# Carbon-13 Magnetic Resonance of Some Branched Alkanes

**Charles J. Carman,*[1a] A. R. Tarpley, Jr.,[1b] and J. H. Goldstein[1b]**

*The B. F. Goodrich Company, Research & Development, Brecksville, Ohio 44141, and the Department of Chemistry, Emory University, Atlanta, Georgia 30322.* *Received March 8, 1973*

ABSTRACT: Natural abundance carbon-13 nmr spectra have been obtained for a series of twelve unique branched alkanes. They represent a series of regular, repeating methylene carbon sequences, between tertiary carbon atoms, with increasing sequence length up to a branched $C_{25}$. They provide a model set for describing monomer sequences in ethylene-propylene copolymers. In addition, they provide a model set for revising the empirical Grant and Paul additive coefficients and corrective terms for predicting $^{13}C$ chemical shifts of alkanes. The resulting revised parameters produce more accurate predictions of cmr spectra of branched alkanes. Two of the compounds demonstrate that conformational structure can produce magnetic nonequivalence between isopropyl methyl carbons even if no asymmetric carbon atom is present in the molecule.

Determination of stereochemistry[2,3] and monomer sequence distribution[4a,b] in ethylene-propylene copolymers and terpolymers by carbon-13 nuclear magnetic resonance (cmr) spectroscopy has been successful because of the relatively large separation of $^{13}C$ chemical shifts. Assignments of $^{13}C$ chemical shifts in these branched, alkane polymers and in branched polyethylene[5] have relied strongly on the pioneering cmr work by Grant and Paul[6] on alkanes. Grant and Paul demonstrated that $^{13}C$ chemical shifts for a sample group of predominantly linear alkanes could be described by a linear equation incorporating empirically determined additivity coefficients. The equation, expressed as

$$\delta_c(k) = B + \Sigma_l A_k n_{k,l} \quad (1)$$

predicts that the $^{13}C$ chemical shift of the $k$th carbon atom is equal to a constant, plus the sum of additive chemical shift coefficients multiplied by the number of carbons in the $l$th position relative to $k$. On this basis, additive coefficients were determined for carbons up to five atoms removed from the $k$th carbon. Furthermore, it was found that correction terms were required to take account of branching effects.

In general, predictions of $^{13}C$ chemical shifts with the additivity coefficients of Grant and Paul are quite good for a saturated hydrocarbon polymer such as an ethylene-propylene copolymer. However, deviations between predicted and observed $^{13}C$ chemical shifts of greater than 1 ppm are noted for some carbons at or near branched sites and result in ambiguities in making structural assignments.[4a,b] This, of course, is not surprising since the coefficients of the correction terms were determined by Grant and Paul on the basis of a very small number of observations involving alkane branching. In addition, the branched alkanes which were used in the Grant and Paul treatment were relatively short-chain molecules and, therefore, probably do not completely represent the $\gamma$ effects and branching effects that might occur in long-chain branched molecules.

As an obvious extension of the previous work of Grant and Paul, we have obtained the natural abundance cmr spectra of a series of 12 highly branched alkanes, the largest of which is a $C_{25}$ hydrocarbon. The unique feature of this set of alkanes is that it is the largest series yet studied which contain regularly repeating methylene sequences between tertiary carbons. Besides enlarging the experimental basis for evaluating additivity effects on $^{13}C$ shifts in branched alkanes, the extended set of molecules provides good models for predicting $^{13}C$ chemical shifts in ethylene-propylene copolymer sequences.

In addition, examples from this series of branched alkanes demonstrate that an asymmetric carbon atom need not be present in a molecule for isopropyl methyl carbons to be magnetically nonequivalent. It will be shown that both rotational conformation and molecular configuration can produce magnetic nonequivalence between what intuitively appear to be identical carbon atoms.

## Experimental Section

All cmr spectra were obtained in the frequency sweep mode at 22.62 MHz with a Bruker Scientific HFX-90 spectrometer. Broad-band proton decoupling was employed in all cases with the aid of a Bruker BSV-2 power amplifier. All $^{13}C$ spectra of the hydrocarbons were obtained on neat samples in 13-mm sample tubes with a 5-mm capillary inserted to allow for external stabilization on the $^{19}F$ resonance of hexafluorobenzene. The probe temperature during broad-band proton decoupling was 48°.

