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# Calculated $\gamma$ Effects on the $^{13}$C-NMR Spectra of 3,5,7,9,11,13,15-Heptamethylheptadecane Stereoisomers and Their Implications for the Conformational Characteristics of Polypropylene

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ABSTRACT: The Suter–Flory rotational isomeric state (RIS) model of polypropylene is employed to calculate the $^{13}$C-NMR chemical shifts expected at the 9-C$^{\alpha}$ and CH$_3$ carbons and at the 8- and 10-CH$_2$ carbons in the various stereoisomers of the polypropylene model compound 3,5,7,9,11,13,15-heptamethylheptadecane (I). Differences in the chemical shifts of the same carbon atom in the various stereoisomers are assumed to be attributable solely to stereosequence-dependent differences in the probability that the given carbon atom is involved in three-bond gauche or $\gamma$ interactions with other carbon atoms. When this approach is followed with a $\gamma$ effect of $-5.3$ ppm for each three-bond gauche C---C interaction, the observed $^{13}$C-NMR spectrum of the central 9-CH$_3$ carbon atom in I, including temperature effects, can be fully explained in terms of the possible stereoenvironments. Consequently, the Suter–Flory RIS model appears to provide an accurate description of the conformational characteristics of polypropylene which permits a detailed understanding of its $^{13}$C-NMR spectrum.

$^{13}$C-NMR spectroscopy[1,2] is currently the most powerful experimental probe used to determine the stereoconfiguration and/or sequence distribution of monomer units constituting vinyl homo- and copolymers. The connections between the stereosequences and $^{13}$C-NMR spectra have been drawn[1] numerous times for many different vinyl polymers. However, it was only recently suggested[3,4] that the observed stereochemical shifts in the $^{13}$C resonance peaks could be attributed to conformational differences among the various stereosequences.

It is apparent from $^{13}$C-NMR studies[4–7] of paraffinic hydrocarbons (see Figure 1a) that the gauche arrangement of carbon atoms separated by three bonds ($\gamma$ substituents) results in an upfield shift ($\gamma$ effect) relative to the shielding experienced in the trans planar conformation (see Figure 1b). Clearly the magnitude of the $\gamma$ effect experienced by a given carbon atom in a vinyl polymer chain should depend on the proportion or probability of those bond conformations which produce a gauche arrangement between the carbon atom of interest and those carbon atoms attached in the $\gamma$ position.

The probability that any given bond in the vinyl polymer adopts a particular rotational state is known[8,9] to be sensitive to the stereosequence of the chain in the vicinity of the bond in question. It is therefore reasonable to expect the $^{13}$C chemical shift pattern observed for a vinyl polymer to be directly related to its conformational characteristics as determined by the stereosequence of the chain.

Bovey[4] was able to approximate the triad structure in the $^{13}$C-NMR methyl spectrum of atactic polypropylene by estimating[10] the number of methyl carbon gauche interactions present in each triad and assigning each a $\gamma$ effect of $-4.3$ ppm. More recently Provasoli and Ferro[11] have attempted to calculate the chemical shifts of the central (9) methyl carbon in the stereoisomers of 3,5,7,9,11,13,15-heptamethylheptadecane (I), a model compound[12,13] for polypropylene.

In addition to the $\gamma$ effect, whose magnitude was least-squares fitted to the observed chemical shifts, the latter authors also considered the deshielding effect of a carbon atom separated by four bonds ($\delta$ substitution) in the syn-axial arrangement with respect to the observed carbon atom (see Figure 1c). They assigned the $\delta$ effect a value of 3 ppm and determined the probabilities of finding bond pairs on either side of C$_9{}^{\alpha}$ in the syn-axial conformation for each of the stereoisomers of I. The three-state [trans (t), gauche$^+$ (g), and gauche$^-$ ($\bar{\text{g}}$)] rotational isomeric state (RIS) model for polypropylene developed by Boyd and Breitling[14] was used to

