Analysis of Nuclear Magnetic Resonance Spectra of Protons in Predominantly Isotactic Polystyrene

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ABSTRACT: NMR chemical shifts have been calculated for methine and aromatic protons of the central $>CHC_6H_5$ group in the all-meso nonad m_8 and in the nonads rrm_6, $mrrm_5$, m_2rrm_4, and m_3rrm_3 containing a single racemic triad, each nonad being situated within an otherwise isotactic (meso) polystyrene chain. The magnetic shieldings by phenyl groups that are first and second neighbors along the chain were computed according to their distances and orientations relative to the resonant proton H* in each conformation of the chain using the ring current representation of the π electrons (Johnson and Bovey, and Waugh and Fessenden) or, alternatively, the magnetic anisotropy of the phenyl group and the McConnell equation. The resulting chemical shifts were averaged over all conformations on the basis of the rotational isomeric state scheme appropriate to polystyrene. Shielding by solvent (tetrachloroethane) was treated empirically by taking averages over the occurrence of phenyl groups in direct apposition to H*, whereby solvent is excluded from H*. The calculations for the methine proton are in excellent agreement with the experimental 300-MHz spectra obtained by Harwood and Shepherd for selectively deuterated, partially epimerized (3%) isotactic polystyrene. The calculations match the observed spectra both in the order of occurrence of the resonances for the various nonads and, approximately, in the magnitudes of the spacings between them. Analogous treatment of the chemical shifts for the aromatic protons in ortho and meta positions is indecisive owing to the extraordinary sensitivity of the shielding to torsional angles in the chain backbone.

The NMR chemical shifts of protons depend on their magnetic environments which, in turn, depend on the conformations of the neighboring bonds and, thus, in vinyl polymers on the stereochemical constitution of the polymer chains. The time-averaged occurrences, or probabilities, of various conformations of the neighboring bonds depend not only on the stereochemical character of the dyad in which the protons are situated, but also in marked degree on the stereochemical character of neighboring dyads, including second and third neighbors and beyond.[2-4] This "long-range" dependence is a consequence of the severe conformational constraints generally prevalent in vinyl chains. Taking this circumstance into account, Flory and Fujiwara[2b,4] calculated the NMR chemical shift spectra of the methylene protons in tetrads for atactic polypropylene and methine protons in pentads for atactic polystyrene.[3] They distinguished various conformations according to the anticipated effect of each on the magnetic shielding of the relevant protons and then calculated the probability of each such conformation.

In polypropylene[2b] the magnetic anisotropy of the chain is much smaller than that of the solvent, *o*-dichlorobenzene, used in the NMR measurements. Hence, only those conformations that preclude magnetic shielding by solvent molecules through juxtaposition of the CHR group of an adjoining dyad to the proton of the methylene group were singled out for consideration. The chemical shifts calculated on this basis led to assignments of each of the ten resonances of methylene protons observed in the spectra of tetrads of various stereochemical structures.[5] All of these assignments were eventually confirmed.[6]

In polystyrene chains the phenyl groups attached to the adjacent substituted C^α atoms are the major source of magnetic shielding. Shielding by a phenyl group depends strongly on its relative orientation as well as on its distance from the proton in question. The theoretical spectra of the methine protons of pentads in atactic polystyrene[3] were estimated by Fujiwara and Flory by considering only those conformations which place a nearest neighboring phenyl in apposition to H. The resulting calculations were in qualitative agreement with the spectra for atactic polystyrene-d_7 observed by Segre et al.[7]

For a more definitive comparison with experiments, these theoretical calculations for atactic polystyrene require refinements as follows:

(i) Owing to the large magnitude of magnetic anisotropy of the phenyl group, the shielding in the conformations other than those which place the phenyl in direct apposition to H may be substantial and, hence, should be taken into account. Shielding by phenyl groups separated by two intervening dyads (second-neighbor shielding) also should be included.

(ii) The shielding parameters for a given conformation should be evaluated more accurately on the basis of the improved analyses now available[8] of molecular geometry in the preferred conformations.

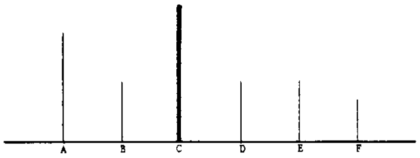
(iii) The shielding by solvent molecules, which are magnetically anisotropic, needs to be considered.