The chemical shifts were measured in all cases using a 120-Hz sweep width and a sweep rate of 3 Hz/sec. Although single scans would have been quite adequate for measurement purposes, eight scans were time averaged for each spectrum using a Fabri-Tek 1074 computer in order to obtain low-noise spectra. All $^{13}C$ chemical shifts were measured relative to external benzene for comparison with the previous data of Grant and Paul. They were then expressed relative to internal $Me_4Si$ by subtracting each chemical shift from 128.76 ppm. This difference in chemical shift between internal $Me_4Si$ and external benzene was obtained by measuring the chemical shifts of 2,4-dimethylpentane and 2,8,14,20-tetramethylhenicosane relative to internal $Me_4Si$, and determining the average difference between the internal and external references for the 15 resonances. The average difference in chemical shifts for the $C_7$ and $C_{25}$ hydrocarbon, which should reflect differences in magnetic susceptibilities, was 0.15 ppm. Under the above experimental conditions it is estimated that the absolute chemical shifts are accurate to 0.1-0.2 ppm, but the uniform conditions employed make the relative chemical shifts internally consistent to at least 0.5 Hz or 0.02 ppm.

2,4-Dimethylpentane was obtained from Aldrich Chemical Co., and 2,5-dimethylhexane from Columbia Organic Chemicals Co. The remaining model compounds were synthesized and purified by Dr. E. C. Gregg, Jr., of The B. F. Goodrich Co., Research & Development. These compounds were: 2,6-dimethylheptane, 2,4,6-trimethylheptane, 2,7-dimethyloctane, 2,8-dimethylnonane, 2,5,8-trimethylnonane, 2,9-dimethyldecane, 2,5,8,11-tetramethyldodecane, 2,6,10,14-tetramethylpentadecane, 2,8,14,20-tetramethylheneicosane, and hydrogenated *cis*-1,4-poly(isoprene).

## Results

The branched alkanes used in the present study are

(1) (a) The B. F. Goodrich Co.; (b) Emory University.
(2) A. Zambelli, G. Gatti, C. Sacchi, W. O. Crain, Jr., and J. D. Roberts, *Macromolecules*, 4, 475 (1971).
(3) W. O. Crain, Jr., A. Zambelli, and J. D. Roberts, *Macromolecules*, 4, 330 (1971).
(4) (a) C. J. Carman and C. E. Wilkes, *Rubber Chem. Technol.*, 44, 781 (1971); (b) C. E. Wilkes, C. J. Carman, and R. A. Harrington, *J. Polym. Sci.*, in press.
(5) D. E. Dorman, E. P. Otocka, and F. A. Bovey, *Macromolecules*, 5, 574 (1972).
(6) D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, 86, 2984 (1964).

