

to minimize irradiation of **2**. From the shortest irradiation times, where the minute concentrations of photoproducts are at the limit of our detection, to the point where much of the starting azide is destroyed, the ratio of **2** to **3** remains constant. This is most consistent with **3** also being a primary photoproduct of **1**. The absence of a matrix effect¹² on the product ratio weakens, but does not eliminate, the possibility that **3** arises from rearrangement of vibrationally hot singlet nitrene **5**. An alternative is that an electronically excited state of **5** (or **2**) directly produces **3**. The facile photochemical conversion of the triplet nitrene **2** to **3** suggests that there may be a readily accessible excited state of the nitrene with a proclivity toward rearrangement.^{16,17}

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(17) The interconversion of triplet phenylnitrene (**2**) and didehydroazepine (**3**) has been proposed before on the basis of ESR results.¹⁸ The thermal interconversion of these species at room temperature has also been postulated to explain certain aspects of the solution photochemistry of phenyl azide.¹⁰

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High-Resolution ¹³C Nuclear Magnetic Resonance Observations of Two Crystalline Model Compounds for Syndiotactic Polystyrene

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Recently synthesized^{1,2} syndiotactic polystyrene (s-PS) has been observed¹⁻⁸ to crystallize into two distinct polymorphs. Melt crystallization produces form I crystals ($T_m = 270$ °C) with an X-ray diffraction fiber repeat of 5.1 Å, which is consistent with a planar-zigzag, all-trans chain conformation. Form II crystals, with an X-ray fiber repeat of 7.5 Å, are obtained by casting films from dilute solutions or by exposure of amorphous, melt-quenched films to certain organic solvent vapors. At ca. 190 °C, form II crystals are transformed into form I crystals via a solid-solid phase transition. The 7.5-Å fiber repeat found for the form II crystals is consistent with a 2₁-helical, ...*ttggttgg*... chain conformation,

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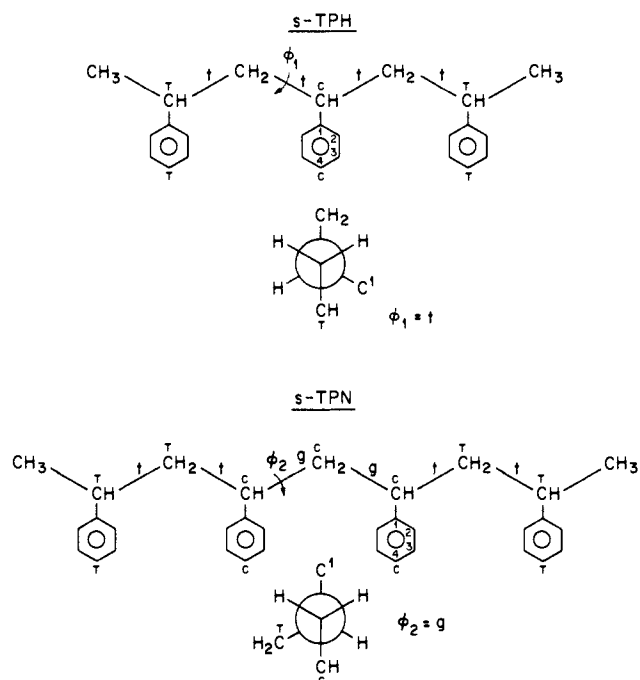


Figure 1. The molecular structure and labeling scheme for s-TPH and s-TPN. Below each structural drawing is a Newman projection illustrating a trans (s-TPH) or a gauche (s-TPN) backbone bond conformation.

