(30) In constructing the line spectrum in Figure 3 corresponding to the calculated ^{13}C chemical shifts, each of the central (C) methine (see Figure 2) carbon resonances had to be shifted downfield by ca. 6.0 ppm, because the C-methine carbon has one additional β-carbon substituent compared to the end (E) methine carbons. This value for the β effect[6–9] was arrived at by comparing the chemical shift difference observed between the C and E methine carbons in each of the TCH isomers and assigning this difference, after correction for the different number of γ effects involving C and E methine carbons, to the β effect between neighboring methine carbons. The value arrived at (6.2 ± 0.5 ppm) is similar to the β effect caused by other tertiary carbon atoms reported in the literature.[6–9] In addition the consistent set of β effects obtained for the TCH isomers also supports $\gamma_{\mathrm{CH,CH_2\ or\ CH_3}} = -5.0$ ppm and $\gamma_{\mathrm{CH,Cl}} = -3.0$ ppm.

(31) I. Ando, Y. Kato, M. Kondo, and A. Nishioka, *Makromol. Chem.*, **178**, 803 (1977).

(32) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972, Chapter 5, p 134.

(33) A. E. Tonelli, *Macromolecules*, **9**, 867 (1976).

(34) A. E. Tonelli, unpublished results cited in ref 35.

(35) H. N. Cheng and F. A. Bovey, *Org. Magn. Reson.*, **11**, 457 (1978).

(36) I. Ando, Y. Kato, and A. Nishioka, *Makromol. Chem.*, **177**, 2759 (1976).

Carbon-13 Chemical Shifts of the Polypropylene "Model" Compounds 3,5-Dimethylheptane and 3,5,7-Trimethylnonane

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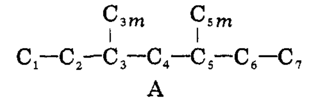
ABSTRACT: ^{13}C-NMR chemical shifts are calculated for the stereoisomers of the polypropylene model compounds 3,5-dimethylheptane (A) and 3,5,7-trimethylnonane (B). Differences in the chemical shifts of the same carbon atom in the various stereoisomers are attributed to stereosequence-dependent differences in the frequency with which the given carbon atom is involved in 3 bond gauche or γ interactions with other carbon atoms. The Suter–Flory RIS model of polypropylene is employed in the evaluation of the number of γ interactions involving each of the carbon atoms in A and B. The calculated ^{13}C chemical shifts are compared to the observed values and those calculated previously for 3,5,7,9,11,13,15-heptamethylheptadecane. This comparison permits an assessment of the utility of A and B as model compounds for polypropylene.

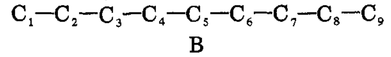
It was recently demonstrated[1,2] that the ^{13}C-NMR spectra of polypropylene can be understood based on the stereosequence sensitive γ effect.[3–6] ^{13}C chemical shifts expected at the 9-C$^{\alpha}$ and CH$_3$ carbons and at the 8 and 10-CH$_2$ carbons in the various stereoisomers of the polypropylene model compound 3,5,7,9,11,13,15-heptamethylheptadecane (C) were evaluated[1] with a 3 bond gauche or γ interaction of −5.3 ppm by employing the rotational isomeric state (RIS) model of polypropylene derived by Suter and Flory.[7] Very good agreement was achieved between the calculated and observed[8–10] chemical shifts for the carbon atoms in C[1] and polypropylene.[2]

Ritter et al.[11] have reported a temperature-dependent study of the ^{13}C chemical shifts of the various stereoisomers of 3,5-dimethylheptane (A) and 3,5,7-trimethylnonane (B),



$$C_1-C_2-\overset{C_{3m}}{\overset{|}{C_3}}-C_4-\overset{C_{5m}}{\overset{|}{C_5}}-C_6-C_7$$

A



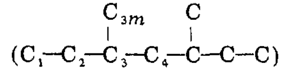
$$C_1-C_2-\overset{C_{3m}}{\overset{|}{C_3}}-C_4-\overset{C_{5m}}{\overset{|}{C_5}}-C_6-\overset{C_{7m}}{\overset{|}{C_7}}-C_8-C_9$$

B

which may also serve as model compounds of polypropylene. They observed throughout the temperature range 150–300 K, and even upon extrapolation to 0 K, that the chemical shift differences between the corresponding carbon atoms in the different stereoisomers do not coincide for compounds A and B. Only the chemical shift differences observed in B correspond to those measured for polypropylene, which seems to render A useless in the study of polypropylene.

