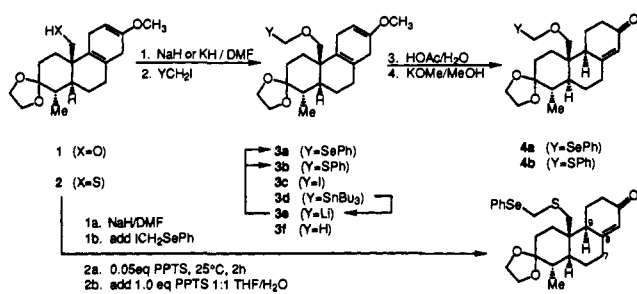
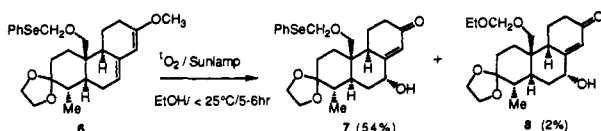


1 equiv of *n*-BuLi in the presence of additives was used in either the sulfenylation or selenylation reactions, a mixture of starting material **3d** (40%), desired product **3a** (29%), and proton-quenched product **3f** (12%) resulted. Fortunately  $\alpha$ -alkoxy stannane **3d** was cleanly selenylated<sup>3</sup> (91% yield of **3a/3f** in a 96:4 ratio) or sulfenylated (75% yield of **3b/3f** in a 92:8 ratio) provided that 2.1 equiv of *n*-BuLi<sup>6</sup> and 4.0 equiv of TMEDA were used to form the  $\alpha$ -alkoxy anion.  $\alpha$ -Alkoxy derivatives **3a,b** were treated with aqueous acetic acid (to generate the  $\beta,\gamma$ -unsaturated ketones) followed by reaction with potassium methoxide in methanol to provide conjugated enones **4a,b** in 46% and 60% overall yield, respectively.

Conversion of mercaptan **2** to compound **5** was accomplished by alkylation with  $\alpha$ -iodomethyl phenylselenide.<sup>7</sup> While aqueous acetic acid hydrolysis quantitatively provided the  $\Delta^{8,9}$   $\beta,\gamma$ -unsaturated ketone, potassium methoxide-mediated conjugation only provided **5** in 15% yield. A preferable method involves PPTs<sup>8</sup>-catalyzed isomerization of **2** to a dienyl ether mixture followed by addition of water to generate **5** (55%) which is easily separated from a 2:1 mixture of the  $\Delta^{8,9}$  and  $\Delta^{7,8}$   $\beta,\gamma$ -unsaturated ketones (23%).



With these precursors in hand, attention was next directed to the introduction of the C-7 oxygen functionality required for the tandem cyclization. Under strictly anhydrous conditions, isomerization<sup>4,9</sup> of **3a** to the thermodynamically more stable conjugated dienyl ether **6** using PPTs occurred in 67% yield. Treatment of the oxidatively-labile dienyl ether **6** with various oxidants such as mCPBA,<sup>10</sup> oxone,<sup>9</sup> or Pd[II]<sup>11</sup> gave a mixture which contained only traces of the desired product **7**. However, when oxidation was carried out with molecular oxygen in a Rayonet reactor (300 nm, Pyrex flask) or using a sun lamp<sup>12</sup> in the absence of sensitizer,  $\gamma$ -hydroxy enone **7** was formed along with a small amount of acetal **8**. Standard reactions<sup>13</sup> effected conversion of **7** to substrates **9a-d**.



Cyclization experiments were conducted as summarized in Table I. These involved slow addition of a 0.1 M solution of tributyl tin hydride in toluene containing 10 mol % AIBN to a

0.01 M solution of the substrate in toluene at reflux.<sup>14</sup> As expected,  $\alpha$ -alkoxy selenide **4a** proved to be far superior to  $\alpha$ -alkoxy sulfide **4b**. By way of contrast,  $\alpha$ -thioselenide **5** afforded a mixture which was enriched in the product resulting from hydride quenching of the  $\alpha$ -thio radical<sup>15</sup> intermediate. Cyclizations of  $\gamma$ -alkoxy enones **7** and **9a** were successful, but attempts to extend the protocol to a tandem cyclization with propargylic ester **9b** produced an exceptionally complex mixture.

