data in Figure 1 may be meaningless in the strict sense of the term. Nevertheless, Figure 1 shows that the presence of lecithin in the system brings about little influence on the monomer reactivity ratios in appearance throughout the copolymerization. Therefore the reactivity ratios in the presence of lecithin are thought to bear a close resemblance to those in the absence of it.

As shown in Figure 2, the rate of copolymerization decreased with an increase in mole fraction of IN in monomer feed in the absence of lecithin. This result can be accounted for by the difference in reactivities of the two monomers, that is, AAc is more susceptible to homopolymerization than IN. Interestingly, the rate of copolymerization was increased by the addition of lecithin, except in the case of homopolymerization of AAc. The rate enhancement by lecithin may be due to a preferable orientation of IN and AAc for the copolymerization.

In addition to the rate enhancement, the copolymer obtained in the presence of lecithin had an optical activity, the sign of which was opposite to that of lecithin. The optical rotatory dispersion (ORD) measurements for the copolymers gave negative plain curves, from which λ_0 values were calculated as about 220 nm, using the simple Drude equation.[6]

Figure 2 also shows specific rotation of the copolymer as a function of the mole fraction of IN in the monomer feed. The absolute value of the specific rotation was increased with an increase in IN monomer units of the copolymer as a result of increasing mole fraction of IN in monomer feed. Needless to say, the asymmetric carbon atoms occur in the copolymers only where IN–AAc or AAc–IN bonds are present. Consequently, the specific rotation of the copolymer must have an interrelation with the run number.[7] The run number of dyad sequences of -IN·AAc- and -AAc·IN- per 100 monomer units, R, is defined as the following equation:

$$R = \frac{200}{2 + r_1x + r_2/x}$$

where x is molar ratio of feed monomers and r_1 and r_2 are monomer reactivity ratios. Figure 3 shows the relationship between the specific rotation of the IN/AAc copolymer and its run number, using r_1 and r_2 values calculated for the copolymerization in the absence of lecithin for the reason described already. In accordance with the relationship, the plot is found to be approximately linear.

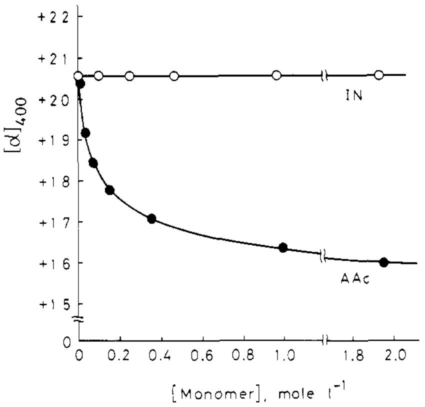

Figure 4. Variation in specific rotation of lecithin: [lecithin] = 3.1 × 10^{-2} mol L^{-1} (c 2.43, benzene); temperature 25 °C.

The asymmetric induction is undoubtly caused by the electrostatic interaction between the polar monomer, AAc, and the polar head group of lecithin. Figure 4 shows the variation in specific rotation of lecithin by addition of AAc. As can be seen from Figure 4, the nonpolar monomer, IN, does not affect the specific rotation of lecithin, whereas the polar monomer, AAc, decreases significantly the specific rotation. This result indicates that there is a fair electrostatic interaction between AAc and lecithin. In conclusion, the asymmetric induction can be considered to be conducted by a stereospecific copolymerization of IN with AAc affected by the chiral surface active substance, lecithin.

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The Carbon-13 Nuclear Magnetic Resonance Methyl Shift in Models of Regioirregular Polypropylene[1]

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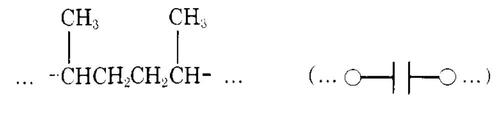
ABSTRACT: Model compounds for irregular arrangements of monomer units in polypropylene have been synthetized. The ^{13}C-NMR spectra have been assigned, considering also the steric structure of the hydrocarbons. An empirical relationship for predicting the ^{13}C methyl shift is proposed, based on constitution and configuration.

