

## Tris(phenylimino)-1,3-diphenyl-1,2,3-propantrione: A Model Compound Implicating a Nonhelical Structure for Poly(*N*-phenylimino)methylene

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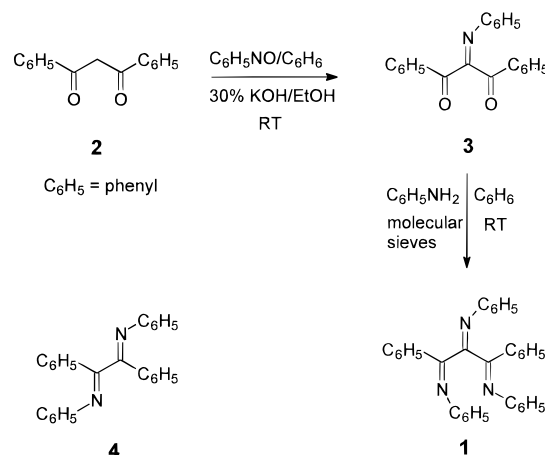
Received March 19, 1997

Recently we showed that poly(*N*-phenylimino)methylene (*N*- $\varphi$ -PIM) aggregates and precipitates when dissolved in an appropriate solvent<sup>1</sup> and that it exhibits three resonance manifolds in the solution <sup>15</sup>N NMR spectrum.<sup>2</sup> Our explanation for these observations was that the “as-prepared” helical conformation<sup>1</sup> of sterically unencumbered *N*- $\varphi$ -PIM unravels in solution. We assumed that the three observed resonance manifolds could be attributed to three conformationally different segments in *N*- $\varphi$ -PIM.<sup>1</sup> We have also confirmed that the “merry-go-round” mechanism<sup>3</sup> is indeed viable,<sup>4</sup> and our results were also consistent with the idea that this mechanism occurs around a Ni(I) ionic center,<sup>5</sup> which delivers the helical conformation found initially. Others have recently shown theoretically<sup>6</sup> that the helical conformation is not the most stable, and thus, we offer this paper as experimental support of this theoretical work.

The syntheses<sup>7</sup> and characterizations<sup>8</sup> of numerous PIM polymers have been reported. The helical conformation exhibited by most sterically constrained PIM polymers has been confirmed<sup>9</sup> and rationalized.<sup>10</sup> The screw-sense-selective polymerizations of aryl-substituted isocyanides have been reported, and it was shown that helical chirality could be induced either in achiral *N*-aryl-PIMs<sup>11</sup> or where the *N*-aryl-substituent included a chiral center that was well removed from the reaction center.<sup>12</sup> Despite these studies, the viability of a rigid rod, 4<sub>1</sub>-helical conformation as the major structural element in the PIM polymers has been questioned.<sup>6,13,14</sup> We will present experimental evidence in this paper that lends credence to these questions.

Small model compounds have been used successfully to mimic the properties of large molecular entities when structural information about the latter is difficult to obtain. Polyketone,  $[-C(O)]_x$ , the hydrolysis product that would be derived from a PIM polymer, is an unknown entity as far as we are aware, and yet, we can predict that it would probably have a helical conformation on the basis of the known structures of model

### Scheme 1



vicinal oligoketones.<sup>15</sup> In this paper, we report the synthesis, characterization, and NMR analysis of the vicinal trimine **1**, tris(phenylimino)-1,3-diphenyl-1,2,3-propantrione. We show that **1** has a unique structure that is consistent with the theoretical predictions recently addressed by Salvadori and co-workers.<sup>6</sup> Thus, we can say with some confidence that sterically unencumbered PIM polymers adopt a geometry in solution that in part includes the predicted *syndio* conformation.<sup>6</sup> We believe<sup>1</sup> this *syndio* conformation corresponds to a transition region between the unraveling helical *s-cis* domain and the linear *s-trans* domain of a random coil *N*- $\varphi$ -PIM.

The preparation of **1** is illustrated in Scheme 1. The starting material, **2**, is easily converted to **3** in 70% yield.<sup>16</sup> Compound **3** can then be converted into **1** at room temperature using an excess of aniline in the presence of molecular sieves. The reaction progress can be monitored by RPLC which shows that the entrance of one aniline occurs relatively rapidly. The entrance of the second aniline is very sluggish, however, requiring a month or more under specific conditions where the mixture was gently swirled occasionally and dry molecular sieves were replenished when RPLC monitoring indicated that the dehydration reaction had ceased. Heating the mixture only exacerbated the decomposition of **1** without improving the kinetics. Despite the gentle conditions the overall yield of **1** from **3** was poor, 4–8%. The reluctance of **1** to form easily by the simple dehydration procedure used can be found in the hydrolytic instability of the compound. We measured the approximate room temperature half-life of **1** in the presence of water, and it was less than 1 min in acidic aqueous ethanol. This is to be compared to the greater than 1 day half-life for hydrolysis of the analogous benzil derivative (**4**) under the same conditions. Once obtained, **1** can be characterized as tris(phenylimino)-1,3-diphenyl-1,2,3-propantrione fairly easily.<sup>17</sup> The <sup>15</sup>N-labeled **1** was prepared using these same methodology and characterization techniques which showed that the phenylimino groups were completely exchangeable.

