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Bridged Dithienylethylenes as Precursors of Small Bandgap Electrogenerated Conjugated Polymers

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Bridged dithienylethylenes (DTEs) bearing solubilizing alkyl chains at various positions (**2**−**5**) have been synthesized by McMurry dimerization of cyclopenta[*b*]thiophen-6-ones. In order to introduce alkyl substituents at different positions of the DTE molecule, the precursor ketones have been prepared by different strategies based on a combination of Mannich or Wittig−Horner reaction and Friedel−Craft intramolecular cyclization. The position and the length of the alkyl substituents exert a strong effect on the ability of the precursor to undergo electrochemical polymerization. Thus, whereas substitution at the α-position of the ethylene linkage (**3**) results in a rapid inhibition of electropolymerization, introduction of alkyl chains at the *β*-position (**4**, **5**) greatly improves the efficiency of the polymerization process. The analysis of the electrochemical and optical properties of the polymers shows that rigidification of the DTE molecule leads to a significant decrease of the oxidation potential and bandgap. A comparative analysis of DTE and its bridged analogues by means of X-ray diffraction reveals, in agreement with experimental and theoretical results, that the observed reduction of both the HOMO−LUMO gap of the precursor and the bandgap of the corresponding polymers are related to a relaxation of bond length alternation in the DTE moiety.

Introduction

The synthesis of narrow bandgap linear *π*-conjugated systems (LCSs) has become one of the main challenges for synthetic chemists involved in the field of organic conductors.[1] Since E_g governs the intrinsic electronic properties of the *π*-conjugated system, progress in this area constitutes the key of many fundamental and technological problems. Thus, in addition to the long term possibility of achieving intrinsic metallic conductivity, the search for small bandgap LCSs is motivated by the optimization of other properties such as the increase of the number of charge carriers in organic field-effect transistors,[2] the possibility to use stable metal electrodes for the fabrication of organic light emitting diodes,[3] or the improvement of electron transmission efficiency when LCSs are used as *π*-conjugating spacers in molecules for nonlinear optics.[4]

Since the first synthesis of poly(isothianaphthene)[1a] the increase of the quinonoid character of the conjugated backbone to the detriment of its aromaticity has represented the main strategy for synthesizing small bandgap conjugated polymers.[1a−e] While this research area remains very active,[5] the past few years have witnessed the emergence of alternative approaches such as the introduction of electron-withdrawing or electron-releasing groups at selected positions of the conjugated chain[1c,g,3,6] or, more recently, the rigidification of the *π*-conjugated system.[1f,7]

Previous works have shown that the bandgap of poly(thienylenevinylene) (PTV) (1.70−1.80 eV)[8] is significantly smaller than that of poly(thiophene) (PT) (2.00−2.20 eV).[9] This lower bandgap is related to the presence of ethylene linkages of defined configuration that (*i*) limit the statistical rotational disorder associated with the interannular rotations around single bonds in PT[10] and (ii) decrease the overall aromatic character of the *π*-conjugated backbone and thus contribute to minimizing *π*-electrons confinement within the aromatic thiophene rings.[11]

In this context, *trans*-dithienylethylenes (DTEs) have recently attracted particular attention as precursors of *π*-conjugated polymers that exhibit some structural features of PTV while retaining the advantages of the

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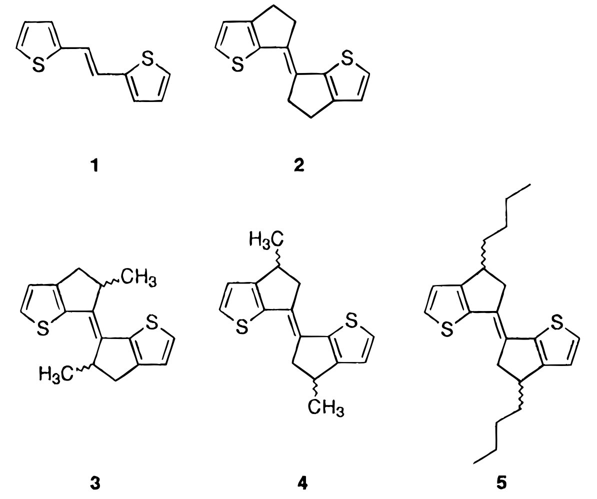
Chart 1



electrochemical polymerization.[12] Thus, the chemical or electrochemical polymerization of DTEs bearing solubilizing alkyl chains at the 3,3′-positions of the thiophene rings leads to polymers with bandgaps around 1.70 eV and conductivities of ~10^{-2} S cm^{-1}.[12] On the other hand, it has been shown that electropolymerization of DTEs or of related oligomers bearing a cyano group at the ethylene linkage leads to conjugated polymers exhibiting both high electron affinity and reduced bandgaps.[6c,f]

We have shown recently that the covalent bridging of the thiophene rings with the central ethylene linkage of DTE leads to a reduction from 1.80 to 1.40 eV of the bandgap of the corresponding polymer.[13] However, this structural modification also produces a considerable decrease of the solubility of the precursor, which has deleterious consequences for the efficiency of the electropolymerization process.

In an attempt to solve this problem, we report here the synthesis of bridged DTEs **2**−**5** (Chart 1) in which solubilizing alkyl groups have been attached at various positions of the molecule.

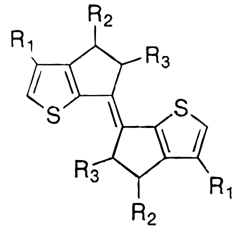
The characterization of the electrochemical and optical properties of the resulting polymers using DTEs **1** and **2** as reference compounds shows that the length and the position of the alkyl chain exert a strong effect on the polymerization reaction and on the structure and properties of the polymer. These results are discussed in the light of the crystal structures of the precursors and of the results of MO calculations.

Results and Discussion

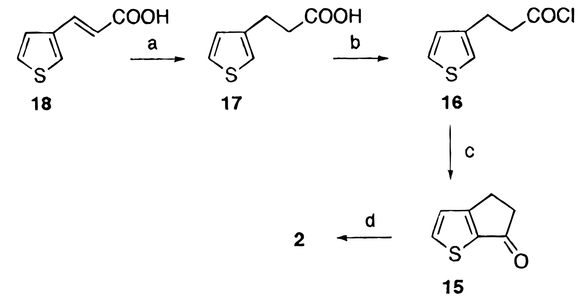
Synthesis of the DTE Precursors. Substitution of the bridged DTE molecule **2** can be envisioned at three different positions R_1−R_3 (Chart 2).