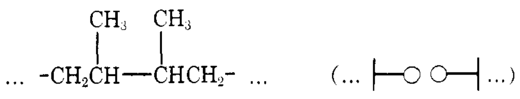
I. Introduction

The highly isotactic polymers of propylene, such as those obtained in the presence of catalytic systems consisting of violet titanium trichloride and organometallic compounds of aluminium, show a very regular chemical arrangement of the monomer units, i.e., head-to-tail.

On the contrary a small amount of head-to-head and tail-



$$\ldots\ \text{-}\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}H\text{-}\ \ldots \qquad (\ldots \circ\!\!-\!\!\dashv\ \vdash\!\!-\!\!\circ \ldots)$$



$$\ldots\ \text{-}CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}H\text{—}\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2\text{-}\ \ldots \qquad (\ldots \vdash\!\!-\!\!\circ\ \circ\!\!-\!\!\dashv \ldots)$$

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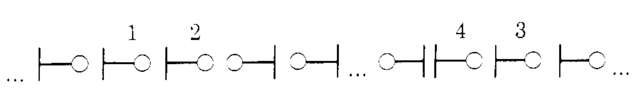
to-tail arrangement is detectable in both syndiotactic and stereoirregular (atactic) polypropylene.[2,3]

Of course the presence of such arrangements must be taken into account while interpreting the ^{13}C-NMR spectrum of the polymer, because this probe is very sensitive both to chemical and steric structure, and, from a detailed knowledge of the structure, information can be drawn on the polymerization mechanism.

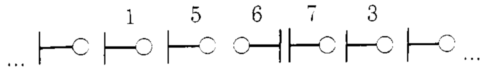
The purpose of this work is first to determine the chemical shift of the methyl group in different alkanes, which may be considered as reasonable models of irregularly arranged polymers of propylene. The other aspect of the work is concerned with the interpretation of the chemical shift of the methyl group in terms of its steric configuration.

The final goal of this work is to provide a basis for the assignment of the signals due to any type of methyl group (neglecting end groups) possibly present in polypropylene containing a small amount of irregularly arranged monomer units.

As discussed in previous papers[2b–6] two limit structures are possible for polymers containing isolated errors in the arrangement of the monomer units:



A



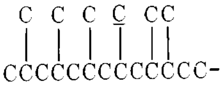
B

In case A the polymer contains blocks of units with head-to-tail orientation (⊢O⊢O) and blocks of units with tail-to-head orientation (O⊣O⊣). The change from one block to the next along the polymer chain should be in principle monitored by the ^{13}C shift of methyls 1, 2, 3, and 4.

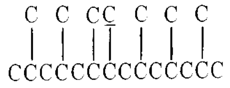
The alternative structure B consists of a polymer having some monomer units with inverted orientation, randomly distributed along the chain. This situation should be in principle monitored by the ^{13}C chemical shift of methyl groups 1, 3, 5, 6, and 7.

It is apparent that the shift of methyls 2 and 4 is diagnostic for structure A whereas the shift of methyls 5, 6, and 7 is diagnostic for structure B.

On the basis of these considerations the following alkanes have been synthesized as models for the seven types of above mentioned methyl groups:



1



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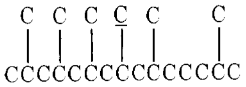

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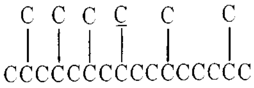

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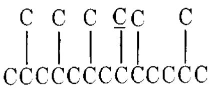

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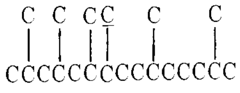
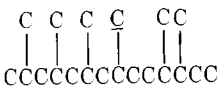


6



7

The methyl groups which are useful as microstructural probes are those underlined in the above formulas. In order to simplify the spectra of the hydrocarbons the underlined methyls were 70% enriched with carbon-13; consequently the spectrum of each sample, which contains all the possible stereoisomers, is expected to show 2^{n-1} enhanced signals (neglecting degeneracies) due to the enriched methyl group, n being the number of asymmetric carbon atoms present in the considered molecule. Numbering of hydrocarbons is consistent with the previous numbering of methyl groups in the polymer.