It appears useful to apply the same procedures, used to successfully evaluate the ^{13}C chemical shifts of the much larger model compound C[1], to compounds A and B in an attempt to also understand their conformational and configurational characteristics. This is carried out in the present report, where the results obtained for A and B are

Table I
Calculated ^{13}C-NMR Chemical Shift Differences $\Delta\nu$ (ppm) for the Carbon Atoms in the Meso and Racemic Isomers of Model Compound A

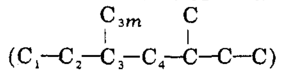


$$(C_1-C_2-\overset{C_{3m}}{\overset{|}{C_3}}-C_4-\overset{C}{\overset{|}{C}}-C-C)$$

carbon atom	$\Delta\nu$,[a] ppm			
	150 K	200 K	250 K	300 K
1	−0.180	−0.170	−0.154	−0.145
2	1.023	1.055	1.012	0.943
3	−0.006	−0.021	−0.037	−0.063
3*m*	−0.724	−0.785	−0.779	−0.753
4	−0.302	−0.297	−0.265	−0.243

[a] Negative values of $\Delta\nu$ indicate that the resonance of the carbon atom in the racemic isomer will occur upfield from its resonance in the meso isomer.

Table II
Comparison of Experimental[5,11] and Calculated ^{13}C Chemical Shift Differences $\Delta\nu$ for the Carbon Atoms in the Meso and Racemic Isomers of Model Compound A

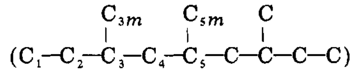


$$(C_1-C_2-\overset{C_{3m}}{\overset{|}{C_3}}-C_4-\overset{C}{\overset{|}{C}}-C-C)$$

carbon atom	$\lvert\Delta\nu\rvert$, ppm			
	150 K		300 K	
	exptl[11]	calcd	exptl[11]	calcd
1		0.18	(0.2)[a]	0.15
2	2.0	1.02	1.15 (1.0)	0.94
3	0.50	0.01	0.14 (0.1)	0.06
3*m*	1.03	0.72	0.71 (0.7)	0.75
4	0.10	0.30	0.16 (0.2)	0.24

[a] Taken from ref 5 where ^{13}C-NMR spectra were recorded in a 50:50 v/v mixture of A-dioxane.

Table III
Calculated ^{13}C-NMR Chemical Shifts ν (ppm) Due to γ Interactions for the Carbon Atoms in the Various Stereoisomers of Model Compound B



$$\begin{array}{c}C_{3m}C_{5m}C\\ (C_1-C_2-C_3-C_4-C_5-C-C-C-C)\end{array}$$

carbon atom	ν, ppm 150 K	 200 K	 250 K	 300 K
2	−3.167,[a] −1.566,[b] −1.909,[c] −1.635[d]	−3.064, −1.800, −1.855, −1.572	−2.905, −1.784, −1.824, −1.529	−2.727, −1.768, −1.797, −1.495
3	−5.274, −5.274, −5.283, −5.274	−5.189, −5.199, −5.226, −5.226	−5.072, −5.088, −5.146, −5.156	−4.945, −4.961, −5.067, −5.040
3*m*	−4.773, −5.735, −5.703, −5.910	−4.802, −5.745, −5.701, −5.918	−4.810, −5.677, −5.645, −5.883	−4.808, −5.592, −5.568, −5.815
4	−3.498, −3.525, −3.565, −3.313	−3.503, −3.501, −3.527, −3.254	−3.514, −3.472, −3.488, −3.223	−3.514, −3.445, −3.459, −3.201
5	−5.274, −5.274, −5.279, −5.284	−5.183, −5.199, −5.231, −5.226	−5.067, −5.088, −5.146, −5.136	−4.924, −4.961, −5.046, −5.040
5*m*	−6.381, −6.609, −6.837, −7.282	−6.270, −6.567, −6.773, −7.303	−6.106, −6.471, −6.657, −7.208	−5.920, −6.339, −6.519, −7.070