The work of Ando et al.[9] on the proton chemical shifts of poly(vinyl chloride) measured in various solvents demonstrates the importance of (iii). After taking account of (i) and (ii) by carrying out the necessary computations they succeeded in identifying the effects of (iii) and found them to be substantial.

Recently, Harwood and Shepherd[10] determined the 300-MHz NMR spectra of partially deuterated isotactic polystyrenes in which protons were retained in one of three selected positions as follows: on the methine carbon, in the ortho positions of the phenyl group, or in the meta positions. They also determined the NMR spectra of each of the three polymers after they had been partially epimerized. A small fraction, ca. 3%, of the α-carbon centers were inverted at random in this process. The racemic triads (rr) thus introduced were surrounded by predominantly meso (m) dyads of the otherwise isotactic chains. The high resolution of the 300-MHz spectrometer used by Harwood and Shepherd[10] and the almost uniform isotactic environments of the racemic triads enabled them to identify five or six well-separated peaks free of extensive overlapping in the spectra of each of the three partially epimerized samples. These resonances were attributed to protons of the central $>CHC_6H_5$ member of the five distinct nonads $m_4{*}m_4$, $r_2m_2{*}m_4$, $mr_2m{*}m_4$, $m_2r_2{*}m_4$, and $m_3r{*}rm_3$, where the location of the resonant proton(s) is denoted by the asterisk.

Harwood and Shepherd's[10] results are presented in Table I. They are represented schematically by the stick diagram above the tabulations of chemical shifts for protons of each of the three kinds. The location of the resonance that is exhibited both before and after epimerization is denoted by C.

Table I
Experimental Chemical Shifts for Protons in Predominantly Isotactic Polystyrene[10]



Line	Proton chemical shifts[a] Methine	Ortho	Meta
A		6.59	7.07
B	2.05	6.53	6.94
C	1.98	6.50	6.89
D	1.90	6.49	
E	1.68	6.35	6.84
F	1.65	6.32	6.81

[a] All values are in units of ppm relative to hexamethyldisiloxane (HMDS). The measurements were made in tetrachloroethane solution at 28 °C by Harwood and Shepherd.[10]

The additional resonances that appear after epimerization are shown in the order of their occurrence in the spectra. The relative intensities of these five peaks are indicated by the length of the sticks, the ratio being 1:2:4 for the shortest (F), the intermediate (B, D, E), and the longest (A), respectively. While the magnitudes of the spacings differ for the methine, ortho, and meta protons, the resonances of greatest and lowest intensities occur at the extremes of the patterns for each.

We have carried out theoretical calculations of the chemical shifts for the methine protons and for the protons of the phenyl group centered in the nonads identified above in an effort to gain a quantitative understanding of them in molecular terms. The well-separated peaks in the spectra of Harwood and Shepherd on the one hand and the controlled stereochemical structures of their samples on the other provide an exceptional opportunity to test theoretical calculations of magnetic shielding averaged over conformations of the chain. The treatment has been improved as indicated in order to overcome deficiencies of previous calculations. The analyses have been carried out in greater detail than heretofore, as warranted by the quality and scope of the experimental results made available to us by Harwood and Shepherd.

Chain Geometry and Rotational States

A detailed description of geometrical parameters and conformational characteristics of polystyrene chains has been presented in a recent paper.[8] The supplements θ' and θ'' of the skeletal bond angles defined in Figure 1 were assigned the values of 66 and 68°, respectively. Lengths l of the skeletal C–C bonds were taken to be 1.53 Å. Geometrical parameters describing the phenyl group were assigned their established values. Repulsions between one of the ortho CH groups of phenyl and one of the H atoms of the neighboring CH_2 group (e.g., between $(CH)_{i-1}{}^{\gamma}$ and H_i in Figure 1) and between the ortho CH and an atom (H) or a group pendant to the adjoining C^{α} (e.g., pendant to C_{i+1} in Figure 1) limit the rotation χ of the phenyl to the range $\chi \approx \pm 20°$.[8,11] The angle χ is measured from the orientation in which the phenyl group is perpendicular to the plane of the adjoining backbone bonds. Conformations in the $\bar{g}$ domain, in the vicinity of $\phi = -120°$ (measured according to the convention relating the rotational sense to the chirality of the bond[12]), are of excessively high energy owing to severe steric interactions involving the planar phenyl group and therefore may be ignored. Hence, two rotational states, trans (t) and gauche (g), with mean locations at $\phi_t \approx 10°$ and $\phi_g \approx 110°$, respectively,[8] suffice for representation of the accessible conformations in polystyrene chains.

