

# 1,4-Di(1,2-di-*tert*-butyl-2-phenylethenyl)benzene and Related Twist-twist Pi Conjugated Stilbene (PPV) Systems

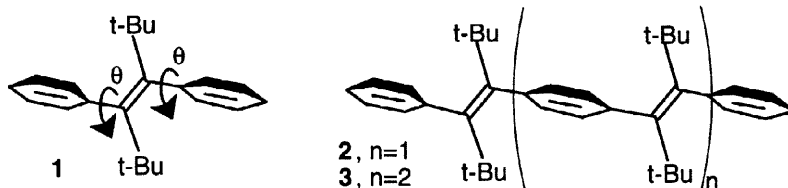
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**Abstract:** Twist-twist, pi conjugated, TTPC, systems are described. The twisted stilbene motif represented by 2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene is extended to systems with five and seven perpendicular pi systems. UV spectra show extension of the chain imparts a regular red shift to the prominent  $\pi \rightarrow \pi^*$  transition. The shift is attenuated compared to planar pi conjugated systems. Extended TTPC systems occur as mixtures of atropisomers with very similar energies. © 1998 Elsevier Science Ltd. All rights reserved.

Connected, perpendicular, multiple, pi systems, such as **1**, are described as twist-twist, pi conjugated, TTPC. As the twist angle,  $\theta$ , moves into the 85–95° range, new opportunities appear for orbital mixing. These replace the lost pi conjugation as the p orbitals flanking the connecting sites become orthogonal. Related systems with this general feature have novel properties: sudden polarization<sup>1-2</sup> and twisted intramolecular charge transfer, TICT.<sup>3-5</sup> This study describes the systematic extension of **1** to **2** and **3**, with five and seven perpendicular pi systems, respectively.



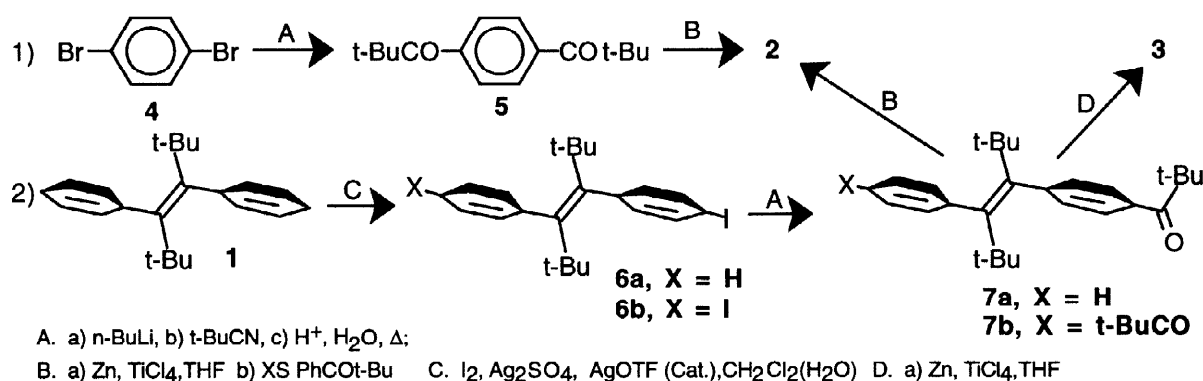
No suitable, simple models of TTPC exist. Although ortho substituents on poly(phenylene)s might be expected to induce this feature, a Cambridge Structural Database search demonstrates the resulting twist angles do not reach 90°. Many phenyl substituted porphyrin metal complexes, such as zinc tetraphenylporphyrin,<sup>7</sup> have the correct geometry, but their complexity and large size make a systematic study difficult. Some other stilbenes are locked into the TTPC geometry by bulky groups<sup>8-12</sup> or cyclic structures.<sup>13-16</sup> The discovery of

**1**, rigidly locked in place by *tert*-butyl groups,<sup>10-11</sup> presents a structural motif for an exploration of TTPC systems.