**Table I**
**Observed and Calculated Carbon-13 Chemical Shifts in Branched Alkanes[a]**

| 1, 2a | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2,4-Dimethylpentane | | | | | | | | | | | |
| 2a | | | | | | | | | | | |
| C C $\sigma_1 = 0.39$[b] | | | | | | | | | | | |
| CCCCC $\sigma_2 = 0.15$[c] | | | | | | | | | | | |
| 1 2 3 | | | | | | | | | | | |
| 22.71 | 25.71 | 49.10 | | | | | | | | | |
| (22.48) | (25.61) | (48.36) | | | | | | | | | |
| [22.78] | [25.99] | [49.17] | | | | | | | | | |
| 2,4,6-Trimethylheptane | | | | | | | | | | | |
| 2a 5 | | | | | | | | | | | |
| C C C $\sigma_1 = 1.13$ | | | | | | | | | | | |
| CCCCCCC $\sigma_2 = 0.58$ | | | | | | | | | | | |
| 1 2 3 4 | | | | | | | | | | | |
| 24.06[d] | | | | | | | | | | | |
| 22.99 | 26.06 | 48.28 | 28.87 | 20.74 | | | | | | | |
| (22.59) | (26.15) | (46.49) | (26.39) | (20.61) | | | | | | | |
| [22.81] | [26.33] | [47.39] | [27.86] | [21.00] | | | | | | | |
| 2,5-Dimethylhexane | | | | | | | | | | | |
| 2a | | | | | | | | | | | |
| C C $\sigma_1 = 0.60$ | | | | | | | | | | | |
| CCCCCC $\sigma_2 = 0.36$ | | | | | | | | | | | |
| 1 2 3 | | | | | | | | | | | |
| 23.09 | 28.96 | 37.57 | | | | | | | | | |
| (23.51) | (28.73) | (36.48) | | | | | | | | | |
| [22.56] | [28.89] | [37.09] | | | | | | | | | |
| 2,5,8-Trimethylnonane | | | | | | | | | | | |
| 2a 6 | | | | | | | | | | | |
| C C C $\sigma_1 = 0.45$ | | | | | | | | | | | |
| CCCCCCCCC $\sigma_2 = 0.28$ | | | | | | | | | | | |
| 1 2 3 4 5 | | | | | | | | | | | |
| 23.01[d] | | | | | | | | | | | |
| 22.79 | 28.69 | 36.86 | 35.18 | 33.70 | 20.01 | | | | | | |
| (22.39) | (28.84) | (36.80) | (34.52) | (32.61) | (20.43) | | | | | | |
| [22.56] | [28.92] | [37.40] | [35.09] | [33.58] | [20.56] | | | | | | |
| 2,5,8,11-Tetramethyldodecane | | | | | | | | | | | |
| 2a 7 | | | | | | | | | | | |
| C C C C $\sigma_1 = 0.72$ | | | | | | | | | | | |
| CCCCCCCCCCC $\sigma_2 = 0.41$ | | | | | | | | | | | |
| 1 2 3 4 5 6 | | | | | | | | | | | |
| 23.62[d] | | | | | 35.85[d] | 20.64[d] | | | | | |
| 23.41 | 29.23 | 37.40 | 35.29 | 34.29 | 35.59 | 20.59 | | | | | |
| (22.39) | (28.84) | (36.90) | (34.52) | (34.72) | (34.94) | (20.43) | | | | | |
| [22.56] | [28.92] | [37.40] | [35.09] | [34.61] | [35.40] | [20.56] | | | | | |
| 2,6-Dimethylheptane | | | | | | | | | | | |
| 2a | | | | | | | | | | | |
| C C $\sigma_1 = 0.39$ | | | | | | | | | | | |
| CCCCCC $\sigma_2 = 0.27$ | | | | | | | | | | | |
| 1 2 3 4 | | | | | | | | | | | |
| 22.65 | 28.21 | 39.68 | 25.35 | | | | | | | | |
| (22.28) | (28.64) | (39.59) | (24.60) | | | | | | | | |
| [22.53] | [28.67] | [39.99] | [25.01] | | | | | | | | |
| 2,6,10,14-Tetramethylpentadecane | | | | | | | | | | | |
| 2a 9 | | | | | | | | | | | |
| C C C C $\sigma_1 = 0.33$ | | | | | | | | | | | |
| CCCCCCCCCCCCCC $\sigma_2 = 0.22$ | | | | | | | | | | | |
| 1 2 3 4 5 6 7 8 | | | | | | | | | | | |
| 23.05 | 28.39 | 39.95 | 24.95 | 37.85 | 33.30 | 37.99 | 25.28 | 20.16 | | | |
| (22.28) | (28.64) | (39.70) | (25.02) | (37.52) | (32.43) | (37.63) | (25.44) | (20.21) | | | |
| [22.53] | [28.67] | [40.02] | [25.32] | [36.96] | [33.14] | [37.99] | [25.63] | [20.50] | | | |