Although these model compounds are not exact reproductions for structural sequences 3, 4, and 6 they may be considered appropriate models for methyls 3, 4, and 6.

II. Experimental Section

Preparations. ^{13}C-enriched hydrocarbons 1 to 8 were synthesized following essentially the same steps described in previous papers for similar hydrocarbons.[6,7] Experimental details will be given in a subsequent paper together with the characterization by GLC and mass spectrometry.

The final steps of the synthesis of 1 to 8 were (a) methylation of the parent ketones with ^{13}C-enriched lithium methyl in diethyl ether and (b) catalytic C–OH hydrogenolysis of the resulting tertiary alcohols (T = 135 °C, p_{H_2} = 30 atm, catalyst = 10% palladium on charcoal, solvent = cyclohexane, in the presence of a trace amount of a halogenated hydrocarbon (1,2,5-trichlorobenzene)).

Compounds 9 and 11 were prepared by reaction of n-pentyllithium in diethyl ether with 2,3-butanedione and 2,5-hexanedione, respectively, with a molar ratio 2 to 1. After hydrolysis the resulting carbinols were subjected to catalytic hydrogenolysis as described above and the reaction products (9 and 11) were recovered by fractional distillation (bp 241 and 273 °C, respectively).

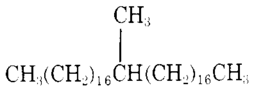
Compound 10 was prepared by coupling in diethyl ether a mixture of meso (80%) and racemic (20%) 1,5-dichloro-2,4-dimethylbutane with n-buthyllithium, in molar ratio 1/2. Also in this case the reaction product was separated by fractional distillation (bp 255 °C).

Spectra. Samples were prepared by dissolving the hydrocarbons in 1,2,4-trichlorobenzene (10% v/v) and by adding 1% of hexamethyldisiloxane (HMD) as an internal reference. Samples were placed in 10-mm o.d. tubes containing a coaxial capillary of deuterated dimethyl sulfoxide for field-frequency stabilization. Spectra were measured with an HX-90 Bruker spectrometer operating at 22.63 MHz in the PFT mode. The temperature of the probe was 140 °C and the variable temperature unit was checked with the ethylene glycol sample before the runs. Dwell time of 184 μs was used with 16K of computer memory for the interferogram, corresponding to an acquisition time of 3 s and to a digital resolution of 0.015 ppm/address. The pulse width was 3.5 μs (the pulse width for a 90 ° pulse for the nucleus being examined is 15 μs). No exponential weighting function of the FID was used.

III. Results and Discussion

The chemical shifts of the ^{13}C-enriched methyls in the examined hydrocarbons are reported in Table I.[22] Configurational stereosequence of each diastereomer hydrocarbon is given by the following: (1) Greek letters denoting the number of bonds between a reference methyl (the observed ^{13}C enriched one) and the other diastereotopic methyl substituents on both sides along the backbone; (2) the two sides of the backbone (relative to the reference methyl) are distinguished by priming the Greek letters denoting the methyl substituents on one of the two sides along the backbone; (3) symbols e (erythro) or t (threo) which mean that one given methyl (for instance the ϵ') in the Fisher projection[20] is on the same side (with respect to the backbone) as the reference methyl or on the opposite side.