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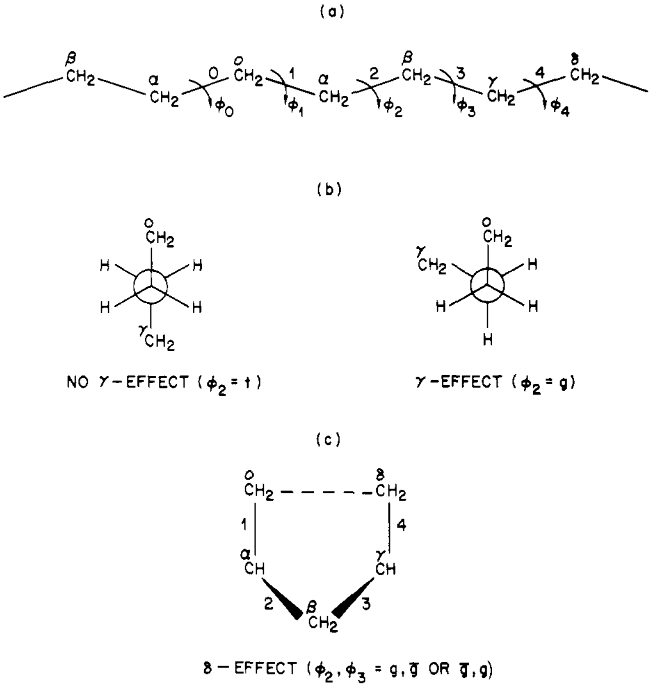

**Figure 1.** (a) Portion of a paraffinic hydrocarbon chain in the all trans, planar zigzag conformation. (b) Newman projections along bond two in (a) illustrating the $\gamma$ effect. (c) Portion of chain in (a) in the g, $\bar{g}$ or $\bar{g}$, g (pentane interference) conformation illustrating the $\delta$ effect.

calculate the bond rotation probabilities for both the $\gamma$ and $\delta$ effects.

Although the overall agreement between the calculated and observed[12,13] chemical shifts for the 9-methyl carbon in I reported by Provasoli and Ferro[11] was good, two features of the calculated chemical shifts are disturbing. In opposition to experiment,[11-13] the calculated chemical shifts give wider syndiotactic than isotactic bands at all temperatures, and the $\gamma$ effect must be increased ca. 10% over the 120 °C interval (20–140 °C) of the experiments to achieve agreement. If the $\gamma$ effect is indeed temperature sensitive, then its utility in the analysis of the conformational and configurational characteristics of vinyl polymers by $^{13}$C-NMR spectroscopy would be severely limited.

For this reason, and because the Boyd–Breitling[14] RIS model of polypropylene is known[15,16] to be inadequate, as is the RIS model[17] used in the preliminary calculations reported by Bovey,[4,10] $^{13}$C chemical shifts of the 9-methyl carbon, $C_9^{\alpha}$, and the 8- and 10-methylene carbons in the stereoisomers of I are recalculated here using the Suter–Flory[18] RIS model of polypropylene. Suter and Flory[18] have recently demonstrated that their RIS model successfully predicts the dimensions and their dependence on stereoregularity and temperature, in addition to the stereochemical equilibrium observed[19] among epimerized oligomers of polypropylene.

**Description of Calculations.** The Suter–Flory[18] RIS model of polypropylene is a five-state model. Each bond in the chain is permitted to adopt any of the t, t*, g*, g, or $\bar{g}$ states corresponding to bond rotation angles of 15, 50, 70, 105, and −115°, respectively. Three-bond gauche interactions leading to $\gamma$ effects can occur in the staggered t, g, $\bar{g}$ rotational states but are absent in the t* and g* eclipsed states. Conformations leading to syn-axial placement of carbon atoms separated by

Table II
Predicted $^{13}$C-NMR Chemical Shift Differences $\Delta\nu$ (ppm) for the 8-Methylene Carbon in 3,5,7,9,11,13,15-Heptamethylheptadecane Stereoisomers ($\gamma$ = −5.3 ppm)

| Stereoisomer | $T$ = 20 °C | $T$ = 80 °C | $T$ = 140 °C |
|---|---|---|---|
| *mrmrmr* | 0 | 0 | 0 |
| *rrmrmm* | −0.196 | −0.164 | −0.127 |
| *rrmrrr* | −0.477 | −0.387 | −0.302 |
| *mrrrrr* | −0.753 | −0.647 | −0.541 |
| *rmmrmr* | −0.925 | −0.843 | −0.758 |
| *mrmmrr* | −0.925 | −0.843 | −0.758 |
| *rmmrrm* | −1.145 | −1.034 | −0.917 |
| *mmmrrr* | −1.447 | −1.261 | −1.081 |
| *rmmmrr* | −1.654 | −1.569 | −1.452 |
| *rmrrrr* | −2.088 | −1.786 | −1.511 |
| *mmmmmr* | −2.200 | −2.009 | −1.791 |
| *mmrrmr* | −2.205 | −1.855 | −1.548 |