We were pleased to find that propargylic ether **9c** underwent clean conversion to the bisannulated product<sup>16</sup> C-H in 50% isolated yield along with a small amount of bridged tetrahydrofuran **D** which likely arises via cyclization of neopentyl alcohol produced by acid-catalyzed fragmentation of the  $\alpha$ -selenyl ether moiety (see table). Similar reaction with *trans*-cinnamyl ether terminator **9d** was less efficient. In this instance, the tetrahydropyranyl-cyclized  $\alpha$ -keto radical intermediate is partitioned between tandem cyclization to C-H and simple reduction to B-H.

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## Electronic Structure and Optical Absorption of Poly(biisothianaphthene-methine) and Poly(isonaphthothiophene-thiophene): Two Low-Band-Gap Polymers

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Recent interest in the search for low-band-gap polymers has been stimulated by the significant intrinsic conductivity and good nonlinear optical properties due to the small gap.<sup>1</sup> Among conjugated polymers, poly(isothianaphthene) (PITN) was known so far to have the smallest energy gap ( $E_g \approx 1.0$  eV) found both experimentally<sup>2</sup> and theoretically.<sup>3</sup> For a related system, polythiophene (PT), it was suggested that the energy gap can be lowered significantly<sup>4</sup> by inserting additional CH units between the monomers (poly(bithiophene-methine), PBTM): the gap of PT is 2.1 eV experimentally<sup>5</sup> and 1.8 eV theoretically,<sup>3</sup> while the theoretical estimation for PBTM is 1.2 eV.<sup>6,7</sup> These systems are

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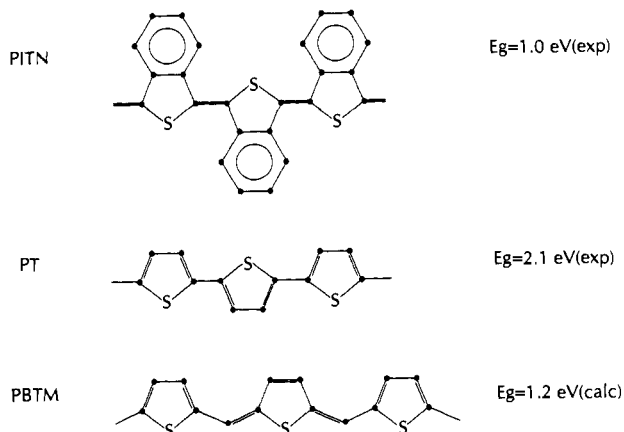
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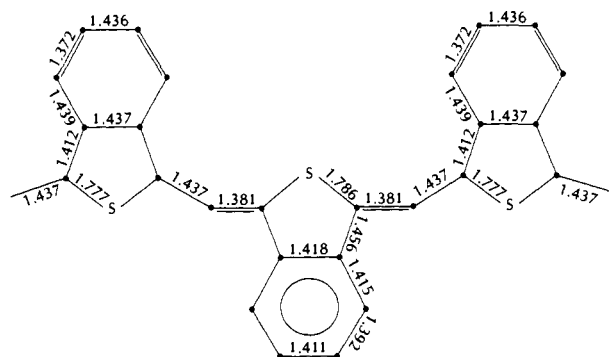
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(13) (a) **7** to **9a**: 4 equiv of Ac<sub>2</sub>O, 10 equiv of Et<sub>3</sub>N, catalyst DMAP, CH<sub>2</sub>Cl<sub>2</sub>, room temperature, 80%. (b) **7** to **9b**: 3 equiv of 3-phenylpropargylic acid, 3 equiv of DCC, catalyst DMAP, CH<sub>2</sub>Cl<sub>2</sub>, -20 °C to room temperature, 72% (cf.: Balas, L.; Jousseau, B.; Langwost, B. *Tetrahedron Lett.* **1989**, *30*, 4525). (c) **7** to **9c**: 50% KOH, 5 equiv of phenylpropargyl bromide, catalyst TBAI, CH<sub>2</sub>Cl<sub>2</sub>, room temperature, 66%. (d) **7** to **9d**: (i) 30% KOH, 5% equiv of cinnamyl bromide, catalyst TBAI, CH<sub>2</sub>Cl<sub>2</sub>, room temperature, (ii) MsCl, Et<sub>3</sub>N, 0 °C (to convert excess cinnamyl alcohol to its mesylate derivative for separation purposes), 55% yield for the two-step procedure (cf.: Kawamoto, K.; Nakai, T. *Chem. Lett.* **1985**, 1719).