Since subsequent polymerization implies the formation of thiophene−thiophene linkages, substitution at R_1 will result in a strong steric interaction between the substituents grafted on adjacent thiophene rings with a departure from planarity and hence a loss of effective conjugation. We therefore focused on the two other possible sites R_2 and R_3 (**3**−**5**) (Chart 1).

Chart 2

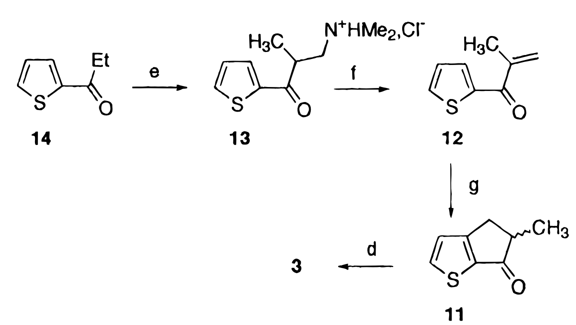


Scheme 1[a]



[a] Reagents: (a) Na/Hg, (b) $SOCl_2$, (c) $AlCl_3$, (d) $TiCl_4$/Zn.

Scheme 2[a]



[a] Reagents: (d) $TiCl_4$/Zn, (e) Me_2NH,HCl/HCHO, (f) Δ, (g) H_2SO_4.

While the various bridged DTEs have been synthesized by McMurry dimerization[14] of the corresponding cyclopenta[*b*]thiophen-6-one (Schemes 1−3), each type of substitution implies the definition of the approriate synthetic strategy for the preparation of the precursor ketone. 1,2-Bis(2-thienyl)ethylene (**1**) was prepared according to the method described in the literature.[15] Cyclopenta[*b*]thiophen-6-one (**15**) was synthesized according to the procedure described by McDowell et al.[16] 3-(3-Thienyl)propionic acid (**17**) obtained by reduction of 3-(3-thienyl)acrylic acid (**18**) by sodium amalgam was converted into the corresponding acid chloride (**16**), which was then subjected to intramolecular Friedel−Crafts acylation to afford the target compound (Scheme 1).

Attempts to synthesize ketone **11** with a methyl group at the R_3 position by direct methylation of **15** with iodomethane in the presence of potassium *tert*-butylate gave mixtures of mono- and dimethylated products that were very difficult to separate. In order to solve this

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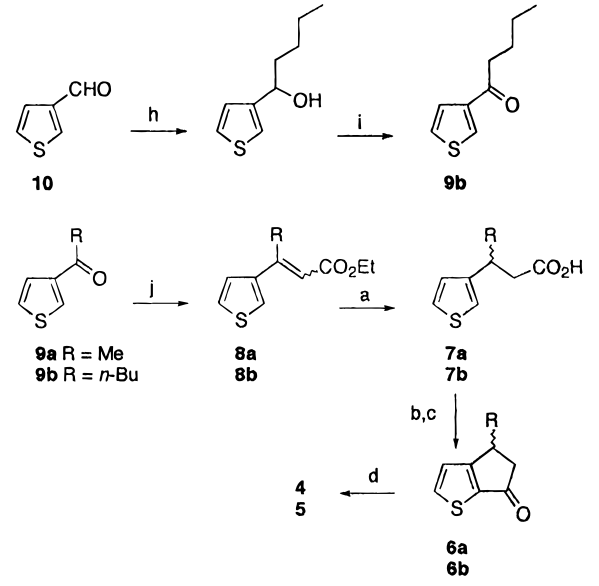
Scheme 3[a]



[a] Reagents: (a) Na/Hg, (b) $SOCl_2$, (c) $AlCl_3$, (d) $TiCl_4$/Zn, (h) *n*-BuMgBr, (i) CrO_3, (j) $(EtO)_2P(O)CH_2CO_2Et$.

problem, we adopted another synthetic strategy based on the method of Burckhalter et al.[17] A Mannich reaction between 2-propionylthiophene, formaldehyde, and dimethylamine chlorohydrate gave the salt **13**, which, upon distillation under reduced pressure, afforded the unsaturated ketone **12**. Due to its strong propensity to polymerize, this latter compound is immediately engaged in the last step, which involves intramolecular cyclization in the presence of concentrated sulfuric acid (Scheme 2).

Ketones **6a** and **6b**, precursors of bridged DTEs **4** and **5** substituted at R_2 with methyl and butyl chains, have been prepared using 3-acetylthiophene (**9a**) and 3-pentanoylthiophene[18] (**9b)** as starting material. This latter compound has been prepared by reaction of *n*-butylmagnesium bromide on 3-thiophenecarboxaldehyde (**10**) followed by oxidation of the resulting secondary alcohol with chromium trioxide (Scheme 3).

Wittig–Horner olefination of **9a** and **9b** with triethyl phosphonoacetate in the presence of *n*-butyllithium afforded the corresponding α-unsaturated esters **8a** and **8b** as a mixture of *Z* and *E* isomers. Saponification of the ester group followed by reduction of the double bond with sodium amalgam and acidification gave the corresponding carboxylic acids **7a** and **7b**. Subsequent conversion into the corresponding acid chlorides and intramolecular Friedel–Crafts acylation yielded the cyclic ketones **6a** and **6b** as racemic mixtures. McMurry reaction of ketones **11**, **6a**, and **6b** gave the substituted target molecules **3**–**5** as a mixture of diastereomers.

Table 1 lists the electrochemical and electronic absorption data of the various DTEs. The values of the anodic peak potentials (Epa1) determined by single scan cyclic voltammetry clearly show that the bridging of the thiophene ring to the ethylene linkage leads to a considerable negative shift of Epa1 from 1.10 to *ca.* 0.70 V, indicative of a parallel decrease in oxidation potential.

Comparison of the electronic spectra of the various bridged DTEs with that of **1** reveals, as previously observed for **2**,[13] a strong intensification of the resolution of the vibronic fine structure typical of rigid conjugated systems.[19] The band maxima undergo a 7–8 nm bathochromic shift indicative of an extension of π-electron delocalization, while as already observed for other rigidified π-conjugated systems,[7,13] these changes are accompanied by the emergence of a new absorption band of weak intensity extending up to the 460–470 nm region.