Table III
Predicted $^{13}$C-NMR Chemical Shift Differences $\Delta\nu$ (ppm) for the 9-$\alpha$ Carbon in 3,5,7,9,11,13,15-Heptamethylheptadecane Stereoisomers ($\gamma$ = −5.3 ppm)

| Stereoisomer | $T$ = 20 °C | $T$ = 80 °C | $T$ = 140 °C |
|---|---|---|---|
| *mmmmmr* | 0 | 0 | 0 |
| *rmmmrr* | −0.095 | −0.080 | −0.069 |
| *mrmmrr* | −0.154 | −0.138 | −0.106 |
| *rmmrrm* | −0.244 | −0.270 | −0.276 |
| *mmmrrr* | −0.254 | −0.281 | −0.286 |
| *rrmrrr* | −0.270 | −0.297 | −0.297 |
| *mrrrrr* | −0.307 | −0.360 | −0.382 |
| *mrmrmr* | −0.313 | −0.350 | −0.350 |
| *rmmrmr* | −0.313 | −0.345 | −0.350 |
| *rrmrmm* | −0.323 | −0.360 | −0.360 |
| *rmrrrr* | −0.334 | −0.392 | −0.424 |
| *mmrrmr* | −0.350 | −0.424 | −0.472 |

Table I
$^{13}$C-NMR Chemical Shift Differences $\Delta\nu$ (ppm) of the 9-Methyl Carbon in 3,5,7,9,11,13,15-Heptamethylheptadecane Stereoisomers

| Stereoisomer | $T$ = 20 °C obsd[11-13] | $\gamma$ = −5.4 calcd | $T$ = 80 °C obsd[11-13] | $\gamma$ = −5.4 calcd | $T$ = 140 °C obsd[11-13] | $\gamma$ = −5.2 calcd |
|---|---|---|---|---|---|---|
| *mmmmmr* | 0 | 0 | 0 | 0 | 0 | 0 |
| *rmmmrr* | −0.389 | −0.328 | −0.302 | −0.278 | −0.216 | −0.214 |
| *mrmmrr* | −0.680 | −0.605 | −0.594 | −0.518 | −0.410 | −0.406 |
| *mmmrrr* | −0.799 | −0.640 | −0.766 | −0.701 | −0.755 | −0.686 |
| *rmmrrm* | −0.799 | −0.735 | −0.831 | −0.756 | −0.755 | −0.717 |
| *rmmrmr* | −0.907 | −0.903 | −0.960 | −0.914 | −0.906 | −0.849 |
| *rrmrrr* | −1.090 | −1.024 | −1.042 | −0.996 | −0.906 | −0.902 |
| *rrmrmm* | −1.252 | −1.222 | −1.176 | −1.169 | −1.036 | −1.042 |
| *mrmrmr* | −1.252 | −1.249 | −1.176 | −1.183 | −1.036 | −1.049 |
| *mrrrrr* | −1.533 | −1.577 | −1.543 | −1.561 | −1.446 | −1.447 |
| *rmrrrr* | −1.824 | −1.837 | −1.748 | −1.765 | −1.575 | −1.600 |
| *mmrrmr* | −2.072 | −2.146 | −1.899 | −1.995 | −1.694 | −1.764 |

**Table IV**
**Predicted $^{13}$C-NMR Chemical Shift Differences $\Delta\nu$ (ppm) for the 10-Methylene Carbon in 3,5,7,9,11,13,15-Heptamethylheptadecane Stereoisomers ($\gamma = -5.3$ ppm)**

| Stereoisomer | $T$ = 20 °C | $T$ = 80 °C | $T$ = 140 °C |
|---|---|---|---|
| *rmrrrr* | 0 | 0 | 0 |
| *mrmmrr* | −0.239 | −0.281 | −0.307 |
| *mrrrrr* | −0.435 | −0.313 | −0.228 |
| *rmmmrr* | −0.604 | −0.557 | −0.509 |
| *mmrrmr* | −0.848 | −0.800 | −0.742 |
| *mmmmmr* | −1.288 | −1.219 | −1.134 |
| *rrmrrr* | −1.336 | −1.140 | −0.970 |
| *rmmrrm* | −1.389 | −1.177 | −0.996 |
| *mmmrrr* | −1.919 | −1.532 | −1.235 |
| *mrmrmr* | −2.279 | −2.003 | −1.754 |
| *rrmrmm* | −2.788 | −2.359 | −1.993 |
| *rmmrmr* | −2.809 | −2.380 | −2.009 |

four bonds (see Figure 1c) are not significantly permitted, resulting in the virtual absence of $\delta$ effects.

