## Synthesis and Structure of (E,E)-[6.2]-(2,5)Thiophenophane-1,5-diene: A New Monomer for Cyclopolymerization.

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Abstract: Synthesis and characterization of the title compound (1) is described. UV and variable temperature <sup>1</sup>H-NMR spectroscopy are used to deduce structural detail of 1 in solution and results are compared to its x-ray structure. 1 shows structural features favorable for cyclopolymerization to form polymers containing stacked aromatic rings.

Polymerization of [6.2]paracyclophane-1,5-dienes<sup>1,2</sup> and (1,n)-bis(*p*-vinylphenyl)alkanes<sup>3</sup> can yield cyclopolymers which exhibit interesting electronic properties, such as semiconductivity when oxidized<sup>2,4</sup> and good photoconductive properties when doped with weak electron acceptors.<sup>5</sup> The electronic properties of these polymers can in principle be enhanced by lowering the oxidation potential of the stacked ring systems, e. g. by replacement of the benzene rings with thiophene rings. Further, cyclopolymerization of [6.2]cyclophane-1,5-dienes is favored by the close proximity of the double bonds but structural details of the resulting cyclopolymer will depend on their exact disposition in the monomer. We report here the synthesis and structural characterization of (*E*,*E*)-[6.2]-(2,5)thiophenophane-1,5-diene (1) for synthesis of new, electronically active cyclopolymers. 1 also serves as a structural model for cyclopolymerization of this type of monomer. To our knowledge, this is the first reported x-ray structure of such a [6.2]-1,5-diene-phane system.

Diene 1 was synthesized from the unsaturated aldehyde<sup>6</sup> 2 (Scheme 1)<sup>7</sup> using literature procedures<sup>8</sup> and was isolated from the residue of pyrolysis of 5 as white crystals in 18% yield,<sup>9</sup> by trituration with hexane, filtration and cooling. Hydrogenation of 1 gave [6.2]-(2,5)thiophenophane (6) in 85% yield.<sup>10</sup> Hydrogenation/desulfurization of 1 with excess Raney Nickel<sup>11</sup> gave cyclohexadecane.<sup>12</sup>

UV spectroscopy has been used to derive structural information for bridged aromatic compounds in solution <sup>13,14</sup> Absorption maxima for  $\pi$ - $\pi^*$  transitions in 1 and model compound<sup>15</sup> 7 occur at 282 ( $\epsilon$ =18,800) and 286 ( $\epsilon$ =12,200) nm, respectively. Calculation of the effective torsional angle between the thiophene ring and the *trans* double bond in 1 using Braude's treatment<sup>14,16</sup> gave a value of 28°. The corresponding torsional angle for the analog of 1 with benzene aromatic rings (8) was calculated to be 35°.<sup>14</sup> This difference likely stems from the absence of eclipsing hydrogens on the side of the sulfur in 1, resulting in a smaller torsional angle and suggesting that the double bonds are in an s-*cis* conformation relative to sulfur. The torsional angle between the thiophene rings and *trans* double bonds in 1 is also reflected in an increase in energy of the  $\pi$ - $\pi^*$  transition, resulting in the hypsochromic shift observed for 1 relative to 7.

Scheme 1. Synthesis of (E,E)-[6.2]-(2,5)Thiophenophane-1,5-diene.



The temperature dependence (-55 °C to 50 °C) of the NMR spectrum of 1 was used to investigate its conformational mobility in solution. At room temperature the [2] bridge methylene proton signals undergo dynamic averaging to give a broad singlet at 2.8 ppm which becomes sharper at higher temperature. At -55°C, this peak is resolved into a complex pattern (broadened multiplets at 3.3 ppm and 2.4 ppm) suggestive of the expected AA'BB'-type system and the multiplet for the [6] bridge methylene proton signals. The activation free energy of exchange ( $\Delta G_C$ ) between the [2] bridge protons was calculated<sup>17</sup> to be 12.3 Kcal/mole ( $T_c = -4$  °C in CDCl<sub>3</sub>,  $\Delta S_c = 3.0$  cal/mol). The thermodynamic parameters and NMR data show that 1 is conformationally mobile. Although the exact nature of this conformational motion is unclear, the data suggest that the thiophene rings (and likely the vinyl groups) undergo inversion in solution above the coalescence temperature and slow down or become fixed below it.  $\Delta S_c$  for 1 is small, suggesting the conformational interconversion does not involve substantial ordering or disordering.