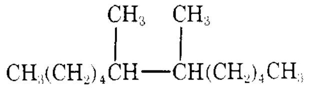
The assignment of the individual lines to the different methyl configurations was obtained by using the procedure outlined here. The chemical shift of the central methyl group in the hydrocarbon 8, determined in the same conditions of



$$\overset{CH_3}{CH_3(CH_2)_{16}CH(CH_2)_{16}CH_3}$$

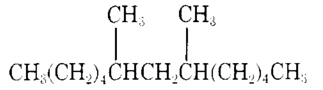
8

the other molecules, resulted at 17.99 ppm from HMD. This shift was compared with that of the side chain methyl groups in the following molecules (for the assignment see later in the text):



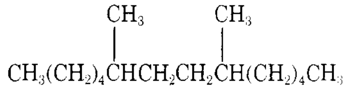
$$\mathrm{CH_3(CH_2)_4\overset{\overset{CH_3}{|}}{C}H{-}\overset{\overset{CH_3}{|}}{C}H(CH_2)_4CH_3}$$

9, meso δ 14.94; racemic δ 13.16



$$\mathrm{CH_3(CH_2)_4\overset{\overset{CH_3}{|}}{C}HCH_2\overset{\overset{CH_3}{|}}{C}H(CH_2)_4CH_3}$$

10, meso δ 18.76; racemic δ 18.21



$$\mathrm{CH_3(CH_2)_4\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{CH_3}{|}}{C}H(CH_2)_4CH_3}$$

11, meso δ 18.15; racemic δ 18.05

hydrogenated polyisoprene[5,9]

12, meso, meso δ 18.00; meso, racemic δ 17.97; racemic, racemic δ 17.94

The comparison shows that the chemical shift of the methyl group in the paraffinic chain **8** is modified by the presence of another methyl group in the γ, δ, ε, and ζ position. Of course this observation is in agreement with the effect described by the empirical rule of Grant[10] for saturated hydrocarbons. However, in addition to this, the present data show that the

Table I
^{13}C Chemical Shift of Model Hydrocarbons (Labeled Methyls)[a]