**Table I** (*Continued*)

| 1, 2a | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2,7-Dimethyloctane | | | | | | | | | | | |
| 2a | | | | | | | | | | | |
| C C $\sigma_1 = 0.24$ | | | | | | | | | | | |
| CCCCCCCC $\sigma_2 = 0.20$ | | | | | | | | | | | |
| 1 2 3 4 | | | | | | | | | | | |
| 22.72 | 28.28 | 39.51 | 28.03 | | | | | | | | |
| (22.28) | (28.53) | (39.50) | (27.71) | | | | | | | | |
| [22.53] | [28.64] | [39.87] | [27.91] | | | | | | | | |
| 2,8-Dimethylnonane | | | | | | | | | | | |
| 2a | | | | | | | | | | | |
| C C $\sigma_1 = 0.22$ | | | | | | | | | | | |
| CCCCCCCCC $\sigma_2 = 0.19$ | | | | | | | | | | | |
| 1 2 3 4 5 | | | | | | | | | | | |
| 22.76 | 28.30 | 39.51 | 27.84 | 30.61 | | | | | | | |
| (22.28) | (28.53) | (39.39) | (27.62) | (30.82) | | | | | | | |
| [22.53] | [28.64] | [39.74] | [27.69] | [30.81] | | | | | | | |
| 2,8,14,20-Tetramethylheneicosane | | | | | | | | | | | |
| 2a 12 | | | | | | | | | | | |
| C C C C $\sigma_1 = 0.32$ | | | | | | | | | | | |
| CCCCCCCCCCCCCCCCCCCCC $\sigma_2 = 0.15$ | | | | | | | | | | | |
| 1 2 3 4 5 6 7 8 9 10 11 | | | | | | | | | | | |
| 23.05 | 28.42 | 39.66 | 27.63 | 30.87 | 27.95 | 37.68 | 33.31 | 37.68 | 27.95 | 30.87 | 20.18 |
| (22.28) | (28.53) | (39.39) | (27.62) | (30.93) | (28.04) | (37.32) | (32.21) | (37.32) | (28.04) | (31.04) | (20.21) |
| [22.53] | [28.64] | [39.74] | [27.69] | [30.84] | [28.00] | [37.71] | [33.08] | [37.71] | [28.00] | [30.87] | [20.50] |
| 2,9-Dimethyldecane | | | | | | | | | | | |
| 2a | | | | | | | | | | | |
| C C $\sigma_1 = 0.26$ | | | | | | | | | | | |
| CCCCCCCCC $\sigma_2 = 0.21$ | | | | | | | | | | | |
| 1 2 3 4 5 | | | | | | | | | | | |
| 22.80 | 28.31 | 39.53 | 27.80 | 30.38 | | | | | | | |
| (22.28) | (28.53) | (39.39) | (27.51) | (30.73) | | | | | | | |
| [22.53] | [28.64] | [39.74] | [27.63] | [30.59] | | | | | | | |
| Hydrogenated *cis*-1,4-poly(isoprene) | | | | | | | | | | | |
| 1 | | | | | | | | | | | |
| C C $\sigma_1 = 0.75$ | | | | | | | | | | | |
| C(CCCC)$_n$CC $\sigma_2 = 0.41$ | | | | | | | | | | | |
| 2 3 4 | | | | | | | | | | | |
| 20.85 | 33.87 | 38.58 | 25.53 | | | | | | | | |
| (20.21) | (32.43) | (37.63) | (25.44) | | | | | | | | |
| [20.50] | [33.14] | [37.99] | [25.63] | | | | | | | | |

[a] All $^{13}C$ chemical shifts are given in ppm downfield from internal $Me_4Si$. The number at the top of each column coincides with the carbon identification shown for each compound. Reading down a column, the first entry is the observed value, the entry in parentheses is that calculated from the Grant and Paul coefficients,[6] and the entry in brackets is that calculated with the modified Grant and Paul coefficients from this work (Table II, second column). [b] $\sigma_1$ is the standard deviation[8] between the observed $^{13}C$ chemical shifts and those predicted using the original Grant and Paul parameters. [c] $\sigma_2$ is the standard deviation[8] between the observed $^{13}C$ chemical shifts and those predicted using the parameters in the second column in Table II. [d] Chemical shift differences reflect nonequivalent carbon atoms.

listed in Table I in an order of increasing, repeating methylene sequences between tertiary carbon atoms. Thus, the compounds represent the following runs of methylene sequences: 1 run of 1, 2 runs of 1, 1 run of 2, 2 runs of 2, 3 runs of 2, 1 run of 3, 3 runs of 3, 1 run of 4, 1 run of 5, 3 runs of 5, 1 run of 6, and $n$ runs of 3. They provide an ideal model set for extending $^{13}C$ chemical shift predictions of methyl-substituted alkanes to a $C_{25}$ aliphatic alkane. The experimental $^{13}C$ chemical shifts found for the branched alkane series are given in Table I as the first entry in each column under the carbon identifications. The corresponding chemical shifts predicted from the Grant and Paul parameters are given in parentheses for comparison. Linear regression analysis[7] was used to calculate new additive chemical shift parameters and correction terms in the Grant and Paul basis. The data included all $^{13}C$ chemical shifts for the alkanes used in the original Grant and Paul analysis[6] in addition to the $^{13}C$ chemical shifts from the present series of branched alkanes. The statistical summary from this regression analysis is presented in Table II. The $^{13}C$ chemical shifts predicted using the new parameters, from the second column in Table II, are given in Table I in brackets below the carbon identifications. Table I also contains, for each compound, a comparison of the standard deviation between the ob-

(7) Regression analysis was performed using the IBM program "Regre" patterned after: B. Ostle, "Statistics in Research," The Iowa State College Press, Ames, Iowa, 1954, Chapter 8.