Figure 1. ORTEP drawing of (E, E)-[6.2]-(2,5)Thiophenophane-1,5-diene. Only one of the enantiomers in the crystal structure is shown. Hydrogen atom positions were not determined.



Information from the x-ray structure of 1 (Figure 1)<sup>18</sup> (solid state) and the above UV and NMR (solution) studies are in good agreement with regard to conclusions about structure and conformation. The position of the double bonds with respect to each other in the solid state show that they are oriented in opposite directions (cross-like geometry) and in the s-*cis* conformation relative to sulfur. 1 is chiral (C<sub>2</sub> symmetry) if the thiophene-ene moieties are conformationally fixed in the solid state at normal temperatures and both enantiomers can be seen in the crystal

structure as distinct molecules in similar conformations. The thiophene rings are *anti* to one another in non-eclipsing cofacial gauche positions (ca. 50° and 60° off eclipsing for each enantiomer, respectively).<sup>19</sup> The torsional angles between the thiophene rings and the *trans* double bonds for each enantiomer were found to be ca. 25° and 21°. The thiophene rings are slightly envelope-shaped with the sulfur atoms being ca. 0.03 Å out of the ring plane, which is normal in thiophene cyclophanes.<sup>19</sup>

These structural results have important ramifications for the potential use of 1 as a monomer for cyclopolymerization. Cyclopolymerizations of 1,5- and 1,6-non-conjugated dienes in conformations similar to that of 1 have been shown to lead to cyclopolymers containing five-membered ring backbones.<sup>1,2,20</sup> It has been suggested that the benzene analog 8 cyclopolymenzes easily due to its fixed structure and close proximity of double bonds.<sup>1</sup> We have carried out NMR studies on 8 which show no peak coalescence from -51 to 21 °C (the normal range for its cationic cyclopolymerization), suggesting that onset of conformational mobility, if any, occurs at higher temperatures. It might be expected that the greater conformational mobility of 1 would hinder analogous cyclopolymerization. Assuming that initiation occurs at C17\* to generate the resonance stabilized carbocation at C16\*, we suggest that clean cyclopolymerization of 1 would most likely occur at low temperature where the structure would be conformationally fixed and the proximity of the reacting centers, C16\* - C17 (3.25 Å, avg. for both molecules in the crystal structure), would facilitate ring closure. From this mode of ring closure we would also expect the protons on C16\* and C17 to be cis to one another, as has been shown in a model compound for the cationic cyclopolymerization of 8.1 Ring closure between C16 - C16\* (3.85 Å avg.) to form a six-membered ring is less likely due to the greater distance between these atoms and the formation of a less stable 2° carbocation intermediate. Attack of cationic initiator at C16\*, followed by bond formation between C17 and C17\*, atthough close (2.66 Å avg.), appears less favorable due to the formation of a strained cyclobutane ring and the need to form an initial, nonresonance stabilized 2° carbocation at C17\*. These structural studies suggest cyclopolymerization of 1 to be favorable under proper conditions and are significant since little structural detail is known about cyclophane cyclopolymers from direct investigations. Initial attempts to cyclopolymerize 1 have been successful and details on its polymerization and polymer properties will be forthcoming.

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## **References and Notes**

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- New Compounds: Compound 3: Oil, bp 93 °C/0.4 mm Hg. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>), δ ppm: 6.70 (d, 1H, J=3.3 Hz, thiophene); 6.5-6.6 (m, 2H, thiophene, vinyl); 5.9 (m, 1H, vinyl); 3.0 (d, 2H, J=7.8 Hz); 2.44 (s, 3H); 2.25 (s, 6H). IR (neat): 765 and 790 (s, CH oop); 950 (s, C=C trans); 1430 (m, thiophene); and 3050 cm<sup>-1</sup> (w, β-hydrogens). MS: m/e 181 (32%, M<sup>+</sup>), 137 (51%), 111 (65%), 58 (100%). Compound 4: mp 158-161 °C (decomp). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>), δ ppm: 7.2 (d, 1H, J=18 Hz, vinyl); 6.96 (d, 1H, J=3.3 Hz, thiophene); 6.67 (d, 1H, J=3.3 Hz, thiophene); 5.95 (m, 1H, vinyl); 4.6 (d, 2H, J=8.1 Hz); 3.4 (s, 9H); 2.47 (s,