Both potential routes, 1) and 2) below, to extended stilbenes **2** and **3** employed the McMurry reaction.<sup>17-18</sup> This reaction proved useful preparing **1**.<sup>19</sup> Route 1) would provide **2** in two steps from commercially available 1,4-dibromobenzene, **4**. Although diketone **5** was quantitatively prepared from **4**, cross-coupling of **5** failed to form **2**. The bright red coupling solution, which appeared in place of the normally blue-black mixture, produced a mixture of reduction products instead.

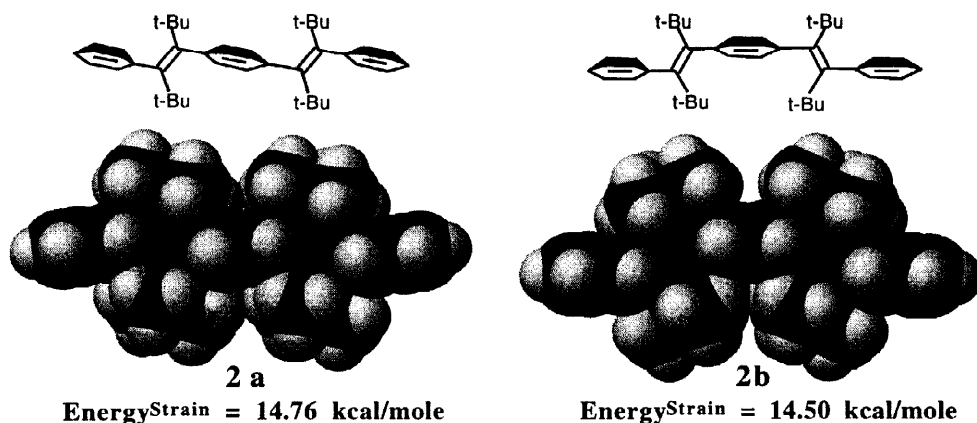
Route 2) began with **1**, which was prepared from *tert*-butyl phenyl ketone.<sup>19</sup> As described in detail elsewhere,<sup>20</sup> iodination of **1** to form **6** required special conditions to avoid decomposition. If these conditions were not used, an intractable black mass was produced, or no reaction occurred.<sup>20</sup> The resulting mixture of **6a** and **6b** was not separated. Instead, it was quantitatively converted into ketone **7**. Isolation of **7a** from **7b** by column chromatography and cross coupling of **7a** with excess *tert*-butyl phenyl ketone gave a 42 % overall yield of **2**<sup>21</sup> from **1**. Similarly **3** was prepared through the coupling of **7a** with itself.<sup>21</sup> The solubility decreased rapidly in the series **1** -> **2** -> **3**.

The <sup>13</sup>C NMR and <sup>1</sup>H NMR spectra of **2** displayed twice as many signals as needed to account for the structure.<sup>21</sup> Evidently **2** was produced as a 2:1 mixture of atropisomers, **2a** and **2b**. As expected, no *Z*-stilbenes were evident from the coupling reaction.<sup>17</sup>



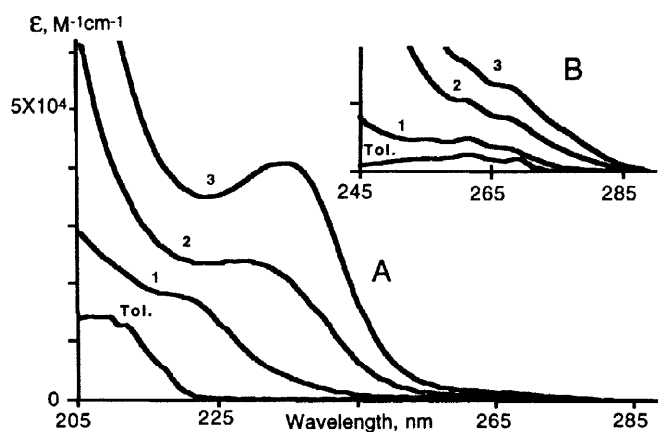
Molecular mechanics calculations represented **2a** and **2b** to have comparable energies,  $\Delta E = 0.26$ .<sup>22</sup> Space filling models, below, show the bulky, *tert*-butyl groups in **2a** and **2b** have sufficient space to avoid one another.