**Figure 1.** Schematic structures and energy gaps of some organic conjugated polymers.



**Figure 2.** Schematic structure and optimized bond lengths of three units of poly(bis(isoindole-1,3-dione)-methine) (PBITNM).

shown in Figure 1. Due to H $\cdots$ H repulsions, the orientation of the rings is trans in all polymers discussed in this paper. According to the orbital interpretations,<sup>3,6-8</sup> the small gap of PITN is due to the combined effects of the perturbations caused by heteroatoms, side rings, and C-C bond relaxations. However, in the case of PBTM a curious cancellation of heteroatomic perturbations occurs. The gap reduction in PBTM relative to polyacetylene (PA) is therefore due to the slight reduction of the bond length alternation<sup>6</sup> of the C-C-C-C backbone.

Since PITN has a lower gap than PT, it appears to be a straightforward idea to modify the structure of the former by introducing the methine linkage. The resulting polymer, PBITNM, is shown schematically in Figure 2. In this communication we present semiempirical calculations on the band structure and optical absorption of PBITNM. The theoretical method we selected for this purpose is based on the model of Longuet-Higgins and Salem (LHS)<sup>9</sup> which physically corresponds to an extended version of the SSH model.<sup>10</sup> In the LHS method, only the  $\pi$ -electrons are considered explicitly in the tight-binding (Hückel) approximation, while the effects of the  $\sigma$ -core are described by an empirical potential. The model is able to describe the effects of geometry changes on the  $\pi$ -electronic structure quite well. Recently, we have reparametrized the LHS model and extended it to treat heteroatoms as well.<sup>11</sup> The method was shown to be sufficiently accurate in predicting energy-gap values for

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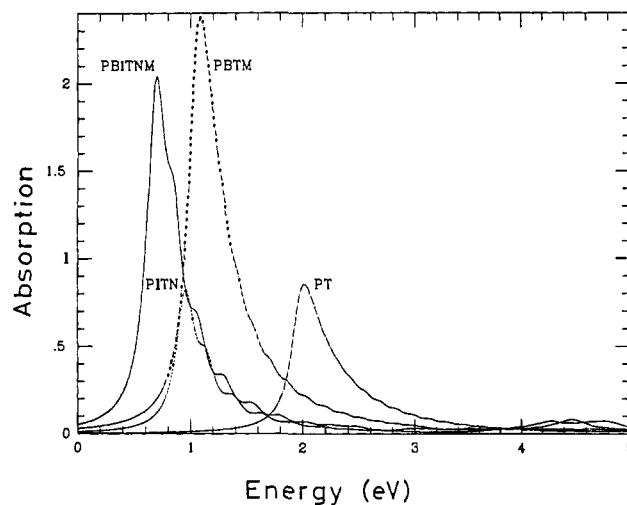
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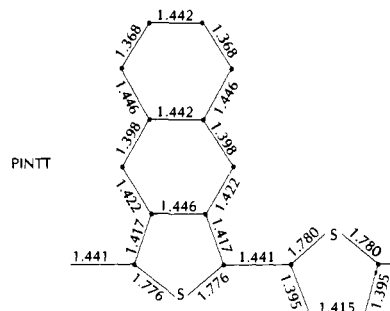
**Table I.** Reliability of the LHS Method for Predicting  $E_g$  (eV), Together with the Predicted  $E_g$  Values of the New Polymers PBITNM and PINTT

polymer	LHS	MNDO + EH	expt
(CH) <sub>x</sub> <sup>a</sup>	1.50	1.53 <sup>b</sup>	1.4-1.6 <sup>c</sup>
PT	1.97	1.83 <sup>d</sup>	2.1 <sup>e</sup>
PITN <sup>a</sup>	1.00	1.16 <sup>d</sup>	1.0 <sup>f</sup>
PINT	1.37	1.50 <sup>d</sup>	1.4-1.5 <sup>g</sup>
PBTM	1.04	1.21 <sup>b</sup>	
PBITNM	0.69		
PINTT	0.54		