	Chemical shift		Assignment			
Compd	Measured	Predicted	ζ	δ	δ′	ε′
1	19.89	19.93	e	e	e	e
	19.72	19.73	t	e	e	e
	19.60	19.60	e	e	e	t
	19.41	19.40	t	e	e	t
	19.19	19.21	e	t	e	e
	19.07	19.08	t	t	e	e
	18.91	18.88	e	t	e	t
	18.88	18.88	e	e	t	e
	18.79	18.75	t	t	e	t
	18.70	18.72	e	e	t	t
	18.70	18.68	t	e	t	e
	18.53	18.52	t	e	t	t
	18.18	18.16	e	t	t	e
	18.03	18.03	t	t	t	e
	18.00	18.00	e	t	t	t
	17.86	17.86	t	t	t	t
			ζ′	δ′	γ	ε
2	15.66	15.82	e	e	e	e
	15.58	15.62	t	e	e	e
	15.30	15.44	e	e	e	t
	15.28	15.24	t	e	e	t
	15.14	15.10	e	t	e	e
	15.12	14.97	t	t	e	e
	14.92	14.72	e	t	e	t
	14.85	14.59	t	t	e	t
	13.78	14.02	e	e	t	e
	13.65	13.82	t	e	t	e
	13.32	13.54	e	e	t	t
	13.27	13.34	t	e	t	t
	13.27	13.30	e	t	t	e
	13.25	13.17	t	t	t	e
	12.90	12.82	e	t	t	t
	12.86	12.69	t	t	t	t
			ζ	δ	δ′	
3	19.58	19.60	e	e	e	
	19.39	19.40	t	e	e	
	18.98	19.05	e	e	t	
	18.88	18.88	e	t	e	
	18.82	18.85	t	e	t	
	18.75	18.76	t	t	e	
	18.30	18.33	e	t	t	
	18.16	18.20	t	t	t	
			ζ	δ	ε′	
4	18.93	18.99	e	e	e	
	18.84	18.89	e	e	t	
	18.75	18.79	t	e	e	
	18.65	18.69	t	e	t	
	18.24	18.27	e	t	e	
	18.14	18.17	e	t	t	
	18.14	18.14	t	t	e	
	18.04	18.04	t	t	t	
			ζ′	δ′	γ	
5	15.54	15.78	e	e	e	
	15.45	15.58	t	e	e	
	15.20	15.06	e	t	e	
	15.11	14.93	t	t	e	
	13.65	14.00	e	e	t	
	13.55	13.80	t	e	t	
	13.27	13.28	e	t	t	
	13.21	13.15	t	t	t	
			ε	γ	ε′	
6	15.08	15.26	e	e	e	
	15.06	15.16	t	e	e	
	14.73	15.16	e	e	t	
	14.69	15.06	t	e	t	
	13.33	13.48	e	t	e	
	13.25	13.38	t	t	e	
	12.84	13.38	e	t	t	
	12.78	13.28	t	t	t	
			ζ	δ	ε′	ζ′
7	19.01	19.04	e	e	e	e
	18.97	18.96	e	e	e	t
	18.87	18.94	e	e	t	e
	18.84	18.86	e	e	t	t
	18.84	18.84	t	e	e	e
	18.78	18.76	t	e	e	t
	18.68	18.74	t	e	t	e
	18.63	18.66	t	e	t	e
	18.32	18.32	e	t	e	e
	18.27	18.24	e	t	e	t
	18.24	18.22	e	t	t	e
	18.16	18.14	e	t	t	t
	18.16	18.19	t	t	e	e
	18.12	18.11	t	t	e	t
	18.08	18.09	t	t	t	e
	18.03	18.03	t	t	t	t
			ζ	δ	δ′	ζ′
AB of ref 7	19.80	19.67	e	e	e	e
	19.58	19.47	e	e	e	t
	19.39	19.27	t	e	e	t
	19.04	18.95	e	e	t	e
	18.90	18.82	e	e	t	t
	18.90	18.75	t	e	t	e
	18.76	18.62	t	e	t	t
	18.35	18.23	e	t	t	e
	18.22	18.10	t	e	e	e
	18.10	17.97	t	t	t	t

[a] Measured from internal HMD.

Table II
Carbon-13 Chemical Shift Additivity Parameters for Diastereomeric Paraffins

	γ	δ	ϵ	ζ
Erythro	−3.05	0.77	0.16	0.05
Threo	−4.83	0.22	0.06	−0.03

R_{ij}	$R_{\delta\zeta}$	$R_{\delta\epsilon}$	$R_{\gamma\epsilon}$
e e	0.02	0.17	−0.12
e t	−0.10	−0.06	−0.40
t e	−0.15	−0.33	−0.14
t t	−0.20	−0.39	−0.52

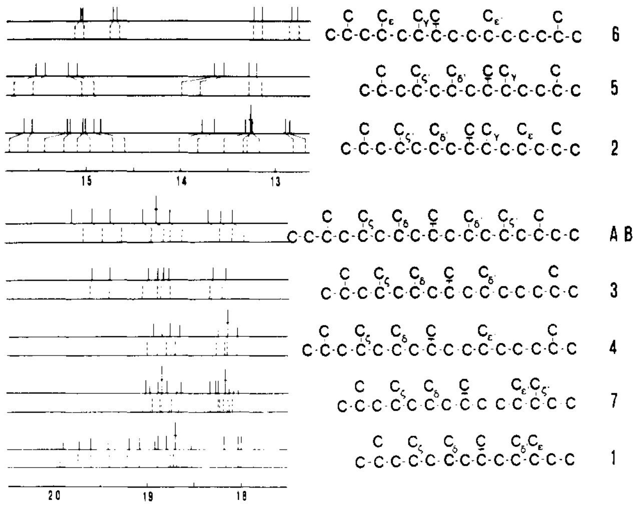


Figure 1. Observed (full line) and predicted (broken line) stick spectra of model compounds of polypropylene.

