

## **<sup>13</sup>C-NMR Determination of Inverted Propylene Units in Polypropylene**

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### **Summary**

The <sup>13</sup>C NMR spectra of regioirregular polypropylene samples were fully interpreted. The complex spectral patterns were shown to originate from inverted propylene sequences and tacticity. The spectra were analyzed by a reaction probability model; both tacticity and the amount of propylene inversion can be determined. The computations have been automated.

### **Introduction**

<sup>13</sup>C NMR analysis of polypropylene has been reported numerous times in the literature (1-4). Most of the efforts have concentrated on tacticity, especially pentad analysis of the methyl resonances. Only a few papers have dealt with inverted propylene sequences (5-8). Yet, many catalyst systems are known to be non-regiospecific (9), and head-to-head and tail-to-tail structures invariably occur to some extent.

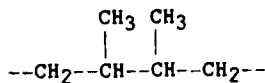
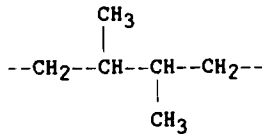
Asakura, Doi, and coworkers (5-7) had previously provided assignments for the spectra of regioirregular polypropylenes. In this work, a reexamination of the <sup>13</sup>C NMR spectra has been made, and a revised and more detailed interpretation produced. On the basis of these revised assignments, analytical schemes have been devised that give more accurate information on propylene inversion and propylene tacticity.

### **Results and Discussion**

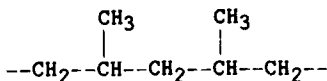
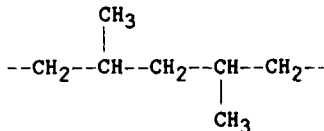
Since we are dealing with stereoirregular and regioirregular polymers, a proper terminology is needed when referring to the various microstructures encountered in the NMR spectra. In this work, two sets of nomenclatures will be used. The first is that of Carman, et al. (10) as expanded by Smith (11) and Doi (7). In this system, S, T, P refer respectively to secondary (methylene), tertiary (methine), and primary (methyl) carbons. Two Greek subscripts are used, referring to the distances the nearest methyl groups are placed from the carbon in question. Where four Greek subscripts appear, they refer to the distances of the two nearest methyl substituents on each side of the given carbon.

In the second nomenclature (12), the polymer chain is represented by 0 and 1, with 0 for methylene and 1 for methyl/methine units. Furthermore, the relative configuration is shown by 1 (for meso placements) and  $\bar{1}$  (for racemic). Where an underlined  $\underline{1}$  occurs, both meso and racemic structures apply. For convenience, tacticity is also represented by m (meso) or r (racemic) with a subscript corresponding to the number of methylene units between the methyls/methines, e.g.

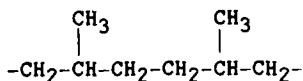
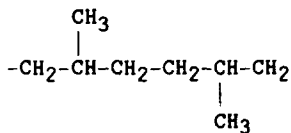
0110

 $m_0$ 01 $\bar{1}$ 0 $r_0$ 

01010

 $m_1$ 010 $\bar{1}$ 0 $r_1$ 

010010

 $m_2$ 0100 $\bar{1}$ 0 $r_2$ 

## II. Spectral Assignments

One may consider stereoirregular and regioirregular polypropylene to be the product of binary copolymerization of head-first polypropylene (01) and tail-first polypropylene (10). Inclusion of configuration (tacticity) produces eight possible equations:



The first four reactions where propylene adds tail-first between the polymer and the catalyst are "secondary insertions" or "2-1 additions"; the last four reactions (with propylene adding head-first) are "primary insertions" or "1-2 additions". The metal-carbon bond in the reactants can be either secondary (Equations 1, 3) or primary (Equations 2, 4). It is apparent that for non-stereoselective polymerizations, all three tacticities ( $m_0/r_0$ ,  $m_1/r_1$ ,  $m_2/r_2$ ) can occur.

The  $^{13}\text{C}$  NMR spectrum for a sample of irregular polypropylene is shown in Figure 1. The spectral features are broad, indicating the presence of complex structures. A major deficiency in the earlier assignments (5-7) is that the effect of tacticity is not taken into account in the regioirregular sequences. Yet, from the above scheme (Equations 1-4) and from the earlier work on ethylene-propylene rubbers (12), it is clear that a complete spectral interpretation must specifically include tacticity. Drawing analogy to ethylene-propylene rubbers (12), one can re-interpret the spectra and provide revised and more detailed assignments. These are given in Table 1. For comparison, the earlier assignments of Doi (7) are also included.