<sup>a</sup>Basis of parametrization. <sup>b</sup>Reference 6. <sup>c</sup>Reference 12. <sup>d</sup>Reference 8. <sup>e</sup>Reference 5. <sup>f</sup>Reference 2. <sup>g</sup>Reference 13.



**Figure 3.** Optical absorption spectrum of PBITNM, compared to those of PT, PBTM, and PITN, calculated by the LHS method.



**Figure 4.** Schematic structure and optimized bond lengths of poly(iso-naphthothiophene-thiophene) (PINTT).

simple  $\pi$ -electron polymers (see Table I).

For PBITNM, we have calculated the optimized bond lengths and the energy levels. Transition energies are evaluated simply as orbital energy differences. Transition moments are evaluated in the dipole velocity formalism. From these data, optical absorption curves can easily be constructed. We considered a superposition of Lorentzian lines with an individual half-width of 0.1 eV at each transition weighted by the squares of transition moments defining the transition intensities.

The calculated optical absorption for PBITNM is shown in Figure 3. The calculations have been performed for an oligomer consisting of 19 unit cells, but we checked also that a chain of 11 unit cells shows practically the same result, so convergence is reached for the gap as a function of the chain length. It is remarkable that the band gap is only  $\approx 0.7$  eV. At the band edges, the density of states is quite high, and the one-electron states are fairly delocalized. The band structure of PBITNM is rather complicated, but the valence and conduction bands seem to be wide enough to allow significant conductivity of the system.

An alternative strategy to lower  $E_g$  is offered by mixing together the repeat units of polymers with significantly different band

gaps.<sup>14</sup> By mixing thiophene and isothianaphthothiophene we arrive at poly(isonaphthothiophene-thiophene), PINTT, as shown in Figure 4. In this polymer the two repeat units are connected by a CC bond of intermediate strength, and the calculated gap is expected to be rather small.

We have to note that there are several factors neglected in the above model which can increase the real energy gap: steric effects which may cause nonplanarity, short conjugated segments due to cross-links, randomly coiled segments, etc. Last but not least, electron-electron interactions and correlation effects may influence the band gap. Nevertheless, the parametrization of our model has been quite successful for several related systems (cf. Table I), which leads us to conclude that the present estimations for the band gaps of PBITNM (0.7 eV) and PINTT (0.5 eV) are not far from reality. Even though the reduced alternation of  $\delta r_{av} = 0.044 \text{ \AA}$  along the main chain for PBITNM would predict a gap of  $1.5 \text{ eV} \times (0.044/0.090) = 0.73 \text{ eV}$  if one based the gap solely on the alternation of the C-C-C-C carbon skeleton, this agreement with the theoretical prediction of 0.69 eV is completely fortuitous. Orbital interpretation of the small gap is in concordance with earlier results.<sup>3,6,8</sup> The frontier orbitals are delocalized over the main chain as well as the side rings and heteroatoms. Although these two materials have not been synthesized yet, syntheses of similar polymers<sup>15a,b</sup> and oligomers<sup>15c</sup> have been reported recently.

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**Supplementary Material Available:** Parameters used in the present study (4 pages). Ordering information is given on any current masthead page.