[a] *mm* isomer. [b] *mr* isomer. [c] *rm* isomer. [d] *rr* isomer.

compared to C and polypropylene.

Calculations

The Suter–Flory[7] RIS model of polypropylene is a five-state model, where each backbone bond 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 γ effects can only occur in the staggered t, g, $\bar{g}$ rotational states.

Consequently, the probabilities of finding all but the terminal bonds in the t, g, $\bar{g}$ states were calculated for A and B. The meso (*m*) and racemic (*r*) isomers of A and the *mm*, *mr*, *rm*, and *rr* isomers of B were treated at temperatures of 150, 200, 250, and 300 K.

The usual matrix multiplication techniques[12] were used to obtain the bond rotation probabilities. These bond rotation probabilities[13] permit the calculation of the number of γ interactions involving each of the carbon atoms in the various stereoisomers of A and B. A γ effect of −5.3 ppm was adopted for each C- - -C γ interaction, based on previous results[1] obtained for model compound C.

Results and Discussion

^{13}C chemical shift differences calculated for the carbon atoms in the meso (*m*) and racemic (*r*) isomers of A are presented in Table I. The calculated chemical shifts cover the temperature range 150–300 K.

Table II compares the calculated chemical shift differences with those measured by Ritter et al.[11] in $CDCl_3$-CD_2Cl_2 (40:60 v/v) solution. At 300 K there is close agreement between predicted and observed chemical shift differences. However, at 150 K the measured chemical shift differences for carbon atoms 2 and 3 between the *r* and *m* isomers of A are significantly larger than those predicted for these two carbon atoms.

Ritter et al.[11] find the chemical shift differences between the *r* and *m* isomers of A to increase considerably (0.3 to 0.8 ppm) for atoms 3, 3*m*, and especially 2 upon lowering the temperature from 300 to 150 K. The calculated chemical shift differences, on the other hand, change by less than 0.1 ppm over the same temperature range. At present we are unable to offer an explanation for this discrepancy, but through observation of the low-temperature ^{13}C NMR spectra of A in several solvents we hope to either confirm or refute the results reported by Ritter et al.[11] at 150 K.

Table IV
Comparison of Calculated ^{13}C Chemical Shifts for the Various Stereoisomers of the Polypropylene Model Compounds[a] A, B, and C

carbon atom	stereoisomer	ν,[b] ppm A	 B	 C[c]
4(A) and $(CH_2)_{8,10}$(C)	*m*	−3.14		−3.02
4(A) and $(CH_2)_{8,10}$(C)	*r*	−3.38		−4.08
5*m*(B) and $(CH_3)_9$(C)	*mm*		−5.92	−5.78
5*m*(B) and $(CH_3)_9$(C)	*mr (rm)*		−6.43	−6.36
5*m*(B) and $(CH_3)_9$(C)	*rr*		−7.07	−7.26

[a] A ≡ 3,5-dimethylheptane; B ≡ 3,5,7-trimethylnonane; C ≡ 3,5,7,9,11,13,15-heptamethylheptadecane. [b] Calculated at 300 K. [c] Dyad and triad chemical shifts are averaged over the various heptads calculated[1] for C.