The largest discrepancies in assignments between this work and those of Doi and Asakura (5-7) are found with the methylenes. For example, in this work a group of bands are found in the 41.0-42.0 ppm region corresponding to  $m_0\text{-S}\beta\alpha\alpha\gamma$  and  $m_0\text{-S}\beta\alpha\alpha\delta$ . The detailed assignments for  $\text{S}\beta\alpha\alpha\gamma$  and  $\text{S}\beta\alpha\alpha\delta$  are indicated in Table 1. The splitting between  $m_0$  and  $r_0$  structures is on the order of 2 ppm. Similar splittings between  $m_0$  and  $r_0$  for

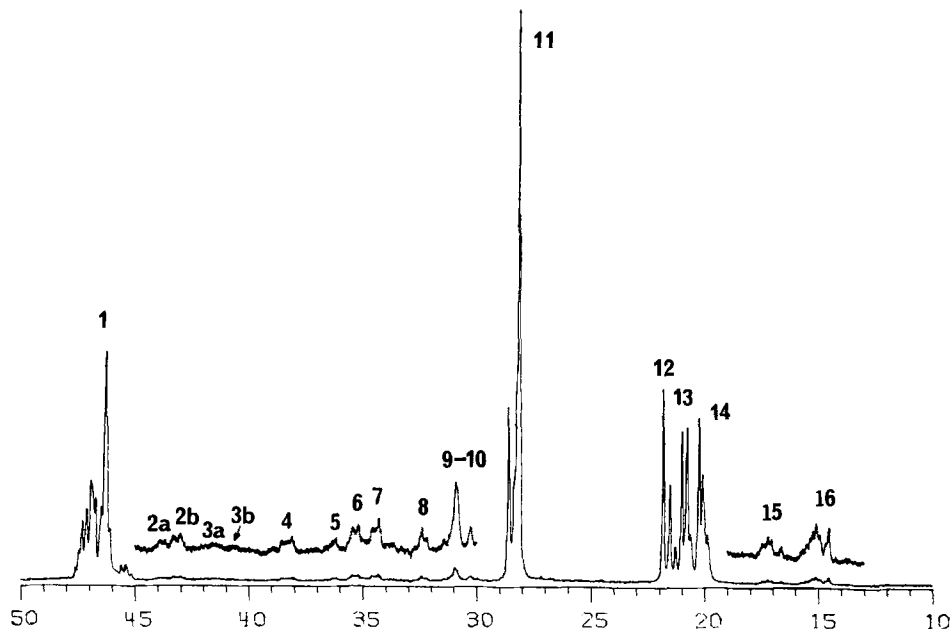


Figure 1:  $^{13}\text{C}$  NMR Spectrum at 90 MHz of a Stereoirregular and Regioirregular Polypropylene