**Table II**
**Regression Analysis of Chemical Shift Parameters**

| C Position, l | $A_l$ (ppm) This Work | $A_l$ (ppm) Grant and Paul[6] |
|---|---|---|
| $\alpha$ | −8.85 ± 0.10 | −9.09 ± 0.11 |
| $\beta$ | −9.51 ± 0.10 | −9.40 ± 0.11 |
| $\gamma$ | 2.34 ± 0.05 | 2.49 ± 0.07 |
| $\delta$ | −0.28 ± 0.04 | −0.31 ± 0.10 |
| $\epsilon$ | −0.03 ± 0.04 | −0.11 ± 0.12 |
| **Cor Term** | **Coef (ppm)** | |
| 1° (3°) | 0.96 ± 0.15 | 1.12 ± 0.21 |
| 2° (3°) | 2.11 ± 0.17 | 2.50 ± 0.24 |
| 3° (2°) | 3.04 ± 0.11 | 3.65 ± 0.17 |
| 1° (4°) | 3.61 ± 0.36 | 3.37 ± 0.35 |
| 4° (1°) | 1.27 ± 0.12 | 1.50 ± 0.12 |
| 4° (2°) | 8.24[a] | 8.36[a] |
| 2° (4°) | 7.14[a] | 7.23[a] |
| 3° (3°) | 9.05[a] | 9.47[a] |
| Number of observations | 113 | 53 |
| Number of independent variables | 13 | 13 |
| Multiple correlation coefficient | 0.9991 | 0.9992 |
| Standard deviation (ppm) | 0.39 | 0.30 |
| Constant term (ppm) | 131.11[b] | 131.18 |

[a] Only a single observation was available[6] and thus a statistical analysis of experimental deviations is not applicable. [b] To calculate relative internal $Me_4Si$, the constant term = 2.35 ppm.

served $^{13}C$ chemical shifts and those predicted using either the original Grant and Paul parameters or the new parameters; where, the following equation[8] was used for standard deviation

$$SD = \sqrt{\Sigma d^2/2(n-1)}$$

## Discussion

As shown in Table I, predicted values of $^{13}C$ chemical shifts, which are based on the original Grant and Paul parameter values, in some cases differ from observed values by as much as 1 ppm. These deviations are particularly noticeable for tertiary carbon atoms at interior branching locations. The deviations are next most noticeable for secondary carbon atoms bonded to carbons at interior branching locations. Since the alkanes used by Grant and Paul included very few cases of branching, it seems reasonable that some of the Grant and Paul correction terms for branching may not be well determined. In fact, only five observations from the Grant and Paul alkane cmr data involve the 1° (3°) term while only three observations involve the 2° (3°) and 3° (2°) terms. The symbols represent: a methyl carbon bonded to a tertiary carbon, 1° (3°), a secondary carbon bonded to a tertiary carbon, 2° (3°), and a tertiary carbon bonded to a secondary carbon, 3° (2°).[6] On the other hand, the present series is characterized by extensive multiple branching. Consequently, the 60 chemical shift values of the present alkane series were combined with the 53 values given by Grant and Paul. The statistical analysis of the resulting combined set of data is shown in Table II. There are now 15, 17, and 16 observations involving the 1° (3°), 2° (3°), and 3° (2°) corrective terms, respectively. A desirable feature of the present results is that they were obtained without increasing the number of parameters used by Grant and Paul. In this way the entire procedure becomes consistent with the convenient empirical approach derived by Grant and Paul as far as both the types and number of branching correction terms are concerned. For example, in 2,4,6-trimethylheptane, the methylene carbon between the two tertiary carbons (C-3 in 2,4,6-trimethylheptane, Table I) is a secondary carbon bonded to two tertiary carbons. Consequently, included in the calculation of the $^{13}C$ chemical shift is two times the 2° (3°) term, the term for a secondary carbon bonded to a tertiary carbon. Similarly, in the same compound, the C-4 tertiary carbon, is bonded to two secondary barbons. Consequently, the predictions of the $^{13}C$ chemical shift for C-4 has incorporated a correction of two times the 3° (2°) term.

Examination of the regression analysis results in Table II shows that the two sets of coefficients and corrective terms are quite similar. The most notable differences are, as might be expected, for the 3° (2°) and 2° (3°) corrective terms. These terms are now statistically more reliable because they are determined from a much larger body of relevant data. From Table I, it should also be noted that the experimental $^{13}C$ chemical shifts for the present series are now predicted with an average standard deviation 0.34 ppm, as compared to an average standard deviation of 0.61 ppm when the original Grant and Paul parameters are used. For the entire set of 113 chemical shifts, the maximum difference between the observed value and the predicted value, using the new parameters, is only about 1 ppm. For example, the difference between the observed and calculated chemical shift for C-5 in 2,6,10,14-tetramethyldecane (Table I) is 0.9 ppm. In fact, most of the deviations are considerably less than 1 ppm.