shielding effect depends on whether the steric relationship between the two methyl groups is meso or racemic and, more in general, erythro or threo. This stereospecific character of the adjacent methyl shielding is responsible for the dispersion of the chemical shift of the methyl group of polypropylene, which has already been correlated with the different pentad configurations.[7,11–13]

The above observations suggest that it may be possible to estimate the chemical shift of a methyl in a paraffinic chain, such as the title compounds and polypropylene itself, through an additivity scheme of the kind introduced by Grant and making allowance for configurational effects.

Following this idea the shift of the methyl is given by the empirical relation

$$\nu = 17.99 + \Sigma N_i P_i + \Sigma R_{ij}$$

where 17.99 is the shift of the methyl 17′ in the parent compound **8**, N_i is the number of methyl groups having a definite distance from and a steric relation with the observed methyl, P is the additivity parameter characterizing both the distance (γ, δ, ϵ, ζ) and the steric relationship (erythro or threo), and R_{ij} is a parameter which describes the effect of the proximity of two methyl substituents and it is dependent on their steric relation.

The values of the parameter P were obtained from the comparison of the shift of methyl in **8** with that of **9, 10, 11,** and **12.** The parameters R were introduced in order to have a better fitting between calculated and observed line positions. The procedure is similar to that followed by Grant, who has also introduced interaction terms in his empirical scheme.

The values of the parameters P and R, used in calculating the line positions in the present work, are collected in Table II; the comparison between observed and predicted line positions is reported in Table I and in Figure 1 for model compounds 1 to 7 and for hydrocarbon AB of ref 7, which is the model compound for steric pentads of regioregular polypropylene.[13]

The results show that the agreement between calculated and observed spectrum is in most cases fairly good, although discrepancies are present, particularly with compounds **2** and **5.** In any case the above procedure allows one to predict the sequence of line positions and consequently to give a self-consistent rationalization of all the signals due to different steric structures in all the observed compounds.

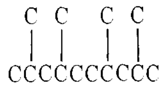
The R parameter reflects the effect on the chemical shift of conformational factors which must certainly be taken into account beside the constitutional and configurational effects. The conformational analysis of these data of the present comunication should be the obvious step forward in the rationalization of the factors governing the ^{13}C chemical shift in hydrocarbon polymers.[14]

Finally we point out that the numerical values of P and R correspond to 140 °C, the typical temperature for measuring polyolefin spectra. A change of their values may be expected for lower temperatures.

Assignment of the Simple Models 9–12. The shielding of the side chain methyl in **9** is very close to that previously measured in *cis*-2-butene/ethylene and in *trans*-2-butene/ethylene copolymers prepared with Ziegler catalysts.[15] The configuration of the 2-butamer units is erythro in *cis*-2-butene copolymers and threo in *trans*-2-butene copolymers.[16,17] Since the methyl of *cis*-2-butene copolymer was observed at lower shielding than that of the trans copolymer it follows, by analogy, that the erythro (or meso) methyl in **9** is to be assigned at lower field than the threo (or racemic) methyl.

The assignment of the methyl in **10** was obtained by examining the spectrum of a sample containing an excess of the meso form over the racemic form.

The assignment of the methyl in **11** was established by comparison with the spectra of the separated meso and racemic forms of the hydrocarbon **13** in which methyl 4′ (≡7′) absorbs at lower field for the meso than for the racemic form.[18]



$$\mathrm{C\overset{C}{C}C\overset{C}{C}CC\overset{C}{C}C\overset{C}{C}C}$$

13

Finally the assignment of hydrogenated polyisoprene is that previously reported[8] in the literature.