Table 1. Electrochemical and UV–vis Spectral Data for Compounds 1–5

compd	λ_{max} (nm)	Epa1 (V/SCE)
1	330, **341**, 360	1.10
2	331, **348**, 367	0.72
3	333, **350**, 369	0.78
4	331, **348**, 368	0.73
5	332, **349**, 369	0.72

Preparation and Properties of the Polymers. The electrochemical polymerization of aromatic-like precursors involves their electrooxidation into the corresponding cation radical followed by a succession of chemical (C) and electrochemical (E) steps according to a (ECCE)n scheme.[9,20] In addition to the chemical reactivity of the cation radical, the efficiency of electropolymerization depends also on the solubility of the precursor molecule and on that of the various oxidized intermediates involved in the polymerization process. However, since oxidation to the cation radical state generally results in a decrease in solubility, it is clear that a poorly soluble precursor will lead to a limited number of couplings, thus preventing the formation of extensively conjugated polymer chains. In the extreme case, highly conjugated and poorly soluble molecules lead to the electrodeposition of the cation radical salt of the precursor itself, as already observed for sexithienyls.[21] In this context, it is clear that, due to their low oxidation potential and hence to the low reactivity of their cation radicals, electropolymerization of DTEs, and especially the bridged ones, can be expected to be more difficult than that of thiophene monomers.

Figure 1 shows the cyclic voltammograms (CV) corresponding to the potentiodynamic polymerization of **2**–**5** by application of recurrent potential scans. In each case, the first CV trace shows an irreversible anodic wave corresponding to the oxidation of the monomer into its cation radical. Subsequent cycling leads to the emergence, at less positive potentials, of a new redox system associated with the oxidation and reduction of the polymer grafted onto the electrode surface. For the unsubstituted DTE **2**, the CV shows narrow anodic and cathodic waves indicative of the formation of a single compound of defined structure. The polymerization CV of **3** and **4** show that introduction of a methyl group in the DTE structure leads to a broadening of the wave and to a slight negative shift of their maximum. However, for **3**, the increase of the wave intensity stops after 12–15 cycles, revealing an inhibition of the polymerization process. Comparison of the polymerization CV of **5** with the previous ones shows that the grafting of the *n*-butyl chain induces a much larger negative shift of the polymer redox system, suggesting the formation of a more conjugated polymer.

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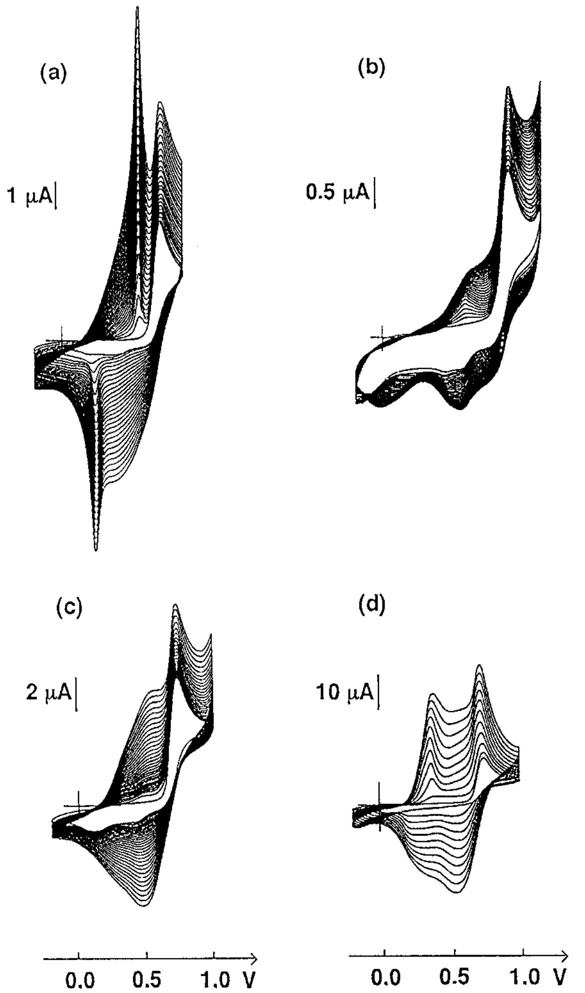

Figure 1. Potentiodynamic electrodeposition curves for the polymers (a) **2**, (b) **3**, (c) **4**, and (d) **5**. 10^{-2} M substrate in 0.1 M TBHP−MeCN, scan rate 100 mV s^{-1}.

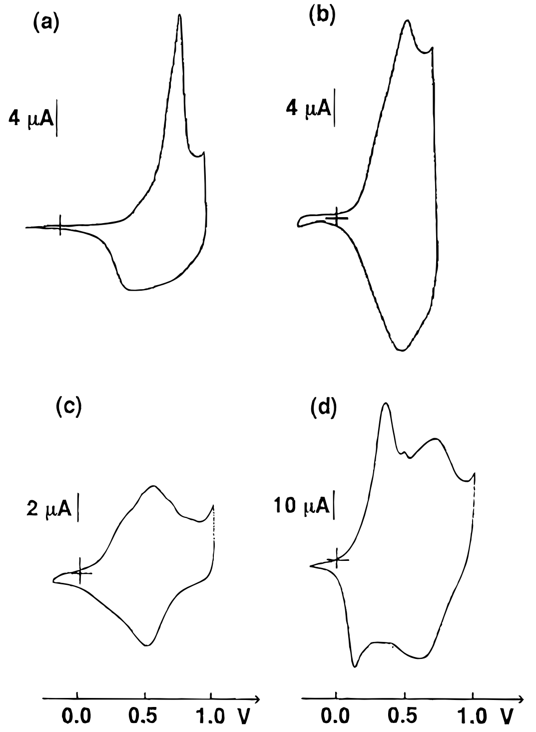

Figure 2. Cyclic voltammograms of the polymers electrodeposited on Pt under the conditions of Figure 1. Electrolytic medium 10^{-1} M TBHP−MeCN, scan rate 100 mV s^{-1}: (a) poly(**1**), (b) poly(**2**), (c) poly(**4**), and (d) poly(**5**).

Table 2. Electrochemical and UV−vis Spectral Data for Poly(1−5)

precursor	Epa (V/SCE)	λ_{max} (nm)	Eg (eV)
1	0.98	500	1.80
2	0.60	500	1.30−1.40
3	0.70	430	
4	0.56	470	1.30−1.40
5	0.34	486	1.30−1.40

Figure 2 shows the CVs of the polymers derived from **1**, **2**, **4**, and **5** recorded in a monomer-free electrolytic medium. Comparison of the CVs of poly(**1**) and poly(**2**) shows that the rigidification of the DTE molecule considerably improves the symmetry of the anodic and cathodic waves and hence the electrochemical reversibility. Concurrently, Epa1 shifts negatively from 1.00 to 0.60 V while a new weak anodic shoulder can be discerned around 0.30−0.40 V. The introduction of a methyl group in the structure leads to an intensification of this shoulder and to a decrease of Epa to 0.56 V. Finally, the CV of poly(**5**) shows that the first wave becomes predominant while Epa undergoes a further negative shift to 0.34 V, which is, to our knowledge, the lowest value ever reported for a poly(DTE) (Table 2).