Studies by Mason[9] as well as Lindeman and Adams[10] outline other approaches to the prediction of $^{13}C$ chemical shifts in linear and branched alkanes. Mason proposes diamagnetic corrections for branching as an explanation for the corrective parameters used in the Grant and Paul model. Although the Mason work is of potential theoretical interest, some predictions based on the reported diamagnetic corrections deviate from the observed $^{13}C$ chemical shifts in branched alkane series in Table I by well over 2 ppm. The error is particularly large for internal tertiary carbons. The Lindeman and Adams work which was based on a relatively large series of linear and branched alkanes outlines a general approach which includes 22 parameters. In addition, these authors point out that another 12 parameters would be required to more adequately describe a molecule in detail.

We have found that the 13 parameters calculated in the present work and given in Table II are adequate to extend the predictions to cmr spectra of more complex hydrocarbon series, such as polymeric branched alkanes, which have structural similarities to the model compounds in Table I. The cmr spectrum prediction of hydrogenated *cis*-1,4-poly(isoprene), using the new Grant and Paul type coefficients, is adequate to provide line assignments (see Table I). In the spectrum shown in Figure 1, there are only four resonances, and there are no ambiguities in assignment. The pair of Greek letters under resonances 3 and 4 is that previously suggested[4] for identification of methylene carbons in ethylene–propylene sequences. The letters signify the number of bonds, in both directions down the molecular chain, separating a given methylene carbon atom from its nearest tertiary carbon atoms. In

(8) W. J. Youden, "Statistical Methods for Chemists," Wiley, New York, N.Y., 1951, Chapter 2.

(9) J. Mason, *J. Chem. Soc. A*, 1038 (1971).
(10) L. P. Lindeman and J. Q. Adams, *Anal. Chem.*, 43, 1245 (1971).

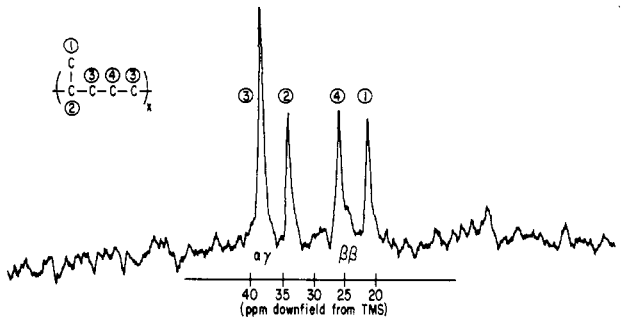


**Figure 1.** Proton noise-decoupled natural abundance 22.62-MHz $^{13}C$ nmr spectrum of hydrogenated *cis*-1,4-poly(isoprene). The spectrum was accumulated at 48° for 64 scans using a sweep width of 40 Hz/cm and a sweep rate of 60 Hz/sec from a 10% (w/v) solution in *o*-dichlorobenzene.

contrast to the spectrum in Figure 1, it has been shown by Carman and Wilkes[4a,b] that more precise predictions of carbon resonances in spectra of ethylene–propylene copolymers and terpolymers are necessary if accurate structural features are to be deduced. The relative $^{13}C$ chemical shifts of the model compounds in Table I, combined with the Grant and Paul predictions, led to the assignments of methyl carbon atoms and tertiary carbon atoms in propylene-centered pentad sequences in ethylene–propylene copolymers.[4a] In addition, these compounds provided a basis for assigning $^{13}C$ chemical shifts of methylene carbon atoms in these same copolymers to methylene carbon atoms in positions $\alpha$, $\beta$, $\gamma$, or greater than $\gamma$ bonds relative to their nearest tertiary carbon atom neighbors.

As shown in Table I, three of the molecules showed nonequivalent isopropyl methyl carbons which were not predicted by the substituent parameters. Differences in $^{13}C$ chemical shifts have been previously reported for methyl carbons in terminal isopropyl groups and were attributed to the presence of an asymmetric carbon atom.[10,11] It was also shown,[11] that the differences in $^{13}C$ chemical shifts decreased as the number of methylene groups between the isopropyl group and the asymmetric carbon increased. In the present study, we observed magnetic nonequivalence between the methyl carbons of isopropyl groups in two molecules which do not contain an asymmetric carbon atom. These compounds are 2,4,6-trimethylheptane and 2,5,8-trimethylnonane.