Table 1.  $^{13}\text{C}$  NMR Assignments for Irregular Polypropylene

No.	Shift (ppm)	Assignment given in this Work		Doi (Ref. 7)
		Designation	Structure	
1a	45.0-47.0	$S_{\gamma\alpha\alpha\gamma}$	$101\dot{0}101$	$S_{\gamma\alpha\alpha\gamma}$
1b		$S_{\gamma\alpha\alpha\delta}$	$101\dot{0}100$	$S_{\gamma\alpha\alpha\delta}$
2a	ca. 43.8	$r_o-S_{\beta\alpha\alpha\gamma}$	$011\dot{0}101$	} $S_{\beta\alpha\alpha\gamma} + S_{\beta\alpha\alpha\delta}$
2b	ca. 43.0	$r_o-S_{\beta\alpha\alpha\delta}$	$011\dot{0}100$	
3a	ca. 41.8	$m_o-S_{\beta\alpha\alpha\gamma}$	$011\dot{0}101$	} n.r. (a)
3b	ca. 41.0	$m_o-S_{\beta\alpha\alpha\delta}$	$011\dot{0}100$	
4a	39.0	$m_o-T_{\alpha\gamma}$	$011\dot{0}01$	$T_{\alpha\gamma}$
4b	38.2	$r_o-T_{\alpha\gamma}$	$0\bar{1}1\dot{0}01$	
5a	36.8	$m_o r_1-S_{\gamma\alpha\beta\gamma}$	$\bar{1}01\dot{0}011 + \bar{1}01\dot{0}0\bar{1}\bar{1}$	n.r. (a)
5b	36.2	$r_o r_1-S_{\gamma\alpha\beta\gamma}$	$\bar{1}01\dot{0}01\bar{1} + \bar{1}01\dot{0}0\bar{1}\bar{1}$	
6	35.0-36.0	$m_o-T_{\alpha\beta}$	$011\dot{0}1$	} $T_{\alpha\beta}$
		$m_1-S_{\gamma\alpha\beta\gamma}$	$101\dot{0}011$	
		$r_1-S_{\gamma\alpha\beta\delta}$	$\bar{1}01\dot{0}0101$	
7	33.7-35.0	$r_o-T_{\alpha\beta}$	$0\bar{1}1\dot{0}1$	} $S_{\gamma\alpha\beta\gamma} + S_{\gamma\alpha\beta\delta}$
		$m_1-S_{\gamma\alpha\beta\delta}$	$101\dot{0}0101$	
8	32.0-32.7	$r_o-S_{\beta\alpha\beta\gamma}$	$011\dot{0}0110$	} n.r. (a)
		$r_o-S_{\beta\alpha\beta\delta}$	$011\dot{0}0101$	
9	30.5-31.5	$m_o-S_{\beta\alpha\beta\gamma}$	$011\dot{0}0110$	} $S_{\beta\alpha\beta\gamma} + S_{\beta\alpha\beta\delta}$ (b)
		$m_o-S_{\beta\alpha\beta\delta}$	$011\dot{0}0101$	
10a	31.5	$T_{\beta\gamma}$	$110\dot{1}001$	n.r. (a)
10b	31.0	$T_{\beta\gamma}$	$010\dot{1}001$	$T_{\beta\gamma}$
11a	29.1	$T_{\beta\beta}$	$110\dot{1}01$	n.r. (a)
11b	29.0-28.1	$T_{\beta\beta}$	$010\dot{1}01$	$T_{\beta\beta}$
12	22.0-21.2	$m_1 m_1-P_{\beta\beta}$	$10\dot{1}01$	} $P_{\beta\beta} + P_{\beta\gamma}$ (c)
13	21.2-20.5	$m_1 r_1-P_{\beta\beta}$ and $m_1-P_{\beta\gamma}$	$10\dot{1}0\bar{1} + 10\dot{1}001$	
14	20.5-19.5	$r_1 r_1-P_{\beta\beta}$ and $r_1-P_{\beta\gamma}$	$\bar{1}0\dot{1}0\bar{1} + \bar{1}0\dot{1}001$	
15	16.5-18.0	$m_o-P_{\alpha\beta}$ and $m_o-P_{\alpha\gamma}$	$011\dot{0}1 + 011\dot{0}01$	$P_{\alpha\beta}$
16	14.5-15.5	$r_o-P_{\alpha\beta}$ and $r_o-P_{\alpha\gamma}$	$0\bar{1}1\dot{0}1 + 0\bar{1}1\dot{0}01$	$P_{\alpha\gamma}$

(a) n.r. = not reported to be present in ref. 7.

(b)  $S_{\beta\alpha\beta\gamma} + S_{\beta\alpha\beta\delta}$  reported to be between 31.0 and 31.9 ppm in ref. 7.(c)  $P_{\beta\gamma}$  noted as uncertain at 19.5-20.0 ppm in ref. 7.

methylenes next to two contiguous methine groups have been observed earlier. For example, Moeller, Ritter, and Cantow (8, 13) in their studies of poly(1,2-dimethyltetramethylene) and model compounds found a 2-ppm difference for their  $C_5$  carbon. A similar splitting was reported for a model compound by Freche, et al. (14).

Further differences in methylene assignments are shown for the 33.7-37.0 ppm region (Figure 2). The spectral assignments have been aided by APT (attached proton test) experiment. It is clear that tacticity spreads out the signals in question and complicates interpretation. Moreover, signals were found (but not previously reported) in the 36.2-37.0 ppm region corresponding to  $r_1$ - $S_{\gamma\alpha\beta\gamma}$ . The complete assignments for this region are indicated in Figure 2 (and also in Table 1).