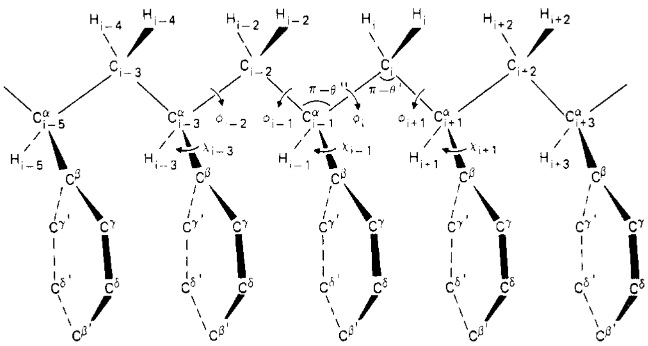


Figure 1. Portion of the isotactic polystyrene chain in the all-trans conformation. A pair of racemic dyads is obtained by exchanging phenyl and H at one of the C^{α}.

Chemical Shifts Due to Shielding by Phenyl Groups in Specified Conformations

In the higher approximation employed in this paper, we consider the diamagnetic shielding of the resonant proton H* by the first- and second-neighboring phenyl groups; e.g., with reference to the methine proton H_{i-1} in Figure 1 we consider shielding effects of phenyl substituents at $i-5$, $i-3$, $i+1$, and $i+3$. On this basis, the averaged chemical shift τ_{Ph} is given by

$$\tau_{\mathrm{Ph}} = \tau_{\mathrm{Ph}}{}^0 + \sum_{\alpha} \delta_{\alpha} p_{\alpha} + \sum_{\alpha\beta} \delta_{\alpha\beta} p_{\alpha\beta} \tag{1}$$

where $\tau_{\mathrm{Ph}}{}^0$ is a constant for protons of a given class, and δ_{α} is the shift parameter due to the phenyl group attached to the adjoining C^{α} atom when the intervening dyad is in the conformation specified by α, whose probability of occurrence is p_{α}; the shift parameter due to the phenyl separated from H* by two dyads (second-neighbor shielding) when the two intervening dyads are in the conformations specified by α and β, respectively, is $\delta_{\alpha\beta}$; the probability of this conformation is $p_{\alpha\beta}$. The summations include both the preceding and the following dyads or dyad pairs. The chemical shifts due to the phenyl groups separated from H* by more than two dyads are negligible when averaged over all conformations, because of the greater distances and variety of orientations. Hence, neglect of magnetic shielding by groups that are more remote in sequence along the chain appears to be well justified.

The contributions δ_{α} and $\delta_{\alpha\beta}$ to the chemical shift depend on the distance of the phenyl group from the resonant proton and on the orientation of the phenyl group in the various conformations for intervening skeletal bonds. An expression for these contributions has been derived by Waugh and Fessenden[13] and by Johnson and Bovey[14] on the basis of the free electron model of Pauling.[15] According to their scheme the shift parameter δ in ppm for a proton located at a point specified by the cylindrical coordinates ρ and z measured from the center of the phenyl group and expressed in units of the phenyl ring radius a, is given by[14]

$$\delta = \frac{ne^2 \times 10^6}{6\pi mc^2 a[(1+\rho)^2 + z^2]} \left[K + \frac{1-\rho^2-z^2}{(1-\rho)^2+z^2} E \right] \tag{2}$$

where e and m are the electronic charge and mass, respectively, c is the velocity of light, n is the number of π electrons ($n = 6$), and K and E are the complete elliptic integrals whose modulus k is given by

$$k^2 = \frac{4\rho}{(1+\rho)^2 + z^2} \tag{3}$$

Table II
Calculated Chemical Shift Parameters δ_α and $\delta_{\alpha\beta}$ for the Methine Proton in Polystyrene[a]