Equilibrating a **2a/2b** mixture at 80° produced a **2a/2b** ratio of 1.2. The phenyl group rotation, which provided the equilibration, occurred at lower temperatures in **2** than the analogous rotation reported for stereochemically labeled **1**.<sup>23</sup>



Recrystallization of a **2a/2b** mixture in benzene produced crystals of a benzene solvate. X-ray analysis of the benzene solvate allowed sufficient refinement to identify **2a** as the *anti* atropisomer depicted above.

The UV spectra of toluene, **1**, **2** and **3**, Figure-A, displayed red shifts in the allowed transition of 10, 11 and 5 nm, respectively, as the system was extended. These shifts were compared to 100, 43 and 26 nm observed for the planer analogs benzene, stilbene, *p*-styrylstilbene and *p,p'*-distyrylstilbene, respectively.<sup>24</sup> ZINDO calculations<sup>21</sup> showed this



**Figure.** UV spectra of toluene, **1**, **2** and **3**: A,  $2.0 \times 10^{-5}$  and B,  $5.1 \times 10^{-4}$  M in cyclohexane.

prominent band involved  $\pi_{C=C} \rightarrow \pi^*_{Ph}$  transitions in **1** - **3**. The forbidden, long wavelength transition, assigned as  $\pi_{Ph} \rightarrow \pi^*_{Ph}$  in **1** - **3**, shows no similar red shift,<sup>25</sup> Inset-Figure. This was in disagreement with the ZINDO predictions. No fluorescence was observed from either **1**, **2**, or **3**.

The feasibility of preparing extended TTPC systems has been demonstrated. They exhibit a) atropisomers b) decreasing solubilities c) red shifted UV spectra and d) no fluorescence. The synthesis of further extended systems with increased solubilities is in progress.

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structure. The generous financial support from the OBOR Research Challenge Program is acknowledged.

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- (21) **2**: Mp 279.0 - 280.5 °C; CHN Calc. C 90.06 %, H 9.94 %, Exp. C 89.90 %, H 9.87 %; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.75(s, 18H), 0.76(s, 18H), 7.12(s, 4H), 7.19-7.31 (m, 10H); <sup>13</sup>C NMR (Cyclohexane-*d*<sub>12</sub>) δ 33.4 (assignments as below), 126.4, 127.0, 130.0, 131.5, 142.3, 144.6, 146.4, 146.6; **2b** <sup>1</sup>H NMR(CDCl<sub>3</sub>) δ 0.71(s, 18H), 0.83(s, 18H), 7.13(s, 4H), 7.19-7.31(m, 10H); <sup>13</sup>C NMR (Cyclohexane-*d*<sub>12</sub>) δ 33.3 (CH<sub>3</sub>), 33.6 (CH<sub>3</sub>), 38.2 (C(CH<sub>3</sub>)<sub>3</sub>), 38.2 (C(CH<sub>3</sub>)<sub>3</sub>), 126.4, 127.0, 130.0, 131.4, 142.4, 144.7, 146.5, 146.6; **3** (Mixture of atropisomers) Mp 420 °C (427 from TGA); HRMS Calculated for C<sub>54</sub>H<sub>72</sub> 720.5610939, Found 720.5610962; MS *m/z*(relative intensity) 720 (M<sup>+</sup>, 0.4), 608 (4), 607 (8), 551 (5), 131 (17), 57 (100); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.87-0.69 (> 7 s, 54H), 7.15-7.09 (m, 8H), 7.31-7.18 (m, 10H).
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