In the 30.0 to 32.7 ppm region,  $T_{\beta\gamma}$ ,  $S_{\beta\alpha\beta\gamma}$  and  $S_{\beta\alpha\beta\delta}$  overlap. The assignments provided in Table 1 form a consistent set and are generally compatible with data on similar compounds in the literature (12-14).

The methines are easier to interpret. Both in this work and in Doi's papers (6-7), the signals at ca. 38.5 ppm are assigned to  $T_{\alpha\gamma}$ . In some of our spectra,  $T_{\alpha\gamma}$  is split into two signals corresponding to  $m_0$ - $T_{\alpha\gamma}$  and  $r_0$ - $T_{\alpha\gamma}$ . The  $T_{\alpha\beta}$  signal has been shown (vide supra) to be spread out over the 33.7-36.0 ppm range. In contrast, Doi's  $T_{\alpha\beta}$  was localized to 35-36 ppm only (7). The assignments of  $T_{\beta\gamma}$  and  $T_{\beta\delta}$  are straightforward (2, 3, 12), except that satellite bands at 31.5 and 29.1 ppm are found corresponding to the 1101-- structures (Table 1).

The methyl assignments given in this work are more involved and certainly different from the earlier work (5-7). The  $^{13}C$  shift positions for  $P_{\beta\delta}$  and  $P_{\beta\gamma}$  follow the earlier scheme for ethylene-propylene rubbers (12). In addition, two smaller bands occur at higher field (14.5-18.0 ppm). The 14.5-15.5 ppm region has been assigned to racemic  $P_{\alpha\beta}$  and  $P_{\alpha\gamma}$ , and the 16.5-18.0 ppm region to meso  $P_{\alpha\beta}$  and  $P_{\alpha\gamma}$ .

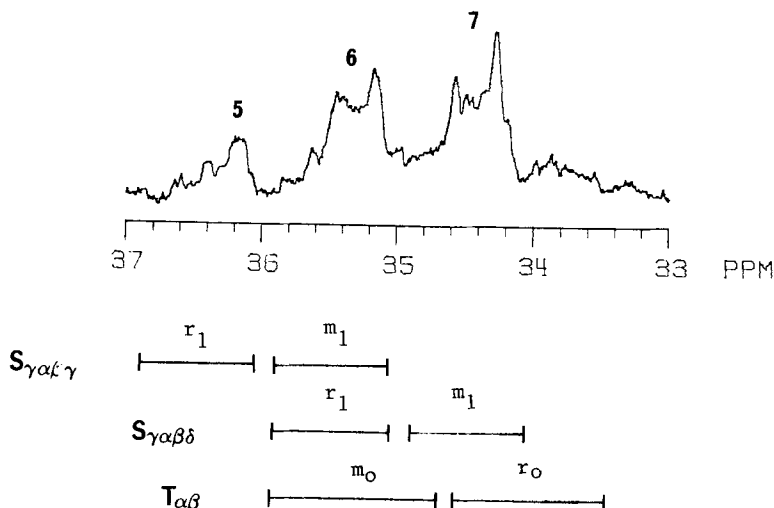


Figure 2: Expanded Plot of the 33-37 ppm region together with assignments.

### III. Computational Schemes

By definition, the dyad and the triad sequences are given by:

$$(0101)+(1010) = S_{\alpha\alpha} = S_{\gamma\alpha\alpha\gamma} + S_{\gamma\alpha\alpha\delta} + S_{\beta\alpha\alpha\gamma} + S_{\beta\alpha\alpha\delta}$$

$$(0110)+(1001) = S_{\alpha\beta} = S_{\gamma\alpha\beta\gamma} + S_{\gamma\alpha\beta\delta} + S_{\beta\alpha\beta\gamma} + S_{\beta\alpha\beta\delta}$$

$$(010101)+(101010) = T_{\beta\beta}$$

$$(010110)+(011010) = T_{\alpha\beta}$$

$$(100101)+(101001) = T_{\beta\gamma}$$

$$(100110)+(011001) = T_{\alpha\gamma}$$

In view of the overlapping spectral lines (especially  $S_{\alpha\beta}$  and  $T_{\alpha\beta}$ ), it is difficult to obtain precise quantitative information from the spectra. For this purpose, some useful relationships are derived:

$$S_{\alpha\beta} = T_{\alpha\gamma} + T_{\beta\gamma}$$

$$T_{\alpha\beta} = S_{\beta\alpha\alpha\gamma} + S_{\beta\alpha\alpha\delta}$$

$$T_{\beta\gamma} = S_{\gamma\alpha\beta\gamma} + S_{\gamma\alpha\beta\delta}$$

$$T_{ij} = P_{ij}$$

$$T_{\alpha\gamma} = S_{\beta\alpha\beta\gamma} + S_{\beta\alpha\beta\delta}$$

$$S_{\gamma\alpha\beta\gamma} = S_{\beta\alpha\beta\delta}$$

These equations can be used to double-check spectral integrations and to confirm the quantitative nature of the spectra. They can also be used to derive dyad and triad sequences through additions and subtractions of spectral areas.