	Conformation	Contribution in ppm
δ_α	meso;tt	−0.04
	meso;tg	−0.15
	meso;gt	0.60
	meso;gg	−0.15
	racemic;tt	0.62
	racemic;tg	−0.14
	racemic;gt	−0.04
	racemic;gg	−0.16
$\delta_{\alpha\beta}$	meso,meso;tt,gt[b]	0.14
	meso,meso;tg,tg	−0.09
	meso,meso;gt,gt	0.10
	meso,racemic;tt,tt	0.27
	meso,racemic;tg,tt	0.06
	meso,racemic;gt,tt	0.12
	racemic,racemic;tt,gt	0.09
	racemic,racemic;tt,tt	0.11

[a] These calculations are for $\Delta\phi = 10°$. The resonant proton is attached to the C^α at the left of the dyad or pair of dyads. [b] The first stereochemical designation (meso or racemic) and the first conformational pair (e.g., tt, tg, etc.) refer to the dyad adjoining the proton.

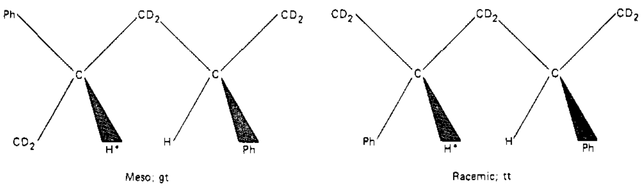


Figure 2. The conformations that directly appose the phenyl group to the methine proton H*.

The π-electron cloud was divided into two rings, one on either side of the plane of the benzene ring.[13,14] In order to reproduce the proton chemical shifts in benzene, Johnson and Bovey[14] fixed the distance between these two rings representing the π cloud at $z = 0.92a = 1.28$ Å.

Alternatively, the shift parameter δ can be calculated from the equation of McConnell,[16]

$$\delta = \Delta g(1 - 3\cos^2\Omega)/3r^3 \qquad (4)$$

where r is the magnitude of the vector connecting the center of the phenyl ring and the proton, Ω is the angle that this vector makes with the normal to the plane of the phenyl, and Δg is the magnetic anisotropy of the phenyl group. Recent results from Zeeman microwave spectra of simple aromatic compounds indicate that $\Delta g = 59.710^{-6}$ erg G^{-1}.[17]

We have employed both methods for evaluating the shift parameters. Differences between results obtained by the two methods were found to be insignificant. The numerical results here reported were calculated according to the former scheme.

Chemical Shift Parameters for Methine Protons in Specified Conformations

Chemical shift parameters δ_α and $\delta_{\alpha\beta}$ were calculated according to eq 2 for each of the conformations tt, tg, gt, and gg, or pair of these conformations. The parameters are sensitive to the torsional angles ϕ_i, ϕ_{i+1} that define the rotational state. In recognition of the correlations of the averaged departures of these two angles from their symmetrical locations,[18] we take $\phi_t = \Delta\phi$ and $\phi_g = 120° - \Delta\phi$. The value of $\Delta\phi$ was varied from 0 to 20°. The chemical shifts also depend on the rotation χ of the phenyl group about its bond to C^α, but to a lesser degree within its allowable range $\chi = \pm 20°$. Calculations were carried out at 10° intervals over this range, and the average was taken of the δ_α thus obtained for each conformation α.

Table III
Conformational Probabilities for the Dyad to the Right of the Central Methine Proton within each Nonad Situated in an Isotactic Chain

Nonad	Probabilities			
	tt	tg	gt	gg
mmmm*mmmm	0.14	0.43	0.43	0.00
rrmm*mmmm	0.11	0.36	0.52	0.00
mmmm*mmrr	0.10	0.59	0.31	0.00
mrrm*mmmm	0.10	0.31	0.59	0.00
mmmm*mrrm	0.07	0.70	0.22	0.00
mmrr*mmmm	0.07	0.22	0.70	0.00
mmmm*rrmm	0.90	0.02	0.01	0.07
mmmr*rmmm	0.90	0.01	0.02	0.07