Table V
Bond Rotation Probabilities for 3,5-Dimethylheptane

bond	$P_{t,g,\bar{g}}$ 150 K *a*	 *b*	 300 K *a*	 *b*
2	0.379	0.341	0.354	0.321
	0.175	0.219	0.160	0.198
	0.035	0.031	0.067	0.061
3	0.552	0.693	0.506	0.663
	0.442	0.302	0.407	0.263
	0.001	0.001	0.014	0.013
4	0.445	0.693	0.438	0.659
	0.549	0.302	0.475	0.286
	0.000	0.000	0.011	0.010
5	0.273	0.241	0.265	0.239
	0.090	0.139	0.102	0.141
	0.273	0.241	0.265	0.239

[a] Meso isomer. [b] Racemic isomer.

Calculated ^{13}C chemical shifts for the *mm*, *mr*, *rm*, and *rr* stereoisomers of model compound B are presented in Table III. Carbons 2, 3*m*, and 5*m* are predicted to show the greatest sensitivity to stereosequence with each expected to show ^{13}C chemical shift differences of ca. 1.0 ppm between the *mm* and *rr* stereoisomers. Unfortunately Ritter et al.[11] do not present detailed ^{13}C chemical shifts for B.

In Table IV ^{13}C chemical shifts calculated for representative, corresponding atoms in model compounds A, B, and C are compared. Chemical shifts calculated for the central methyl carbons in B and C agree closely for each stereoisomer. On the other hand, the central methylene

Table VI
Bond Rotation Probabilities for 3,5,7-Trimethylnonane

	$P_{t,g,\bar{g}}$							
	150 K				300 K			
bond	*a*	*b*	*c*	*d*	*a*	*b*	*c*	*d*
2	0.410	0.381	0.317	0.333	0.370	0.357	0.308	0.318
	0.139	0.165	0.286	0.227	0.141	0.156	0.213	0.201
	0.037	0.035	0.029	0.030	0.070	0.068	0.058	0.060
3	0.438	0.519	0.781	0.720	0.425	0.489	0.722	0.674
	0.555	0.474	0.215	0.275	0.476	0.419	0.206	0.251
	0.001	0.001	0.000	0.001	0.014	0.014	0.012	0.013
4	0.559	0.477	0.781	0.720	0.519	0.452	0.727	0.672
	0.454	0.516	0.214	0.275	0.382	0.456	0.201	0.253
	0.001	0.001	0.001	0.000	0.016	0.014	0.014	0.013
5	0.643	0.768	0.507	0.654	0.567	0.716	0.476	0.636
	0.351	0.227	0.487	0.341	0.339	0.211	0.439	0.290
	0.001	0.001	0.001	0.000	0.016	0.014	0.013	0.013
6	0.354	0.766	0.489	0.654	0.379	0.705	0.466	0.635
	0.639	0.229	0.505	0.341	0.528	0.223	0.449	0.290
	0.000	0.000	0.000	0.000	0.011	0.010	0.011	0.010
7	0.285	0.231	0.268	0.246	0.273	0.234	0.262	0.242
	0.072	0.154	0.099	0.131	0.091	0.149	0.106	0.137
	0.285	0.231	0.268	0.246	0.273	0.234	0.262	0.242

[a] *mm* isomer. [b] *mr* isomer. [c] *rm* isomer. [d] *rr* isomer.

Table VII
Bond Probabilities for 3,5,7,9,11,13,15-Heptamethylheptadecane at 300 K