Probabilities of finding bonds 6, 7, 8, 9, 10, and 11 in the t, g, and $\bar{g}$ states were calculated for the various stereoisomers of model compound I at $T$ = 20, 80, and 140 °C using the Suter–Flory RIS model of polypropylene and the usual matrix multiplication techniques.[20] These bond rotation probabilities permit calculation of the number of $\gamma$ interactions involving the $C_9{}^{\alpha}$, $(CH_3)_9$, $(CH_2)_8$, and $(CH_2)_{10}$ carbons.

At each temperature the value for the $\gamma$ effect was chosen to minimize the mean least-squares deviation between the observed[11–13] and calculated $^{13}$C-NMR chemical shifts for the 9-$CH_3$ carbon in the various stereoisomers of compound I.

## Results and Discussion

The calculated and observed chemical shift differences ($\Delta\nu$) for the 9-methyl carbon in the stereoisomers of I are presented in Table I. Agreement between observed and calculated chemical shifts, as indicated by mean least-squares differences [0.0043 ppm$^2$ (20 °C), 0.0025 ppm$^2$ (80 °C), 0.0013 ppm$^2$ (140 °C)], is as good as previously reported by Provasoli and Ferro,[11] at all temperatures. The greater spreads observed in the isotactic bands relative to the syndiotactic bands are, unlike the results of Provasoli and Ferro,[11] reproduced by the present calculated chemical shifts. Furthermore, this agreement is achieved without consideration of $\delta$ effects[21] or the necessity to make the $\gamma$ effect temperature dependent ($\gamma = -5.2$ to $-5.4$ from $T$ = 20–140 °C).

Tables II–IV contain the predicted chemical shift differences expected for the 8-methylene, 9-$\alpha$, and 10-methylene carbon atoms in the various stereoisomers of the polypropylene model compound I obtained with a $\gamma$ effect of −5.3 ppm. The range of chemical shifts calculated for the 8- and 10-methylene carbons in the various stereoisomers is comparable to or larger than those predicted and observed for the 9-methyl carbon. On the other hand, the 9-$\alpha$ carbon is expected to resonate at nearly the same frequency in each of the stereoisomers of I with a maximum calculated spread in chemical shifts of ca. 0.4 ppm. Both of these predictions are borne out by the $^{13}$C-NMR spectrum[4] of atactic polypropylene, where the widths of the methylene and methyl carbon regions are seen to be comparable, while the $\alpha$-carbon region is considerably contracted by comparison.

The present calculations lend considerable support to the notion that the $^{13}$C-NMR chemical shift differences among the various stereosequences in polypropylene are due principally to the $\gamma$ effect, which in turn depends directly upon the conformational characteristics of a given stereosequence. Suter & Flory's[18] RIS model appears successful in its description of the conformational characteristics of polypropylene as manifested by the correct prediction of the number of $\gamma$ effects and the resulting $^{13}$C chemical shifts. This success is achieved with a temperature insensitive $\gamma = -5.2$ to $-5.4$ and is independent of longer range conformational interactions such as the $\delta$ effect.[21]

The failure of Provasoli and Ferro's[11] calculations can therefore be directly attributed to the inadequacies of the Boyd and Breitling[14] RIS model of polypropylene. It would appear that the Suter–Flory[18] RIS model, coupled with the notion that the $\gamma$ effect is the source of chemical shift difference, can provide a detailed description of the $^{13}$C-NMR spectra of polypropylenes of varying stereosequence. It is hoped that this approach can be applied to other vinyl polymers with equal success, because the ability to predict $^{13}$C-NMR spectra will mean that we understand both the configurational and conformational characteristics of these polymer chains, knowledge which is central to the understanding of their physical properties.

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