This steady decrease of Epa from poly(**1**) to poly(**5**) suggests that the grafting of alkyl chains on the rigid DTE backbone considerably improves the efficiency of the electropolymerization process, thus allowing the formation of more extended π-conjugated structure.

Figures 3 and 4 show the electronic absorption of the undoped polymers on ITO. The spectrum of poly(**1**) shows a λ_{max} at 500 nm and an absorption edge at 685 nm corresponding to a bandgap (E_g) of *ca.* 1.80 eV, in agreement with previous works.[12,13] In addition to a main band with a λ_{max} around 500 nm, the spectra of the polymers derived from the rigid DTEs exhibit an additional broad absorption band extending to the 900−1000 nm region. Similar spectral features have already been observed for other small bandgap polymers.[1c,f,6a,c,d] Although the shape of these spectra makes it difficult, a precise determination of the bandgap (E_g) values around 1.30−1.40 eV can be estimated from the long-wavelength absorption onset.

A further comparison of the spectra of Figures 3 and 4 shows that the intensity of the near-IR absorption is significantly lower for poly(**4**) and poly(**5**) than for poly(**2**). This result appears in contradiction with the extension of conjugation length indicated by the low Epa values for poly(**4**) and poly(**5**). Consequently, it seems rather unlikely that these different spectral features exactly reflect the intrinsic electronic properties of the polymers. In fact, electrodeposition of homogeneous films of poly(**4**) and poly(**5**) on ITO was found considerably more problematic than for poly(**1**) and poly(**2**). Although the origin of this difficulty is not clearly understood, it seems plausible that the presence of alkyl substituents in a plane orthogonal to that of the π-conjugated system can perturb the grafting of the polymer onto the ITO surface. Such a behavior has already been reported for other nonplanar monomers.[22] Another possible relevant factor could involve the increase of the lipophilicity of the

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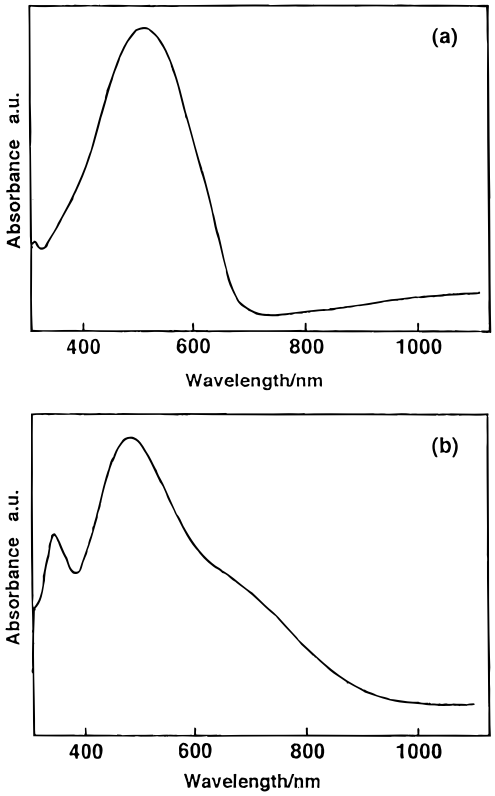

Figure 3. Electronic absorption spectra of the undoped polymers on ITO: (a) poly(**1**) and (b) poly(**2**).

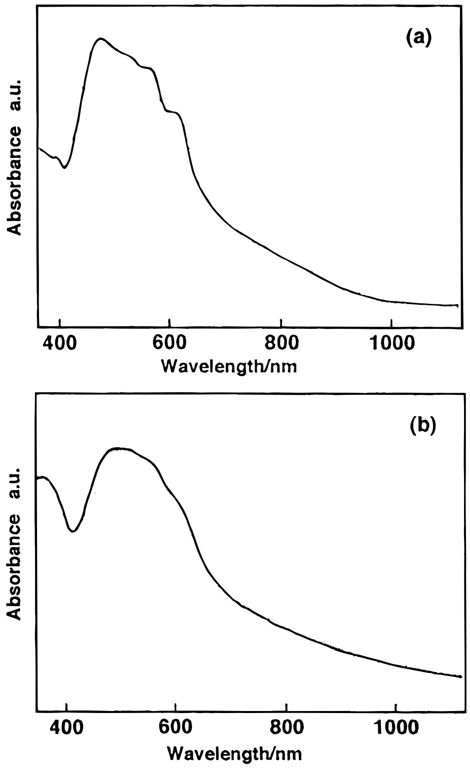

Figure 4. Electronic absorption spectra of the undoped polymers on ITO: (a) poly(**4**), and (b) poly(**5**).

precursor, which makes more difficult the grafting onto the hydrophilic ITO surface as observed for poly(thiophenes) substituted by long alkyl chains.[23]

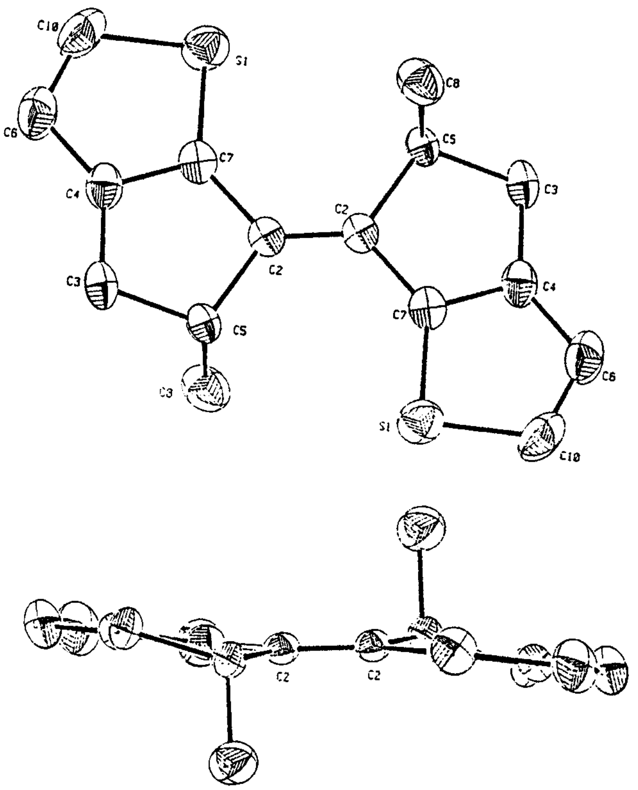

Figure 5. ORTEP view of **3**.