We suggest that a reasonable interpretation of the observed nonequivalence can be attributed to differences in rotational conformations in the molecules. Demonstration of magnetic nonequivalence of isopropyl methyl carbons can be shown by considering the planar zigzag conformation of 2,4,6-trimethylheptane and 2,5,8-trimethylnonane shown in Figure 2a,b. The methyls designated as $CH_3(a)$, $CH_3(b)$, and $CH_3(c)$ represent the three possible relationships the isopropyl methyl can have, relative to the internal methyl carbon. Although the isopropyl methyl carbons would be rapidly interchanging position, due to rotation, the distances between an isopropyl methyl group and an internal methyl group are not equal. This spatial relationship can be verified with Dreiding molecular models. Furthermore, the molecular models show that differences in the distances from the internal methyl carbon to the three positions the isopropyl methyl carbons can experience are less when a second methylene carbon is added between the tertiary carbon atoms.

The difference in $^{13}C$ chemical shift between the nonequivalent methyl carbons is 1.07 ppm if one carbon atom

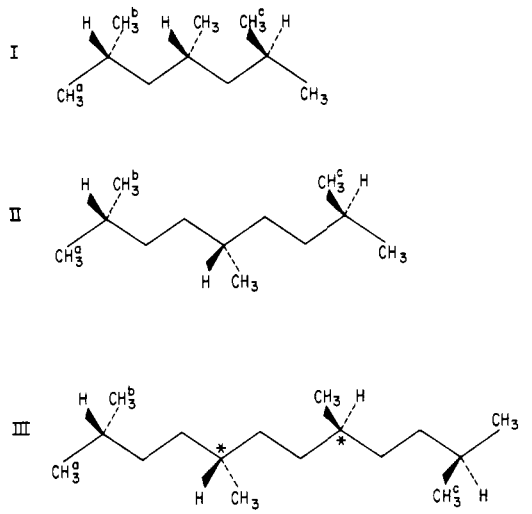


**Figure 2.** Planar zigzag representation of 2,4,6-trimethylheptane (I), 2,5,8-trimethylnonane (II), and 2,5,8,11-tetramethyldodecane (III). Asymmetric carbon atoms are designated with an asterisk.

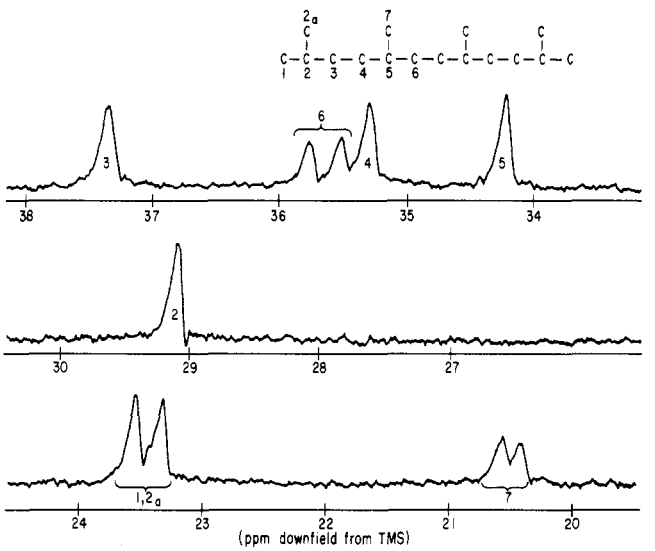


**Figure 3.** Proton noise-decoupled natural abundance 22.62-MHz $^{13}C$ nmr spectrum of neat 2,5,8,11-tetramethyldodecane. The spectrum was accumulated at 48° for 8 scans using a sweep width of 2 Hz/cm and a sweep rate of 3 Hz/sec.

separates the tertiary carbon atom and the isopropyl group, or 0.22 ppm if two carbon atoms separate the isopropyl group and a tertiary carbon atom. These results are in exact agreement with the relative $^{13}C$ chemical shift differences reported[11] for isopropyl methyl carbons in branched alkanes containing an asymmetric carbon atom. As can be seen in Table I, no differences were observed in $^{13}C$ chemical shifts of the isopropyl carbons if the number of methylene carbon atoms between the tertiary carbon atoms exceeds two. It is also noteworthy that the 1.07 ppm difference in isopropyl methyl chemical shift for compound I in Figure 2 is the same order of magnitude as the 1.00 ppm difference in $^{13}C$ chemical shifts for the methyl carbons in racemic and meso-2,4-dichloropentane.[12] In those compounds there is also one methylene carbon atom separating the tertiary carbon atoms. Interactions between carbons with trans and gauche conformations seemed to provide a plausible explanation of the cmr

(11) J. I. Kroschwitz, M. Winokur, H. J. Reich, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 5927 (1969).