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### Synthesis and Reactivity of Bis-Stannylenes Adducts of Zirconocene and (1,1'-Dimethyl)zirconocene. X-ray Crystal Structure of $(C_5H_4CH_3)_2Zr[Sn[CH(SiMe_3)_2]_2]_2$

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The formation and transformation of transition metal to main group element bonds are important steps in a variety of processes including metal mediated hydrometalation cycles,<sup>1</sup> dehydrogenative polymerizations,<sup>2</sup> and semiconductor growth.<sup>3</sup> New methods for generating such bonds are thus of interest, particularly in cases where existing synthetic procedures do not work efficiently. For example, although group 4-silicon compounds have found extensive application in some of the above-mentioned processes,<sup>2,4</sup>

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group 4-tin derivatives remain virtually unknown,<sup>5</sup> primarily due to a lack of synthetic technology.<sup>6</sup> Herein we report the synthesis of a new Zr-Sn complex via a route that takes advantage of zirconium's strong Lewis acidity and the propensity of two carbene-like fragments to couple. The resulting metal-metal bonds are stabilized by a significant  $\pi$  component as indicated by a short Zr-Sn distance.

In situ generated "zirconocene"<sup>7</sup> was trapped while warming a THF solution of  $Cp'_2Zr(n-Bu)_2$ <sup>8</sup> ( $Cp' = C_5H_5$  (a),  $C_5H_4CH_3$  (b)) to room temperature from  $-78 \text{ }^\circ\text{C}$  in the presence of 2 equiv of Lappert's monomeric stannylenes  $Sn[CH(SiMe_3)_2]_2$ <sup>9</sup> (Scheme I). During warming, a slow darkening of the reaction mixture was observed. Upon stirring at room temperature for 1 h, removal of the THF followed by extraction with hexanes yielded a deep blue filtrate from which red-purple microcrystals of  $Cp'_2Zr[Sn[CH(SiMe_3)_2]_2]_2$  (**1a** and **1b**) could be isolated in 40-55% yield. Although the reaction proceeded in better than 80% yield based on crude product returns, isolated yields were lower owing to the high solubility of both **1a** and **1b** even in hydrocarbon solvents.<sup>10</sup>

The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectral data obtained for **1a** and **1b** (supplementary material) indicated that 2 equiv of stannylenes were incorporated into the products. Originally it was anticipated that the bulky nature of the stannylenes would prevent coordination of the second equivalent; nevertheless, when the reaction was performed with 1 equiv of stannylenes, only lower yields of **1a** were obtained. An X-ray diffraction analysis<sup>11,12</sup> on crystals of **1b** confirmed that the formally Zr(II) center had accommodated two stannylenes donors and possesses pseudo-tetrahedral geometry with a 2-fold axis bisecting the Cp-Zr-Cp and Sn-Zr-Sn' angles. The  $CH(SiMe_3)_2$  groups on tin are positioned above and below the plane defined by Sn-Zr-Sn', an orientation which aligns the empty p-orbitals on the two Sn atoms for maximum  $\pi$  overlap with the filled  $1a_1$  orbital of the  $Cp_2Zr^{II}$  fragment.<sup>13</sup> Additionally, the alkyl groups are bent back slightly ( $9.67^\circ$ ) from the Zr-Sn vector, i.e., the Sn atom sits  $0.155 \text{ \AA}$  above the plane defined by Zr, C(7), and C(8). Though these structural features favor a  $\sigma$  interaction between the two tin p-orbitals (I, Scheme I), it appears that steric interaction between the alkyl groups has arrested Sn-Sn bond formation in this complex; the large separation of  $4.236 \text{ \AA}$  indicates that any Sn-Sn interaction is weak.<sup>14</sup>

The most interesting datum is the Zr-Sn distance of  $2.8715 (11) \text{ \AA}$ . A handful of group 4 metal-tin complexes have been structurally characterized<sup>5c,f</sup> and typically the M-Sn bond is long

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(12) Selected bond distances ( $\text{Å}$ ) and angles (deg) with estimated standard deviations in parentheses: Zr-Sn,  $2.8715 (11)$ ; Zr-Cp<sub>cent</sub>,  $2.196 (8)$ ; Sn-Sn',  $4.236 (2)$ ; Sn-Zr-Sn',  $95.06 (4)$ ; Cp<sub>cent</sub>-Zr-Cp<sub>cent</sub>',  $131.5 (3)$ ; C(7)-Sn-C(8),  $102.4 (2)$ ; C(7)-Sn-Zr,  $135.9 (2)$ ; C(8)-Sn-Zr,  $120.5 (2)$ .

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