Larger scale electropolymerizations were performed, and the four-probe conductivity of the resulting powdery deposits was measured on compacted pellets. While poly(**2**) shows a four-probe conductivity of 1–2 × 10^{-2} S cm^{-1}, comparable to that of poly(**1**),[12,13] poly(**5**) exhibits a significantly higher value of 0.15 S cm^{-1} consistent with the more extended conjugation length indicated by electrochemical data.

These various results show that, whereas the rigidification of the DTE molecule leads to a significant decrease of the oxidation potential and bandgap of the resulting polymer, the position and the size of the alkyl group exert a strong influence on the electropolymerization process and on the structure and electronic properties of the resulting polymer. Thus, while substitution at R_2 improves the efficiency of polymerization, substitution at R_3 inhibits the process. These different behaviors suggest that substitution affects the geometry of the conjugated structure and hence the electronic distribution within the DTE molecule. In order to gain more detailed information on this point, single crystals of **3** and **5** have been analyzed by X-ray diffraction.

X-ray Structure and MO Calculations. Figures 5 and 6 show the ORTEP views of the meso forms of **3** and **5** which crystallize preferentially (see the Experimental Section). Molecules **1**,[24] **3**, and **5** belong to the C_i molecular point group. For **1** and **5** the thiophene ring is almost planar and there is a dihedral angle (θ) of 3° between the thiophene ring average plane and the C_2–$C_{2'}$ double bond. For **3**, the steric interaction induced by the methyl groups at R_3 leads to a distortion of the conjugated path with an increase of θ to 8° while the C_5 atom is pushed out of plane. Although the inhibition of polymerization observed for **3** is probably related to these various distortions of the DTE molecule, the relationships between the observed phenomenon and the geometry of the precursor are not clearly understood yet.

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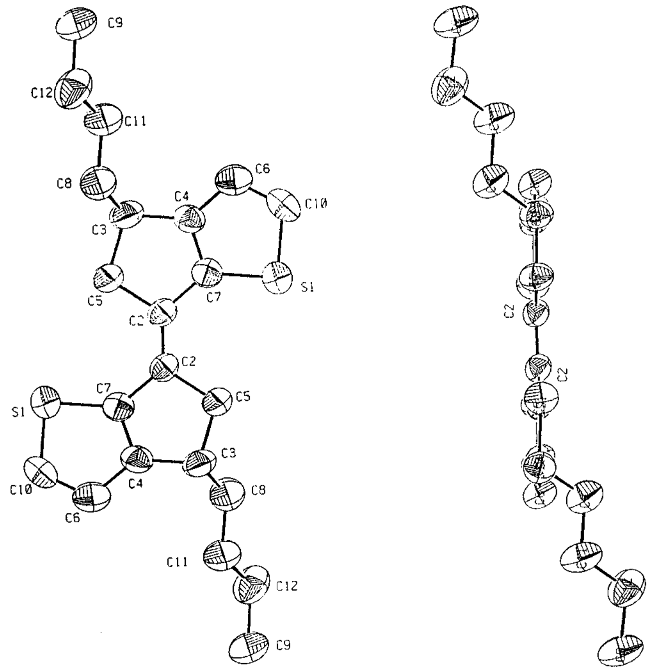

Figure 6. ORTEP view of **5**.

Table 3. Bond Distances along the Conjugated Path for Molecules 1,[24] 3, and 5

compd	C6−C10	C6−C4	C4−C7	C7−C2	C2−C2′	δr (Å)
1	1.350(8)	1.44(1)	1.40(1)	1.457(7)	1.309(8)	0.095
3	1.365(7)	1.416(6)	1.377(6)	1.455(5)	1.325(6)	0.080
5	1.350(1)	1.409(8)	1.356(8)	1.440(7)	1.335(6)	0.078

Comparison of the bond distances along the conjugated path for molecules **1**, **3**, and **5** (Table 3) shows that the bridging of the DTE molecule induces a deformation of the thiophene ring with shortening of the C6−C4 and C4−C7 bonds.

These modifications are larger for **5** than for **3**, suggesting that steric interaction between the methyl group and the thiophene ring contributes to limit the deformability of the latter. On the other hand, the length of the C7−C2 single bond in the linker group decreases by 0.017 Å, while that of the C2−C2′ central double bond increases by 0.026 Å. These various bond length modifications lead to a decrease of the difference between the average length of single and double bonds (δr) from 0.095 Å for **1** to 0.078 Å for **5**.

As discussed in numerous theoretical works, the degree of bond length alternation (BLA) related to δr represents the main contribution to the existence of a finite bandgap in linearly π-conjugated polymers.[25] In this regard, the relaxation of BLA induced by the rigidification of the DTE molecule can be expected to play a major role in the observed reduction of the polymer bandgap.

Table 4. Computed Values of HOMO LUMO Energies and Electronic Absorption Data for 1, 3, and 5

compd	E_{HOMO} (eV)	E_{LUMO} (eV)	$\lambda_{\max}$ (nm)	HOMO−LUMO %	*f*
1	−8.58	−0.63	344	78	0.54
3	−8.19	−0.59	361	78	0.58
5	−8.16	−0.59	361	82	0.67

In order to confirm this conclusion, AM1 calculations[26,27] have been performed using the X-ray structural data of molecules **1**, **3**, and **5**. The computed values in Table 4 show that the bridging of the DTE molecule leads to a 0.42 eV increase of the energy level of the HOMO, which nicely agrees with the 0.40 V decrease of Epa (Table 1).

Theoretical electronic absorption data show that DTE molecules are characterized by a strong singlet−singlet π,π^* transition (where the HOMO−LUMO transition is preponderant) with high oscillator strength (*f*). As expected, the bridging of the DTE molecule leads to a red shift of $\lambda_{\max}$ and to an increase of *f*. These results and the invariance of E_{LUMO} confirm, in agreement with experiment, that the relaxation of BLA induced by the rigidification of the DTE molecule leads to an increase of E_{HOMO} and to a parallel decrease of the HOMO−LUMO energy gap.