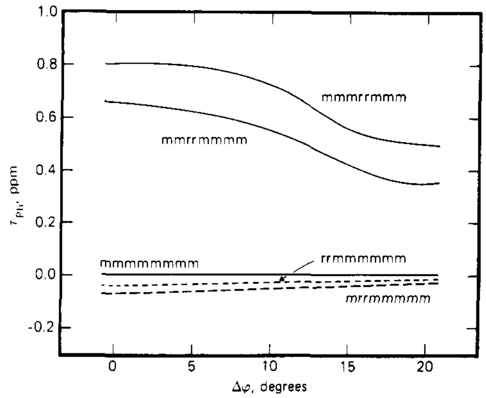


Figure 3. Chemical shift spectra for the central methine proton within each of the indicated nonads due to shielding by first-neighbor phenyls only, plotted against the locations of the rotational states specified by $\phi_t = \Delta\phi$ and $\phi_g = 120° - \Delta\phi$. Each nonad is embedded within a long isotactic (i.e., all-meso) chain. All values are relative to those for the all-meso nonad. They were computed for a range of phenyl rotation χ of ±20°.

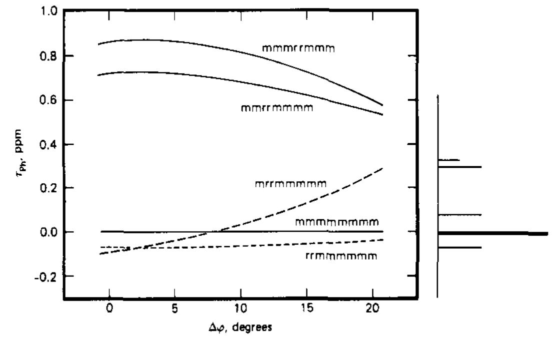


Figure 4. Chemical shift spectra for the central methine proton of the indicated nonads due to the first- and second-neighbor phenyls, plotted against $\Delta\phi$; see the legend to Figure 3. The experimental results of Harwood and Shepherd[10] are shown by the stick diagram on the right-hand ordinate.

Results for δ_α and $\delta_{\alpha\beta}$ with $\Delta\phi = 10°$ are presented in Table II. Here the resonant proton H* is on the left-hand side of the dyad, or pair of dyads, and the shielding phenyl group or groups occur to the right in the specified stereochemical sequence and conformation.

The values of δ_α and $\delta_{\alpha\beta}$ in Table II clearly demonstrate that the meso;gt and the racemic;tt states for the first-neighboring dyads, which place the phenyl in direct apposition to H, make the major contributions to the total chemical shift; see Figure 2. In some conformations, however, shielding by the second-neighbor phenyl group is comparable to the contribution of the first neighbor and, hence, needs to be taken into account.

Averaged Chemical Shifts for Methine Protons Due to Shielding by Phenyls

The conformational probabilities p_α and $p_{\alpha\beta}$ required by eq 1 were computed for the nonad embedded between two sequences of 100 meso dyads each. Thus, the stereochemical structures of the chains considered are expressed by m_{208} and $m_{100+i}r_2m_{106-i}$ where $0 \leq i \leq 3$, the methine proton at the center of the chain being the one of concern in each instance. The 2 × 2 statistical weight matrices of ref 8 furnished the basis for these computations, which were carried out using the matrix multiplication method.[18] All calculations were for a temperature of 28 °C, except as noted otherwise.

Table III presents the probabilities p_α for the dyad to the right of the central methine proton in the indicated nonads. The probabilities of the tg and gt conformations for the adjoining meso dyad are strongly affected by placement of an rr triad in their vicinity. For example, presence of rr as the third neighbor to the left increases the probability of the gt conformation from 0.43 for an all-meso sequence to 0.52. It is increased to 0.59 when rr occurs as the second neighbor and to 0.70 when it adjoins the central methine. Thus, the "long-range" influence of neighbors[2b,4] is clearly demonstrated. Similar effects are manifested in the probabilities $p_{\alpha\beta}$ which are calculated for the pair of dyads that separate the second-neighbor phenyl from the proton H* but are not presented here.

From the shift parameters and the conformational probabilities, the chemical shift τ_{Ph} due to the phenyls may be evaluated for each nonad according to eq 1. First we consider only the shielding due to the adjacent phenyl groups. The resulting chemical shifts, expressed relative to the chemical shift for the all-meso nonad, are shown in Figure 3 as a function of $\Delta\phi$ within the range $0 \leq \Delta\phi \leq 20°$. Inclusion of the second-neighbor shielding due to phenyls separated by two intervening dyads from the central proton yields the results similarly represented in Figure 4.