Extensive analyses by conventional 1-D or 2-D NMR techniques on natural abundance and <sup>15</sup>N-enriched samples of **1** have been carried out in order to determine the structure and

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(17) Compound **1** exhibits the following properties: mp = 122–124 °C; TLC (silica) *R<sub>f</sub>* = 0.45 (20% EtOAc/hexane); RPLC (C<sub>18</sub>) *R<sub>f</sub>* = 35.2 min (20% H<sub>2</sub>O/CH<sub>3</sub>OH); FTIR (KBr)  $\nu_{C=N}$  = 1627 cm<sup>-1</sup>; UV-vis (CH<sub>3</sub>-CN)  $\lambda_{max}$  = 224 nm ( $\epsilon$  = 4.1 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>), 250 nm ( $\epsilon$  = 3.0 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>), 348 nm ( $\epsilon$  = 6.7 × 10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>); MS (natural abundance sample) *m/z* = 463 (M<sup>+</sup> and base peak), <sup>15</sup>N-enriched sample *m/z* = 466 (66%), *m/z* = 465 (29%), *m/z* = 464 (5%). Anal. Calcd for C<sub>33</sub>H<sub>25</sub>N<sub>3</sub>: C, 85.53; H, 5.40; N, 9.07. Found: C, 85.51; H, 5.27; N, 8.95. See the text for NMR analysis.

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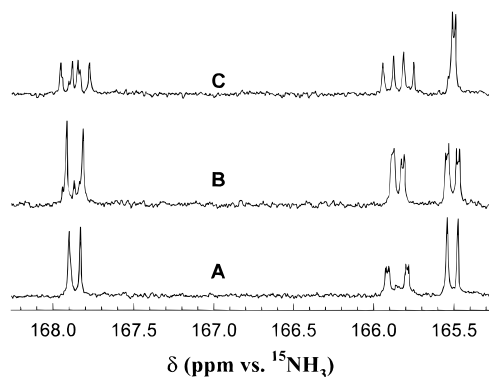
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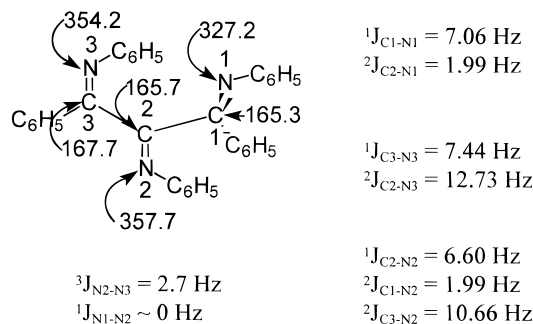


**Figure 1.** Selective irradiation of the  $^{15}\text{N}$  NMR resonances of an  $\sim 70\%$   $^{15}\text{N}$ -enriched sample of **1**. Observation of the changes that occur in the  $^1\text{H}$ -decoupled  $^{13}\text{C}$  NMR spectrum of the three imine carbon resonances with a second channel decoupling  $^{15}\text{N}$  at the following: (A) 357.7 ppm (N2); (B) 354.2 ppm (N3); (C) 327.2 ppm (N1). The 1-D  $^{13}\text{C}$  NMR spectrum of this  $^{15}\text{N}$ -enriched sample exhibited the following imine resonances:  $\delta = 167.7$  ppm (dd) C3;  $\delta = 165.7$  ppm (m) C2;  $\delta = 165.3$  ppm (dd) C1. See Figure 2 for the atom labels.