The tacticity can be determined from the appropriate regions of the  $^{13}\text{C}$  NMR spectra. Thus,  $m_0$  can be obtained from either the 40-44 ppm region ( $S_{\beta\alpha\alpha\gamma} + S_{\beta\alpha\alpha\delta}$ ), the 38.0-39.5 ppm region ( $T_{\alpha\gamma}$ , if resolved), or the 14.5-18.0 ppm region ( $P_{\alpha\beta} + P_{\alpha\gamma}$ ). Likewise, an estimate of  $m_1$  can be obtained from the 19.5 to 20.0 ppm region ( $P_{\beta\beta} + P_{\beta\gamma}$ ).

### IV. Reaction Probability Model

In NMR spectra with overlapping signals, the best analytical approach (in the view of this author) is the computerized reaction probability model proposed earlier (15-18). In this case, the second order Markovian probabilities will be used. Again regioirregular polypropylene is regarded as the copolymer of head-first propylene (p) and tail-first propylene (q).

$$\alpha = P_{ppp}$$

$$\beta = P_{ppq}$$

$$\gamma = P_{qpp}$$

$$\delta = P_{qqp}$$

$$\bar{\alpha} = P_{ppq}$$

$$\bar{\beta} = P_{ppq}$$

$$\bar{\gamma} = P_{ppq}$$

$$\bar{\delta} = P_{qqq}$$

where  $P_{ijk}$  is the probability of monomer  $k$  adding to a polymer chain end terminating in units  $i$  and  $j$ .

The theoretical expressions for the signal intensities can be derived (Table 2). The theoretical intensities are compared with the observed intensities through a simplex optimization process (15), thereby producing the best-fit values for the probability parameters ( $\alpha, \beta, \gamma, \delta$ ). Using these optimized  $\alpha, \beta, \gamma$ , and  $\delta$ , one can obtain the composition, and the dyad and the triad comonomer sequences:

$$p = (01) = k (\bar{\alpha} + \gamma) \delta$$

$$q = (10) = k (\bar{\beta} + \delta) \bar{\alpha}$$

$$pp + qq = (0101) + (1010) = k (\bar{\alpha}\bar{\beta} + \gamma\delta)$$

$$pq = (0110) = k (\bar{\alpha}\delta)$$

$$qp = (1001) = k (\bar{\alpha}\delta)$$

$$ppp + qqg = (010101) + (101010) = k (\bar{\alpha}\bar{\beta}\bar{\delta} + \alpha\gamma\delta)$$

$$ppq + pqq = (010110) + (011010) = k (\bar{\alpha}\gamma\delta + \bar{\alpha}\bar{\beta}\delta)$$

$$qpp + qqp = (100101) + (101001) = k (\bar{\alpha}\gamma\delta + \bar{\alpha}\bar{\beta}\delta)$$

$$qpq + pqp = (100110) + (011001) = k (\bar{\alpha}\bar{\gamma}\delta + \bar{\alpha}\bar{\beta}\delta)$$

In the above equations, the normalization constant  $k = (\bar{\alpha}\bar{\beta} + 2\bar{\alpha}\bar{\delta} + \gamma\delta)^{-1}$ . To reduce the second order to the first order Markovian statistics, one simply drops the first subscript, thus:

$$P_{pp} = \alpha = \gamma; \quad P_{qp} = \beta = \delta$$

$$P_{pq} = \bar{\alpha} = \bar{\gamma}; \quad P_{qq} = \bar{\beta} = \bar{\delta}$$

The product of reactivity ratios is given by:  $r_p r_q = \left(\frac{1}{P_{pq}} - 1\right) \left(\frac{1}{P_{qp}} - 1\right)$