A comparison of theoretical spectra in Figure 3 with those in Figure 4 clearly demonstrates the significance of second-neighbor shielding. In Figure 3 only two peaks, mmmrrmmm and mmrrmmmm, have higher values of τ_{Ph} than the all-meso sequence; the order of the peaks does not change with $\Delta\phi$. When second-neighbor shielding is included (Figure 4), the chemical shift τ_{Ph} for the mrrmmmmm nonad increases with $\Delta\phi$, and for $\Delta\phi > \sim 8°$ it is larger than τ_{Ph} for the all-meso sequence. Thus, for the range $\sim 8 < \Delta\phi < \sim 15°$ the relative locations of the theoretical spectra are in agreement with the experimental results, also shown in Figure 4 by the stick diagram along the right-hand ordinate representing the values in Table I. This range of $\Delta\phi$ includes the value $\Delta\phi \approx 10°$ estimated from conformational energy calculations.[8] The relative intensities of the peaks thus identified are consistent with the intensities predicted from symmetries of the respective nonads containing an rr pair. However, the theoretical spectra are spread over a range about twice that of the observed spectra.

Table IV
The Chemical Shifts for the Central Methine Proton of Nonads Situated within Isotactic Polystyrene[a]

Nonad	τ_{Ph}[b]	$\sum_\alpha q_\alpha$	Calcd τ[b]	Obsd τ[b]
mmmmmmmm	0.00	0.86	(0.00)	
mmmrrmmm	0.82	1.80	(0.33)	0.33
mmrrmmmm	0.68	1.60	0.30	0.30
mrrmmmmm	0.03	0.81	0.06	0.08
rrmmmmmm	−0.06	0.83	−0.04	−0.07

[a] All calculations are for $\Delta\phi = 10°$ and a temperature of 28 °C. Values quoted are averages over χ confined to the range ±20° (see text). [b] These values are in units of ppm relative to the all-meso nonad.

Solvent Effects

The magnetic anisotropy of the solvent, tetrachloroethane, used for the NMR measurements is presumed to be relatively large and may be comparable to phenyl in this respect. We proceed on the assumption that the shielding by solvent molecules is of short range and, hence, that only those conformations need to be considered in which close contacts between H* and solvent molecules are precluded by the presence of an interfering group of the chain. The adjacent phenyl group displaces solvent from the environs of H* in the gt conformation of the meso dyad and, likewise, in the tt conformation of the racemic dyad; see Figure 2. The CD_2 group is proximate to H* in the meso;tg conformation (and also in racemic;$t\bar{g}$ which, however, is strongly disfavored). The CD_2 group is less effective than phenyl in this respect owing to its small size. Hence, we consider only those conformations in which the phenyl group is apposed to H*.

On this basis, the shielding by solvent molecules, τ_s, is expressed by

$$\tau_s = \tau_s^0 - \delta_s \sum_\alpha q_\alpha \tag{5}$$

where τ_s^0 is a constant, δ_s is the shift parameter due to solvent molecules which are displaced when the phenyl group intervenes, and q_α is the probability of such a conformation. The total chemical shift τ due to shielding by phenyl groups attached to the chain and to the solvent is

$$\begin{aligned}\tau &= \tau_{\mathrm{Ph}} + \tau_s \\ &= \tau^0 + \sum_\alpha \delta_\alpha p_\alpha + \sum_{\alpha\beta} \delta_{\alpha\beta} p_{\alpha\beta} - \delta_s \sum_\alpha q_\alpha \end{aligned} \tag{6}$$

The value of δ_s cannot be readily evaluated. In the analysis of NMR spectra of atactic polypropylene, Flory and Fujiwara[2b] estimated that $\delta_s = 0.37$ ppm for the solvent o-dichlorobenzene excluded by the CHR group in certain conformations (δ_s corresponds to $\delta\nu_a$ in their notation). Here we assign δ_s the value such that the calculated chemical shift for the symmetric nonad $m_3r_2m_3$ relative to that for the all-meso sequence matches the experimental value, 0.33 ppm. These two peaks are unambiguously identified by their relative intensities.