(12) C. J. Carman, A. R. Tarpley, Jr., and J. H. Goldstein, *J. Amer. Chem. Soc.*, 93, 2864 (1971).

**Table III**
**Relative $^{13}C$ Chemical Shifts of Nonequivalent Carbons Which Result from Conformational and Configurational Interactions**

| Compound | $\Delta^{13}C$ (ppm) | | |
|---|---|---|---|
| | Terminal[a] $CH_3$ | Internal[b] $CH_3$ | Internal[c] $CH_2$ |
| 2,4,6-Trimethylheptane(I)[d] | 1.07 | | |
| 2,5,8-Trimethylnonane(II)[d] | 0.22 | | |
| 2,5,8,11-Tetramethyldodecane(III)[d] | 0.21 | 0.15 | 0.26 |

[a] Isopropyl methyl carbons. [b] Methyl carbons internal along the molecular chain, away from the chain ends. [c] Methylene carbons internal in the molecular chain, between asymmetric carbons. [d] I, II, and III refer to the structures in Figure 2.

spectra of the diastereoisomers of the dichloroalkanes.[12] Consequently, it is reasonable that conformational interactions may be reflected in the cmr spectra of methyl substituted alkanes that are structurally analogous. These data also substantiate[11] that even though 1,5 $CH_3$–$CH_3$ interactions (I, Figure 2) and 1,6 $CH_3$–$CH_3$ interactions (II, Figure 2) are weaker than the usual steric effects[13-15] reported for 1,4 $CH_3$–$CH_3$ interactions, the longer range interactions are sufficiently strong to be detected using cmr.

Compound III (2,5,8,11-tetramethyldodecane) in Figure 2 is interesting because this compound contains nonequivalent carbon atoms due to both conformational and configurational effects. The difference in chemical shifts for the terminal methyl carbons is 0.21 ppm. The fact that this value is essentially the same as that observed for II, suggests that a common origin for magnetic nonequivalence exists, and this obviously cannot be the presence of an asymmetric carbon atom. However, III has diastereoisomers. Consequently, the internal methyl carbons and the two methylene carbons, between the internal tertiary carbons, can reside in magnetically nonequivalent configurations. Such nonequivalence would be because the chemical environment of the meso isomer would be different than that of the racemic isomer. The natural abundance cmr spectrum of 2,5,8,11-tetramethyldodecane is shown in Figure 3. The relative areas of the internal methyl and methylene carbons are equal as one would expect, *e.g.*, because of equal populations of methyl group configurations.

The relative differences in $^{13}C$ chemical shifts resulting from different molecular configurations are summarized in Table III. These are compared to the relative differences in $^{13}C$ chemical shifts resulting from molecular conformation. These data add to the growing evidence that cmr spectroscopy can be used to distinguish differences between extremely subtle molecular structures. These data also show that the interpretation of methyl carbon resonances in cmr spectra may be complicated because conformational interactions can exist even in the absence of an asymmetric carbon atom, and thus cause magnetic nonequivalence to be present. This finding may prove useful in the interpretation of very complex cmr spectra of biological systems where multiple resonances are common.[16,17]

**Acknowledgment.** We thank Dr. E. C. Gregg, Jr., of The B. F. Goodrich Co. for providing the model compounds. We acknowledge Professor S. Krimm of the University of Michigan for helpful discussions on the effects of molecular conformations and configurations. Our thanks also to The B. F. Goodrich Co. for permission to publish this work and to the National Institutes of Health for partial support of that work carried out at Emory University.

(13) D. M. Grant and B. V. Cheney, *J. Amer. Chem. Soc.*, **89**, 5315 (1967).
(14) D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 6612 (1967).
(15) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Amer. Chem. Soc.*, **92**, 1338 (1970).
(16) W. Horsley, H. Sternlicht, and J. S. Cohen, *J. Amer. Chem. Soc.*, **92**, 680 (1970).
(17) D. E. Dorman and J. D. Roberts *J. Amer. Chem. Soc.*, **93**, 4463 (1971).