- m/e 519 (32%, 2M+-I), 196 (100%, M+-I), 137 (63%). Hydroxide 5 was not isolated.
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- Compound 1: mp (hexane) 106-108 °C (decomp).<sup>1</sup>H-NMR (300 MHz, CDCl3, ambient), δ ppm: 6.71 (d, 2H, J=3.6 Hz, thiophene); 6.62 (d, 2H, J=3.6 Hz, thiophene); 6.10 (d, 2H, J=15.9 Hz, vinyl); 5.35 (m, 2H, vinyl); 2.84 (br s, 4H, [2]-bridge methylenes); 2.45 (m, 4H, [6]-bridge methylenes). <sup>13</sup>C-NMR (300 MHz, Gated Decoupling, CDCl3), δ ppm: 144.7, 144.1 (thiophene ipso); 133.3, 125.5 (thiophene); 125.0, 124.1 (vinyl); 33.2 ([2]-bridge methylenes); 31.6 ([6]-bridge methylenes). IR (KBr): 770, 790 (s); 950 (s, C=C trans);1430 and 1460 (m, thiophene); and 3000 cm<sup>-1</sup> (w, β-hydrogens). MS: m/e 272 (100%, M<sup>+</sup>), 136 (100%), 110 (11%). Anal. Calcd for C1<sub>6</sub>H1<sub>6</sub>S<sub>2</sub>: C, 70.54; H, 5.91. Found: C, 69.39; H, 5.90.<sup>21</sup> UV (hexane): λ<sub>max</sub> 282 (18800), sh 320 (3774).
- Compound 6: Waxy solid, mp (EtOH) 28-30 °C. <sup>1</sup>H-NMR (300 MHz, CDCl3), δ ppm: 6.64 (d, 2H, J=3.4 Hz, thiophene); 6.60 (d, 2H, J=3.4 Hz, thiophene); 2.9 (s, 4H, [2]-bridge methylenes); 2.6 (m, 4H, thenylic); 1.5 (m, 4H); 1.2 (m, 4H, [6]-bridge methylenes). IR (KBr): 775 and 780 (s); and 1430 cm<sup>-1</sup> (m, thiophene); 3050 cm<sup>-1</sup> (w, β-hydrogens). MS: m/e 276 (100%, M<sup>+</sup>), 123 (83%), 110 (100%), 97 (27%).
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- 18. Both enantiomers of 1 are found in the unit cell as independent molecules. Only half of each independent molecule is unique because both are situated at a crystallographic two-fold axis. Therefore, the total number of molecules in the unit cell is four. We note with interest that crystallization of a racemic mixture in an acentric space group (P2<sub>1</sub>2<sub>1</sub>2) in this manner is highly uncommon. Crystal cell data for 1 (slow cooling from hexane):  $C_{16}H_{16}S_2$ ; orthorhombic, space group  $P2_{1}2_{1}2$ ; a = 11.860(4), b = 10.936(3), c = 11.179(4) Å; V = 1449.9 Å<sup>3</sup>;  $M_r = 274.25$ ;  $\rho_{calcd} = 1.256$  g cm<sup>-3</sup>; Z = 4; F(000) = 576;  $\lambda(MoK\alpha) = 0.71069$  Å;  $\mu = 3.0$  cm<sup>-1</sup>. Cell dimensions and intensities of 2555 reflections were measured at room temperature ( $2\theta_{max} = 50^{\circ}$ ,  $\pm h$ , k, h on an Enraf-Nonius CAD-4 diffractometer. The structure was solved by direct methods and refined anisotropically by full-matrix least squares. The data did not allow location of hydrogen atoms and they were not included in the refinement. In general all the atoms displayed high thermal motion and data collected at low temperature data (-110 °C) did not afford improvement. All calculations were carried out with use of the SHELX-76 program. For 1010 unique observed reflections (I > 2\sigma (I)) the final refinement parameters were R = 0.068,  $R_w = 0.065$ , and GOF = 2.8, where R =  $\Sigma(IF_0I IF_cI)/\Sigma IF_0I$ ,  $R_w = [\Sigma W(IF_0I IF_cI)^2 / \Sigma W IF_0I^2]^{1/2}$ , and GOF =  $[\Sigma W(IF_0I IF_cI)^2/((m-n))]^{1/2}$ .
- Note that the conformation between the rings in the more rigid [2.2]thiophenophane is intermediate gaucheeclipsed, the torsional angle being 34.4° (Keehn, P. M.; Rosenfeld, S. M. Cyclophanes; Academic Press: New York; 1983, pp. 160-161).
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