conformation of **1** in  $\text{CDCl}_3$  solution. The  $^1\text{H}$  NMR spectrum exhibits seven complex resonance manifolds centered at  $\delta = 6.53$  (2H), 6.70 (2H), 6.79 (2H), 6.96 (3H), 7.19 (11H), 7.50 (3H), and 7.99 (2H) ppm. The natural abundance,  $^1\text{H}$ -decoupled  $^{13}\text{C}$  NMR spectrum of **1** shows 20 resonances in which the three imine carbons appear at  $\delta = 167.7$ , 165.7, and 165.3 ppm, while the five *ipso* carbons of the five phenyl rings appear at  $\delta = 150.6$ , 149.4, 148.2, 138.2, and 133.6 ppm. The remaining  $^{13}\text{C}$  NMR resonances of the *o*-, *m*-, and *p*-carbons of the five phenyl rings appear between  $\delta = 119.5$  and 130.7 ppm. The  $^1\text{H}$ -decoupled  $^{15}\text{N}$  NMR spectrum of enriched **1** exhibits two doublets and a singlet centered at  $\delta = 357.86$  ( $J = 2.7$  Hz), 354.17 ( $J = 2.7$  Hz), and 327.17 ppm respectively (vs  $^{15}\text{NH}_3$ ).

The assignment of conformation in **1** is based primarily upon the observed vicinal  $^{15}\text{N}$ - $^{15}\text{N}$  couplings. The  $^{15}\text{N}$  NMR chemical shift at 327.17 ppm is a singlet, and this is consistent with **1** having an isolated and magnetically uncoupled imino moiety. Assuming a Karplus-like relationship,<sup>18</sup> this isolated imine must be attached at a nearly  $90^\circ$  dihedral angle via a single covalent bond to the remainder of **1** which is composed of an *s-trans*-conjugated and coupled diimine segment. The assignment of an *s-trans* diimine moiety is based on the observation of  $^3J(^{15}\text{N}-^{15}\text{N}) = 2.7$  Hz between the other two nitrogen atoms, consistent with literature precedence.<sup>19</sup>

Qualitative confirmation of the orientation of the isolated imine segment with respect to the conjugated *s-trans* segment can be found by determining  $J_{\text{CN}}$ . Observation of the  $^1\text{H}$ -decoupled imino  $^{13}\text{C}$  resonances while selectively irradiating the  $^{15}\text{N}$  resonances leads to the spectra shown in Figure 1. The assignments are shown in Figure 2 using, as a reference, the lowest energy conformation found from a molecular mechanics calculation.<sup>20</sup> The  $^2J_{\text{CN}}$  coupling constant information is qualitatively consistent with the two segments being very nearly uncoupled and at  $\sim 90^\circ$  in **1** ( $^3J_{\text{CN}}$  data would have been more



**Figure 2.** The dominant structural conformation found in **1** and the relevant assignments of the NMR chemical shifts and coupling constants of its molecular backbone.

conclusive but this was not observed because the coupling is less than the line width). Thus, our observations and conclusions are consistent with the proposed *syndio* model<sup>6</sup> of Salvadori et al.

The observation that **1** assumes the predominant conformation shown in Figure 2 is powerful evidence that vicinal oligoimines preferentially occupy a *syndio* niche as the lowest energy conformation when sterically unconstrained. The class of molecular entities in which **1** can be included are collectively known as cross-conjugated systems. Recent results from other laboratories that have investigated the crystalline<sup>21</sup> and gas<sup>22</sup> phase molecular structures of related cross-conjugated systems confirm our solution observations. Combining these experimental observations allows us to conclude that end-group effects and aromatic-stacking possibilities seem to play only small roles in determining the ultimate overall thermodynamically most stable conformation available to a cross-conjugated system. Therefore the implication is that extended cross-conjugated systems achieve greatest stability by incorporating *s-trans* segmental portions as the prime constituent of the molecular backbone.

The above observation is consistent with our proposal that sterically unencumbered *N-φ*-PIM contains a *syndio*-like conformation that we previously called the transition domain connecting helical *s-cis* segments and linear *s-trans* segments. Even though the PIM polymers can be prepared so that the helical conformation predominates initially,<sup>4</sup> manipulation of these "as-prepared" materials<sup>1</sup> has the potential of unraveling this helix, especially when the substituent is sterically undemanding, i.e., the rigid rod character of some PIM polymers is not established.<sup>14</sup> Anticipated applications<sup>13a</sup> for the PIM polymers will thus have to account for the fact that rigid rod character will most likely only be maintained when the *N*-substituent of PIM polymers is sterically demanding.

**Acknowledgment.** The authors thank Dr. Gregory A. Nemeth of Dupont-Merck Pharmaceutical Company, Experimental Station #3, Wilmington, DE, for obtaining the NMR spectra shown in Figure 2. We also thank Mr. Amin Kamil of Pfizer Pharmaceutical Company, Groton, CT, for mass spectral data on samples of **1**. The advice of Professor D. D. Traficante is warmly acknowledged. We are most grateful for financial support from the US Army under the AASERT program, grant no. DAAH0494G0150.

JA970880Q

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