Table I. Relative $\delta(^{13}\text{C})$'s Expected for Crystalline s-TPH and s-TPN on the Basis of γ -Gauche Shielding Effects

Methylene Carbons ^a	
$\delta_{\text{CH}_2}^{\text{C}}(\text{s-TPN})$ and $\delta_{\text{CH}_2}^{\text{C}}(\text{s-TPH})$	should be downfield from $\delta_{\text{CH}_2}^{\text{C}}(\text{s-TPN})$ by $\gamma_{\text{CH}_2, \text{CH}} \approx 5$ ppm
Quaternary Aromatic Carbon ^a	
$\delta_{\text{C}^1}^{\text{C}}(\text{s-TPN})$ and $\delta_{\text{C}^1}^{\text{C}}(\text{s-TPH})$	should be downfield from $\delta_{\text{C}^1}^{\text{C}}(\text{s-TPH})$ by $\gamma_{\text{C}^1, \text{CH}} \approx 2.5$ ppm

^a See Figure 1 for labeling of carbons and Newman projections of s-TPH and s-TPN.

as was found previously⁹ for syndiotactic polypropylene. High-resolution, solid-state ¹³C NMR spectra¹⁰ of forms I and II s-PS are consistent with the proposed ...*tttttttt*... and ...*ttggttgg*... chain conformations.

Well before the synthesis of s-PS, Jasse et al.^{11,12} reported the X-ray-derived structure of the single crystals of the syndiotactic isomers of 2,4,6-triphenylheptane (s-TPH) and 2,4,6,8-tetra-phenylnonane (s-TPN). s-TPH was found to crystallize in the planar-zigzag, all-trans, *tttt* conformation, while the *ttggtt* conformation was adopted by s-TPN in its crystals. In this communication we report the preliminary high-resolution, solid-state ¹³C NMR spectra of both s-PS model compounds and compare their ¹³C chemical shifts to those observed for forms I and II s-PS. The conformationally sensitive γ -gauche shielding effects¹³ on ¹³C chemical shifts [$\delta(^{13}\text{C})$] are utilized to discuss the crystalline conformations of forms I and II s-PS by way of comparison to the ¹³C NMR spectra observed for crystalline s-TPH and s-TPN.

The structures and labeling scheme to describe s-TPH and s-TPN are presented in Figure 1 together with Newman projections along backbone bonds in the *t* and *g* conformations. On the basis of the demonstrated¹³ sensitivity of ¹³C chemical shifts

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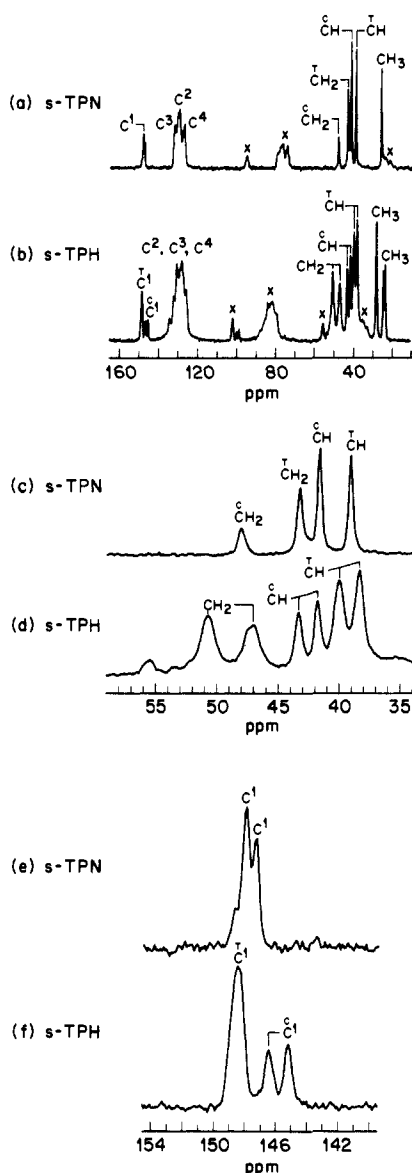


Figure 2. CPMAS/DD ^{13}C NMR spectra of crystalline s-TPH (b) and s-TPN (a) recorded at room temperature at 50.3 MHz on a Varian XL-200 spectrometer equipped with a Doty Scientific solids probe. Both samples were spun at the magic angle at a speed of ca. 2.5 kHz; a 40 kHz rf field strength was applied for 200 ms to achieve ^1H dipolar decoupling; and a 2.5-ms cross-polarization contact time was employed. Both spectra were referenced to external poly(oxyethylene) which resonates¹⁵ at 89.1 ppm from TMS. Resonances marked with an X are the spinning sidebands of the aromatic carbon resonances. Expansions of the CH_2 and CH region of the s-TPN and s-TPH spectra are shown in parts c and d, while expansions of the C^1 region are shown in parts e and f.