Conclusion

Bridged DTEs substituted by solubilizing alkyl groups have been synthesized. The analysis of the electropolymerization of these new precursors and of the structure and properties of the resulting π-conjugated polymers has shown that rigidification of DTE allows a significant decrease of the oxidation potential and bandgap of the polymer. The interpretation of these results in the light of structural and theoretical analyses has shown that the observed narrowing of both the HOMO−LUMO gap of the precursor and bandgap of the polymer are consecutive to a relaxation of bond length alternation, thus confirming that the rigidification of the π-conjugated system constitutes an efficient strategy for bandgap control.

Although introduction of solubilizing alkyl chains on the precursor molecule can greatly enhance the efficiency of the polymerization process and the conjugation length of the polymer, the position and the size of the substituent appear to be as crucial and lead in some cases to undesired effects such as inhibition of polymerization or perturbation of the electrodeposition process. A possible answer to this latter problem can involve the chemical polymerization of these rigid precursors or the synthesis of longer oligomers based on these structures. Work in this direction is now in progress in our laboratory.

Experimental Section

Electrochemical experiments were carried out with a PAR 273 Potentiostat-Galvanostat in a three-electrode single compartment cell equipped with platinum microelectrodes of 7.85 × 10^{-3} cm^2 area, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE). Electropolymerizations were performed in acetonitrile solutions (HPLC grade) containing 0.01 M of precursor and 0.1 M of tetrabutylammonium hexafluorophosphate (TBAHP) (Fluka puriss). Solutions were deaerated by nitrogen bubbling prior to each experiment, which was run under a nitrogen atmosphere. Films for optical and electrical characterization were grown from the same electrolytic solutions using indium−tin oxide (ITO)-coated glass electrodes. UV−vis absorption spectra were recorded on a Lambda 2 Perkin-Elmer spectrometer.

X-ray Structural Analyses.[31] **Crystal Data for 3:** $C_{16}H_{16}S_2$, MW = 272.43, monoclinic, *P*21/*n*, Z = 2, *a* = 6.453(4) Å, *b* = 14.350(5) Å, *c* = 7.510(3) Å, β = 98.50(8)°, *V* = 688(1) Å^3, λ = 0.71069 Å.

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Data Collection. The data were collected by the zig-zag ω scan technique on an Enraf-Nonius Mach III diffractometer: $2.5° \leq \Theta \leq 30°$, $t_{max} = 40$s, range h, k, l ((h 0,9; k 0,20; l −10,10), intensity controls without appreciable decay (0.2%) gives 2230 reflections from which 1199 were independent with $I > 3\sigma(I)$. **Structure Refinement.** After Lorentz and polarization corrections the structure was solved with direct methods (SIR), which reveal all the non-hydrogen atoms. After anisotropic refinement of all the C and S atoms, the coordinates of H atoms were determined from the Hydro program. The whole structure was refined by full-matrix least-squares techniques (use of F magnitude; U_{ij} for S and C atoms, x, y, z and B fixed for H; 82 variables and 1199 observations, weighting $\omega = 1/\sigma(F_0)^2 = [\sigma^2(I) + (0.04F_0{}^2)^2]^{-1/2}$) with the resulting $R = 0.062$, $R_w = 0.080$.

Crystal data for 5: $C_{22}H_{28}S_2$, MW = 356.58, monoclinic, $P21/n$, $Z = 2$, $a = 11.891(7)$ Å, b = 5.284(15) Å, $c = 15.89(2)$ Å, $\beta = 100{,}98(7)°$, V = 980(3) Å^3, $\lambda = 0.710\,69$ Å. **Data Collection.** Data collection was carried out by the zig-zag ω scan technique $2.5° \leq \theta \leq 30°$, on an Enraf-Nonius Mach III diffractometer. Conditions of measurements were $t_{max} = 40$ s, range h, k, l (h 0,16 ; k 0,7 ; l −22,22). Intensity control reflections were measured every 2 h without appreciable decay (0.15%). A total of 3182 independent reflections were collected from which 1071 correspond to $I > 3\sigma(I)$. **Structure Refinement.** After Lorentz and polarization corrections the structure was solved by direct methods (SIR), which reveal all the non-hydrogen atoms. After anisotropic refinement of all the C and S atoms, the coordinates of H atoms were determined from the Hydro program. The whole structure was refined by full-matrix least-squares techniques (refinement on F, x, y, z, U_{ij} for S and C atoms, x, y, z, and U fixed for H atoms; 109 variables and 1071 observations, weighting scheme: non-Poisson contribution with $w = 1/\sigma(F_0)^2 = 4F_0{}^2/[\sigma(I)^2 + (0.04F_0{}^2)^2]$ with the resulting $R = 0.078$, $R_w = 0.090$. All calculations were performed using the MolEN package.

Theoretical Calculations. AM1 calculations[26,27] have been based on X-ray structures; however, since some hydrogen atoms were not experimentally defined, hydrogen atoms of all molecules were optimized at the AM1/RHF level. Ionization potential values (IP) are obtained with the AM1/RHF method through the Koopmans theorem.[28] Theoretical electronic spectra have been computed at the AM1/PECI level following the Franck−Condon approximation. Single plus pair double excitations[29,30] are included in the CI procedure. Microstates are constructed from a 2 s molecular orbital window spanning, the frontier orbitals (13 occupied and 12 vacant), 469 microstates (corresponding to 313 singlet configurations), are built into the configuration procedure. The window is large enough to include most of the π,π^* molecular orbitals in the CI procedure.

***N*,*N*-Dimethyl-*N*-[2-methyl-3-oxo-3-(2-thienyl)propyl]-ammonium Chloride (13)**. A mixture of 2-propionylthiophene (1.5 g, 10.70 mmol), dimethylamine hydrochloride (1.13 g, 13.91 mmol), formaldehyde (0.43 g, 14.12 mmol), ethanol (1.7 mL), and concd HCl (0.02 mL) was refluxed for 4 h. After the mixture was cooled to rt, a white precipitate was filtered and dried to give 1.21 g (49%) of the title compound, mp 154−156 °C (lit.[17a] mp 154−156 °C), which was immediately used for the next step.

2-Methyl-1-oxo-1-(2-thienyl)-2-propene (12). Distillation of **13** under reduced pressure yielded 0.57 g (59%) of a clear yellow oil that must be rapidly used for the next step due to a strong propensity to polymerize: bp 118−119 °C/19 mmHg, (lit.[17] bp 118−120 °C/19 mmHg). ^{1}H NMR ($CDCl_3$) δ 2.07 (s, 3H), 5.80 (s, 2H), 6.93−7.80 (m, 3H).