Chemical Check of Assignments. The synthesis of hydrocarbons starting from ketones of known stereoisomeric composition provides a partial check of the assignments, although in Pd-catalyzed hydrogenolysis (see Experimental Section) partial isomerization can occur, especially on a substituted carbon closer than three bonds to the oxygen.[19] Actually the concentration of different stereoisomeric ketones could be correlated with the intensity of the signals in the spectrum of the synthetized hydrocarbons. Figure 2 shows for instance the spectra of ^{13}C-enriched methyls of 3, 4, and 1. These hydrocarbons were prepared from ketones containing different diastereomers[23] in decreasing concentrations as follows: 2,4,6,10,14-pentamethylpentadecan-8-one (**3**) diastereomer content $4^+, 6^+, 10^- > 4^+, 6^+, 10^+ > 4^+, 6^-, 10^- > 4^+, 6^-, 10^+$; 2,4,6,11,15-pentamethylhexadecan-8-one (**4**) diastereomer content $4^+, 6^+, 11^+ > 4^+, 6^+, 11^- > 4^+, 6^-, 11^+ > 4^+, 6^-, 11^-$; 3,4,8,10,12-pentamethyltridecan-6-one (**1**) diastereomer content $3^+, 4^+, 8^+, 10^+ = 3^+, 4^+, 8^-, 10^- > 3^+, 4^-, 8^-, 10^- = 3^+, 4^-, 8^+, 10^+ > 3^+, 4^+, 8^-, 10^+ = 3^+, 4^+, 8^+, 10^- > 3^+, 4^-, 8^-, 10^+ = 3^+, 4^-, 8^+, 10^-$.

These diastereoisomer compositions can be compared with the intensities of the lines in the spectra of Figure 2 consid-

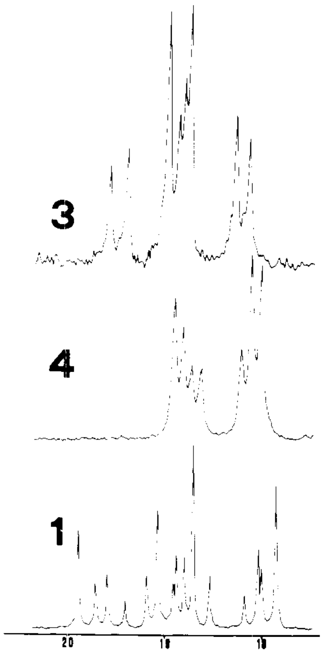


Figure 2. ^{13}C spectra of enriched methyls of hydrocarbons **3**, **4**, and **1**.

ering that each ketone stereoisomer gives two diastereomer hydrocarbons depending on the + or − configuration of the new asymmetric carbon (i.e., of that linked to the labeled methyl). Hydrocarbon stereoisomers are named from the steric relation between the carbon bearing the enriched methyl and each one of the others.

IV. Conclusions

The results of this work show the following: The ^{13}C chemical shift of the methyl group in irregular arrangements of polypropylene is in some cases very close to that of the regular polymer, and this fact must be considered in the interpretation of the fine structure of the signals in this region of the spectrum. The ^{13}C chemical shift of the methyl group can be rationalized by an empirical additivity scheme which considers both constitutional and configurational factors.

The assignments obtained with this approach are in agreement with the synthesis of some of the model compounds starting from intermediates of known stereochemical structure. However, for a further understanding of the present data the chemical shift should be correlated with the conformation.

Finally the above assignments, particularly those of the model compounds for tail-to-tail arrangements, give further information on the mechanism of stereo and regiospecific control of propylene polymerization.[24]

References and Notes

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(22) In the table is included for comparison the spectrum of the model of polypropylene, already assigned.[7]
(23) Diastereomers are denoted according to the relative configuration of substituted carbons: these are denoted by + and − so that the substituents bearing equal signs are erythro (on the same side in the Fisher projection) and those bearing different signs are threo (on different sides in the Fisher projection).
(24) After this work was completed a paper[21] appeared in the literature with assignments of **9–12** in agreement with the present results.