The calculated chemical shifts τ_{Ph} due to shielding by phenyl groups in the various nonads relative to their effect in the all-meso sequence are presented in the second column of Table IV. In these calculations and those that follow $\Delta\phi = 10°$. The combined expectations $\Sigma_\alpha\, q_\alpha$ of the occurrence of a phenyl group in apposition to H* are given in the third column. Coincidence of the calculated chemical shift τ with the value observed for $m_3r_2m_3$ requires $\delta_s = 0.52$ ppm for polystyrene in tetrachloroethane. The chemical shifts τ calculated on this basis for the remaining nonads are presented in the fourth column of Table IV. These calculated chemical shifts, corrected for shielding by the solvent according to eq 6, are

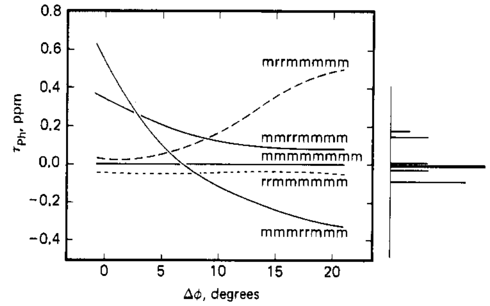


Figure 5. Chemical shift spectra for the central ortho-aromatic protons of the indicated nonads, situated in an otherwise isotactic chain, due to the first- and second-neighbor phenyls plotted against $\Delta\phi$; see the legend to Figure 4.

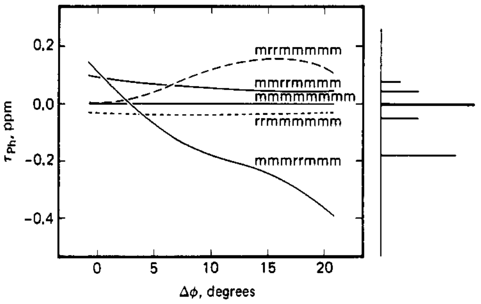


Figure 6. Chemical shift spectra for the central meta-aromatic protons of the indicated nonads, situated in an otherwise isotactic chain, due to the first- and second-neighbor phenyls plotted against $\Delta\phi$; see the legend to Figure 4.

in good agreement with the experimental results given in the last column. Not only do the theoretical chemical shifts occur in the correct order, they are also of the correct magnitude.

Variations in the range of phenyl ring rotation $\Delta\chi$ from 0 to ±30° have only a minor effect on the calculated spectra. The total spread in τ_{Ph} of the spectra decreased from 0.97 to 0.79 ppm when $\Delta\chi$ was increased from 0 to ±30°. Introduction of racemic dyads at random among the 200 units appended at the ends of the nonad up to a proportion of 10% did not appreciably affect the theoretical spectra. An increase of the temperature from 28 to 140 °C likewise had little effect.

Aromatic Protons

The averaged chemical shifts for the ortho- and meta-aromatic protons within each nonad were calculated according to eq 1, which takes account of shielding by phenyl groups, following the procedures described above for the methine proton. The torsional angle χ for the rotation of the phenyl group was confined to the range of ±20°. Mean values of the chemical shifts were calculated for the two ortho protons and for the two meta protons. The resulting nonad spectra for the ortho and meta protons are shown in Figures 5 and 6, respectively, as functions of $\Delta\phi$. They are again expressed relative to the resonance for the all-meso sequence. The corresponding exprimental results are indicated by the stick diagrams on the right-hand ordinates.

The calculated spectra for both the ortho and meta protons are extremely sensitive to the choice of $\Delta\phi$. In fact, they are so sensitive that the representation of the chain conformations with a fixed value of $\Delta\phi$ may be an oversimplification. Qualitative agreement with experiments would be obtained for $\Delta\phi \approx 0°$, except for the additional peaks observed at $\tau_{Ph} < 0$ whose intensities are twice those expected for an asymmetric nonad. The source of these observed resonances is not known. Consideration of possible nonrandomness of the epimerization also did not resolve the difficulty. The large variation of the calculated spectra with the value of $\Delta\phi$ together with the probable effects of solvent shielding, which cannot be accounted for by any simple treatment in case of aromatic protons, render the theoretical analysis of the chemical shift spectra for the aromatic protons subject to large uncertainties.

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