	$P_{t,g,\bar{g}}$											
bond	*mmmm-mr*	*rrrrrm*	*rrrrmr*	*rrrmrr*	*mmmrrr*	*mmrmrr*	*mrmmrr*	*rmmmrr*	*rmmrrm*	*mmrrmr*	*mrmrmr*	*rmmrmr*
6	0.513	0.645	0.654	0.626	0.464	0.367	0.797	0.588	0.559	0.396	0.768	0.546
	0.376	0.283	0.274	0.301	0.432	0.544	0.140	0.319	0.351	0.510	0.167	0.365
	0.017	0.012	0.012	0.011	0.016	0.012	0.013	0.016	0.015	0.013	0.012	0.014
7	0.478	0.441	0.636	0.713	0.586	0.794	0.374	0.471	0.539	0.733	0.468	0.568
	0.409	0.267	0.291	0.218	0.320	0.142	0.538	0.427	0.369	0.196	0.451	0.344
	0.017	0.012	0.012	0.012	0.016	0.013	0.012	0.016	0.015	0.014	0.012	0.014
8	0.470	0.662	0.634	0.720	0.363	0.791	0.573	0.746	0.408	0.719	0.473	0.379
	0.416	0.267	0.294	0.210	0.543	0.146	0.340	0.422	0.500	0.211	0.447	0.534
	0.017	0.012	0.011	0.013	0.013	0.012	0.014	0.016	0.013	0.011	0.012	0.012
9	0.523	0.635	0.712	0.472	0.757	0.440	0.539	0.582	0.729	0.685	0.763	0.792
	0.367	0.292	0.219	0.443	0.174	0.479	0.371	0.325	0.200	0.244	0.172	0.145
	0.017	0.012	0.012	0.013	0.014	0.012	0.014	0.016	0.014	0.011	0.012	0.013
10	0.425	0.633	0.720	0.471	0.745	0.506	0.407	0.367	0.716	0.696	0.763	0.789
	0.465	0.295	0.210	0.444	0.188	0.416	0.502	0.540	0.214	0.232	0.171	0.148
	0.016	0.011	0.013	0.013	0.011	0.012	0.013	0.013	0.011	0.013	0.013	0.012
11	0.600	0.708	0.468	0.721	0.623	0.710	0.744	0.758	0.681	0.479	0.448	0.436
	0.303	0.223	0.447	0.209	0.305	0.220	0.187	0.173	0.248	0.435	0.469	0.482
	0.016	0.012	0.013	0.013	0.011	0.013	0.013	0.014	0.011	0.013	0.012	0.012

carbons in A and C have considerably different expected chemical shifts for the *r* stereoisomer.

On the basis of this comparison, it seems fair to say that A is not a suitable model compound for polypropylene, while the central portion of B does mimic the conformational and configurational properties of polypropylene. Ritter et al.[11] reached a similar conclusion based on their ^{13}C NMR measurements. Quantitative evaluation of the number of gauche arrangements between carbon atoms γ to each other with $\gamma = -5.3$ ppm seems to adequately describe the ^{13}C NMR chemical shifts of model compounds B and C[1] and polypropylene[2] in addition to the ^{13}C chemical shifts of A which, however, cannot be used to model polypropylene.

Appendix

Bond rotation probabilities for 3,5-dimethylheptane and 3,5,7-trimethylnonane are given in Tables V and VI.

Bond probabilities for 3,5,7,9,11,13,15-heptamethylheptadecane at 300 K are given in Table VII.

References and Notes

(1) A. E. Tonelli, *Macromolecules*, **11**, 565 (1978).
(2) A. E. Tonelli and F. C. Schilling, in preparation.
(3) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).
(4) D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1964).
(5) L. P. Lindeman and J. Q. Adams, *Anal. Chem.*, **43**, 1245 (1971).
(6) F. A. Bovey, "Proceedings of the International Symposium on Macromolecules", Rio de Janeiro, July 26–31, 1974, E. B. Mano, Ed., Elsevier, Amsterdam, 1975, p 169.
(7) U. W. Suter and P. J. Flory, *Macromolecules*, **8**, 765 (1975).
(8) A. Zambelli, P. Locatelli, G. Bajo, and F. A. Bovey, *Macromolecules*, **8**, 687 (1975).
(9) G. Gatti and A. Zambelli, cited in ref 10.
(10) A. Provasoli and D. R. Ferro, *Macromolecules*, **10**, 874 (1977).
(11) W. Ritter, M. Möller, and H.-J. Cantow, *Makromol. Chem.*, **179**, 823 (1978).
(12) P. J. Flory "Statistical Mechanics of Chain Molecules", Interscience, New York, 1969, Chapter III.
(13) See Tables V–VII for bond rotation probabilities.