4,5-Dihydro-5-methyl-6*H*-cyclopenta[*b*]thiophen-6-one (11). Compound **12** (0.57 g, 3.76 mmol) was added dropwise to 3.2 mL of concd H_2SO_4 at rt. The mixture was stirred for 2 h and cooled to 0 °C, and cold water was added. After extraction with ether, the organic phase was dried over $CaCl_2$, the solvent evaporated, and the residue chromatographied on silica gel (CH_2Cl_2) to provide 0.46 g (81%) of a pink oil: bp 95 °C/2 mmHg (lit.[17] bp 95.5 °C/2 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.36 (d, $^3J = 7.5$ Hz, 3H); 2.62 (dd, $^3J = 2.8$ Hz, $^2J = 17.15$ Hz, 1H), 3.05 (dq, $^3J = 2.8$ Hz, $^3J = 7.05$ Hz, $^3J = 7.5$ Hz, 1H); 3.29 (dd, $^2J = 17.15$ Hz, $^3J = 7.05$ Hz, 1H), 7.04 (dd, $^3J = 4.7$ Hz, 1H), 7.91 (dd, $^3J = 4.7$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 16.5, 32.4, 47.0, 123.7, 139.2, 140.3, 166.8, 199.8; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 263 (4.14); IR (Nujol) 1702 cm^{-1}; MS (EI) 152 ($M^{\bullet+}$).

3-Pentanoylthiophene (9b).[18] In a three-necked flask fitted with a condenser and a dropping funnel were introduced Mg shavings (2.62 g, 108 mmol) and 5 mL of dry Et_2O under N_2 atmosphere. A solution of 1-bromobutane (13.56 g, 99 mmol) in 25 mL of Et_2O was added dropwise in 0.5 h. After 0.5 h of stirring, a solution of 3-thiophenecarboxaldehyde (**10**) (10.09 g, 90 mmol) in 30 mL of Et_2O was added in 1 h. After 1 h of reflux and 20 h of stirring at rt, the mixture was poured into a mixture of ice−water (200 mL) and concd HCl (30 mL). After dilution with Et_2O (100 mL), the organic phase was separated and the aqueous phase was extracted with Et_2O. The organic phases were gathered, dried ($MgSO_4$), and evaporated *in vacuo* to afford an oil corresponding to the intermediate alcohol. The latter was dissolved in acetic acid (110 mL), and a solution of chromium(VI) oxide (6.47 g, 65 mmol) in 135 mL of acetic acid/water (2:1) was added dropwise. After 1 h of stirring and further addition of water (100 mL), the mixture was extracted with Et_2O and the organic phase was slowly poured into a saturated aqueous solution of Na_2CO_3 until neutralization. The organic phase was washed with water, dried ($MgSO_4$), and evaporated *in vacuo*. The resulting oil was purified by a flash chromatography on silica gel (CH_2Cl_2) to give 11.57 g (77%) of a yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3H, $J = 7.3$ Hz), 1.31−1.49 (m, 2H), 1.65−1.78 (m, 2H), 2.88 (t, 2H, $J = 7.4$ Hz) 7.31 (dd, 1H, $J = 5.0$, 3.0 Hz), 7.55 (dd, 1H, $J = 5.0$, 1.3 Hz), 8.04 (dd, 1H, $J = 1.3$, 3.0 Hz); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.4, 26.4, 39.6, 126.2, 126.96, 131.7, 142.4, 195.0; MS (EI) 168 ($M^{\bullet+}$); IR (KBr) 1674 cm^{-1} (C=O). Anal. Calcd for $C_9H_{12}OS$: C, 64.25; H, 7.19; S, 19.05. Found: C, 63.77; H, 7.19; S, 19.30.

Ethyl (*E* and *Z*)-3-(3-Thienyl)-2-butenoate (8a). To a solution of triethyl phosphonoacetate (33.60 g, 150 mmol) in anhydrous THF (120 mL) was added a solution of *n*-BuLi 2.5 M in hexane (63 mL, 158 mmol) dropwise at −50 °C under N_2 atmosphere over a period of 2 h. After 30 min of stirring, a solution of 3-acetylthiophene (**9a**) (6.31 g, 50 mmol) in anhydrous THF (120 mL) was added in 1 h, and the mixture was allowed to warm to rt and stirred for 45 h. After successive addition of 3 M aqueous NH_4Cl (80 mL) and aqueous 1 M HCl (80 mL), the mixture was diluted with Et_2O (100 mL), the organic phase was separated, and the aqueous phase was extracted with Et_2O. The combined organic phases were then washed with water, dried ($MgSO_4$), and evaporated *in vacuo*. The product was chromatographed on silica gel (CH_2Cl_2/petroleum ether (1:1)) to give 9.39 g (96%) of a yellow oil corresponding to a mixture of the Z and E isomers. First eluted isomer: ^{1}H NMR ($CDCl_3$) δ 1.32 (t, 3H, $J = 7.1$ Hz), 2.58 (d, 3H, $J = 1.2$ Hz), 4.21 (q, 2H, $J = 7.1$ Hz), 6.23 (q, 1H, $J = 1.2$ Hz), 7.31 (d, 2H, $J = 2.1$ Hz), 7.48 (t, 1H, $J = 2.1$ Hz); ^{13}C NMR ($CDCl_3$) δ 14.26, 17.13, 59.73, 115.23, 124.17, 125.13, 126.12, 143.30, 148.87, 167.10. Second eluted isomer: ^{1}H NMR ($CDCl_3$) δ 1.20 (t, 3H, $J = 7.1$ Hz), 2.20 (d, 3H, $J = 1.4$ Hz), 4.10 (q, 2H, $J = 7.1$ Hz), 5.88 (q, 1H, $J = 1.4$ Hz), 7.16 (dd, 1H, $J = 5.0$, 1.3 Hz), 7.26 (dd, 1H, $J = 5.0$, 2.9 Hz), 7.41 (dd, $J = 2.9$, 1.3 Hz); ^{13}C NMR ($CDCl_3$) δ 14.0, 26.8, 59.9, 117.2, 124.2, 124.3, 127.9, 139.8, 148.0, 166.1; MS (EI) 196 ($M^{\bullet+}$) IR (KBr) 1708 cm^{-1} (C=O). Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.20; H, 6.16; S, 16.34. Found: C, 61.25; H, 6.25; S, 16.46.