Although highly informative, the entire computation is complex and tedious. In order to alleviate this computational difficulty, a computer program (called FIT33) has been written in BASIC language. The program consists of two parts: the first part deals with the tacticities, and the second part calculates the sequences via the reaction probability model. The user enters the spectral intensities and can choose either first or second order Markovian statistics. The program then calculates the optimal values of reaction probability parameters, from which the optimized composition (i.e., level of propylene inversion), as well as dyad and triad sequence distributions are computed. An example of the fitted results is shown in Table 3 for a sample with 3% propylene inversion. The data can be fitted equally well with a first order Markovian model with  $P_{pq} = 0.0307$ ,  $P_{qp} = 0.9036$ , and  $r_1 r_2 = 35$ .

The use of the computerized approach considerably simplifies the calculations involved and minimizes computational errors. An advantage of the reaction probability approach is that all spectral integrals are used, thus maximizing the information content of the spectra and improving the accuracy of the final result. Furthermore, the present approach provides a means to determine the conformity of the polymerization to the first or second order Markovian statistics.

Table 2. Second-Order Markovian Reaction Probability Parameters

<u>No.</u>	<u>Shift(ppm)</u>	<u>Assignments</u>	<u>2nd Order Markov</u>
1	45.0-47.0	$S_{\gamma\alpha\alpha\gamma} + S_{\gamma\alpha\alpha\delta}$	$\alpha\gamma\delta + \bar{\alpha}\bar{\beta}\bar{\delta}$
2-3	40.5-44.0	$S_{\beta\alpha\alpha\gamma} + S_{\beta\alpha\alpha\delta}$	$\bar{\alpha}\gamma\delta + \bar{\alpha}\bar{\beta}\bar{\delta}$
4	38.0-39.5	$T_{\alpha\gamma}$	$\bar{\alpha}\beta\delta + \bar{\alpha}\bar{\gamma}\delta$
5-7	33.7-37.0	$T_{\alpha\beta} + S_{\gamma\alpha\beta\gamma} + S_{\gamma\alpha\beta\delta}$	$2\bar{\alpha}\gamma\delta + 2\bar{\alpha}\bar{\beta}\bar{\delta}$
8-10	30.0-33.0	$T_{\beta\gamma} + S_{\beta\alpha\beta\gamma} + S_{\beta\alpha\beta\delta}$	$2\bar{\alpha}\delta$
11	28.0-29.1	$T_{\beta\beta}$	$\alpha\gamma\delta + \bar{\alpha}\bar{\beta}\bar{\delta}$
12-14	19.5-22.0	$P_{\beta\beta} + P_{\beta\gamma}$	$\gamma\delta + \bar{\alpha}\bar{\beta}$
15-16	14.5-18.0	$P_{\alpha\beta} + P_{\alpha\gamma}$	$2\bar{\alpha}\delta$
<u>Total</u>			$3\bar{\alpha}\bar{\beta} + 6\bar{\alpha}\bar{\delta} + 3\gamma\delta$

Table 3. FIT33 Analysis of Irregular Polypropylene

Line	1	2-3	4	5-7	8-10	11	12-14	15-16
Area	100	3.2	1.5	7.0	10.7	97.7	103.4	6.5
$\alpha = 0.9695,$ $\beta = 0.8975,$ $\gamma = 0.9685,$ $\delta = 0.8590$								
$p = 0.967$ $pp + qq = 0.941$ $ppp + qqq = 0.909$ $q = 0.033$ $pq = 0.295$ $ppq + pqq = 0.316$ $m_0/r_0 = 30/70$ $qp = 0.295$ $qpp + qqp = 0.316$ $qpq + pqp = 0.274$								

### Experimental Section

The polymer samples used were all experimental samples prepared with Ziegler-Natta catalysts. The  $^{13}\text{C}$  NMR spectra were obtained on 30% (w/v) solutions in 1,2,4-trichlorobenzene/ $d_6$ -benzene at 90.55 MHz at 100°C on a Nicolet NT 360 WB spectrometer equipped with a Nicolet 1280 computer. The instrumental conditions used were: 1 pulse experiment; 65° pulse; 4 sec. pulse delay,  $\pm$  3000 Hz sweep width; and quadrature detection. All chemical shifts reported herein are referenced to TMS at 0 ppm.

The reaction probability model calculations were carried out on the Nicolet 1280 computer by the FIT33 program. The structure of the program is similar to the EPCO program reported earlier (15).

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