observed in solid-state polymer ^{13}C NMR spectra to their solid-state conformations, we expect the pattern of ^{13}C resonances summarized in Table I. The central (C) methylene carbons in s-TPN and the methylene carbons in s-TPH should resonate downfield from the terminal (T) methylenes in s-TPN, because the T CH_2 's (s-TPN) are shielded by the gauche arrangement of their γ -substituents [$\text{CH}(\text{C})$'s] (see Figure 1), while the central CH_2 's in s-TPN and the s-TPH methylenes are trans to their γ - $\text{CH}(\text{T})$'s and are not shielded. The difference in methylene carbon chemical shifts should be ca. 5 ppm ($\gamma_{\text{CH}_2, \text{CH}}$), judging from previous experience.^{13,14}

The methylene carbons in all-trans, planar-zigzag form I s-PS are not shielded by their γ - CH 's, and they resonate at 48.4 ppm¹⁰ very near the central CH_2 's in s-TPN and the s-TPH methylenes.

In form II s-PS the methylene carbons resonate at 49.1 and 38.1 ppm reflecting 0 and 2 gauche shielding arrangements with their γ - CH 's, respectively, in the ...*ttggttgg*... conformation proposed for this s-PS polymorph. The terminal CH_2 carbons in s-TPN resonate at 43.5 ppm (see Figure 2), or midway between the CH_2 carbons in form II s-PS, because these T CH_2 's are gauche to a single γ -substituent, $\text{CH}(\text{C})$.

The four quaternary, aromatic carbons of s-TPN [$\text{C}^1(\text{C})$ and $\text{C}^1(\text{T})$] and the two terminal quaternary, aromatic carbons of s-TPH [$\text{C}^1(\text{T})$] should resonate downfield from the central C^1 in s-TPH, because $\text{C}^1(\text{C})$ in s-TPH is shielded by two $\gamma_{\text{C}^1, \text{CH}}$, while the other C^1 carbons possess only a single $\gamma_{\text{C}^1, \text{CH}}$ interaction (see Figure 1). This additional shielding ($\gamma_{\text{C}^1, \text{CH}}$) should^{13,14} move $\delta(\text{C}^1(\text{C}))$ in s-TPH ca. 2.5 ppm upfield from the remaining quaternary carbons in both s-PS model compounds.

The CPMAS/DD ^{13}C NMR spectra of crystalline s-TPH and s-TPN are presented in Figure 2. It is clear from their comparison¹⁶ that the methylene and quaternary, aromatic carbon chemical shifts follow the pattern expected (Table I) from consideration of their crystalline conformations in terms of γ -gauche shielding effects. As a consequence, our previous analysis¹⁰ of the ^{13}C chemical shifts observed in the high-resolution, solid-state ^{13}C NMR spectra of forms I and II s-PS is confirmed, and the conclusion that forms I and II s-PS adopt the ...*ttttttt*... and ...*ttggttgg*... conformations, respectively, receives further support.

(16) Note the doubling of most resonances in the CPMAS/DD ^{13}C NMR spectrum of s-TPH shown in Figure 2b. This most likely reflects the fact that two s-TPH molecules form the asymmetric unit of its crystalline unit cell, and each experiences different intermolecular packing interactions. A single s-TPN molecule constitutes the asymmetric unit in its crystalline unit cell, and as expected we observe only single resonances for each carbon type (see Figure 2a).

Palladium-Catalyzed Carboannulation of 1,3-Dienes by Aryl Halides

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Carboannulation processes are among the most important reactions in organic synthesis, but few have proven very general in scope.^{1,2} The addition of arylpalladium species to 1,3-dienes is known to afford π -allylpalladium compounds,³ and extensive work

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