Ethyl (*E* and *Z*)-3-(3-Thienyl)-2-heptenoate (8b). This compound was prepared using the above-described procedure from triethyl phosphonoacetate (24 g, 107 mmol), *n*-BuLi 1.6

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[30] A modified version of VAMP 4.3 has been used for the PECI calculations because VAMPS. S1 computes erroneous values of the transition dipole moment and oscillator strength.

[31] The author has deposited atomic coordinates for 3 and 5 with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

M in hexane (70.3 mL, 113 mmol), and 3-pentanoylthiophene (6 g, 36 mmol) except that completion of the reaction was achieved by an additional 24 h of reflux, yield 8.23 g (97%) of a yellow oil corresponding to a mixture of *Z* and *E* isomers. First eluted isomer: ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 3H, $J = 7.2$ Hz), 1.32 (t, 3H, $J = 7.1$ Hz), 1.37−1.57 (m, 4H), 3.05 (t, 2H, $J = 7.8$ Hz), 4.21 (q, 2H, $J = 7.1$ Hz), 6.16 (s, 1H), 7.28 (dd, 1H, $J = 5.2, 1.4$ Hz), 7.32 (dd, 1H, $J = 5.2, 2.8$ Hz), 7.48 (dd, 1H, $J = 2.8, 1.4$ Hz); ^{13}C NMR ($CDCl_3$) δ 13.88, 14.27, 22.97, 30.72, 31.76, 59.70, 115.00, 123.95, 125.63, 126.09, 142.42, 154.20, 166.70. Second eluted isomer: ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3H, $J = 7.1$ Hz), 1.17 (t, 3H, $J = 7.2$ Hz), 1.25−1.47 (m, 4H), 2.46 (t, 2H, $J = 6.9$ Hz), 4.07 (q, 2H, $J = 7.1$ Hz), 5.86 (s, 1H), 7.05 (dd, 1H, $J = 4.5$ and 1.6 Hz), 7.25−7.30 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.8, 14.0, 22.1, 30.0, 40.0, 59.8, 117.1, 123.3, 124.4, 128.0, 139.5, 153.4, 166.2; MS (EI) 238 ($M^{\bullet+}$); IR (KBr) 1709 cm^{-1} (C=O). Anal. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61; O, 13.43; S, 13.45. Found: C, 65.35; H, 7.71; O, 13.41; S, 13.17.

4,5-Dihydro-6*H*-cyclopenta[*b*]thiophen-6-one (15). 3-(3-Thienyl)acrylic acid (Lancaster) (10 g, 65 mmol) was dissolved in 140 mL of 0.6 M aqueous NaOH, and 2% sodium amalgam (200 g) was added portionwise in 1 h. After 0.5 h of stirring, the mixture was acidified with 50% aqueous HCl and extracted with ether. The organic phase was washed with water, dried over $CaCl_2$, and evaporated, giving 10.7 g of a pale yellow oil that crystallized. A solution of thionyl chloride (15 mL, 210 mmol) in 200 mL of anhydrous ether was added, and the mixture was refluxed for 3.5 h. Removal of the solvent and thionyl chloride in excess by evaporation under reduced pressure gave a brown oil that was dissolved in 150 mL of CS_2. After transfer in a dropping funnel, this solution was added dropwise to a suspension of $AlCl_3$ (8.7 g, 65 mmol) in 100 mL of CS_2. The mixture was stirred for 20 h at rt, refluxed for 2 h, and then poured into a mixture of concd HCl (100 mL) and ice-water (200 mL). The aqueous phase was extracted with CH_2Cl_2, and the organic phase was washed with water, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on silica gel (petroleum ether/Et_2O 4:1) to afford 5 g of a white solid, yield 56% based on **18**: mp 89−90 °C (lit.[16] mp 90−91 °C); ^{1}H NMR ($CDCl_3$) δ 2.90−3.10 (m, 4H), 7.05 (d, 1H, $^3J = 4.85$ Hz), 7.89 (d, 1H, $^3J = 4.85$ Hz); ^{13}C NMR ($CDCl_3$) δ 23.9, 41.2, 123.9, 140.5, 141.1, 170.0, 197.3; MS (EI) 138 ($M^{\bullet+}$); IR (KBr) 1685 cm^{-1} (C=O); UV−vis (CH_2Cl_2) λ_{max} nm (log ϵ) 262 (4.21).

4-Methyl-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-6-one (6a). An aqueous solution of NaOH 10% (130 mL) was added to a solution of ester **8a** (9.25 g, 47 mmol) in 150 mL of EtOH, and the resulting mixture was refluxed for 2 h. After dilution with water (100 mL), 3% sodium amalgam (128.5 g) was added portionwise at rt in 3 h and the mixture was stirred for 20 h. Hg was separated by decantation, and the reaction mixture was slowly acidified at 0 °C with concd HCl (65 mL). After extraction of the aqueous phase with CH_2Cl_2, the organic phase was washed with water, dried ($MgSO_4$), and evaporated *in vacuo* to afford 7.83 g (46.06 mmol) of the crude carboxylic acid as a yellow oil. After addition of thionyl chloride (13.80 mL) in Et_2O (185 mL), the mixture was refluxed for 3 h. Solvent evaporation gave the crude acid chloride (8.46 g, 44.9 mmol). The latter was dissolved in CS_2 (100 mL), and this solution was added dropwise to a mixture of $AlCl_3$ (7.77 g, 58.3 mmol) in CS_2 (150 mL) under N_2. After 4 h of reflux, the mixture was cooled to 20 °C and poured into a mixture of concd HCl (100 mL) and ice−water (200 mL). The aqueous phase was extracted with CH_2Cl_2, and the organic phase was washed with water, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on silica gel (petroleum ether/Et_2O 4:1) to afford 2.94 g of a yellow oil, yield 41% based on **8a**: ^{1}H NMR ($CDCl_3$) δ 1.35 (d, 3H, $J = 7.3$ Hz), 2.53 (dd, 1H, $^2J_{gem} = 18.4$ Hz and $^3J = 2.5$ Hz), 3.18 (dd, 1H, $^2J_{gem} = 18.4$ Hz, $^3J = 6.7$ Hz), 3.31−3.44 (m, 1H), 7.04 (d, 1H $^3J = 4.8$ Hz), 7.87 (d, 1H, $^3J = 4.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 20.7, 31.4, 49.8, 122.9, 140.2, 140.6, 174.0, 196.6; MS (EI) 152 ($M^{\bullet+}$); IR (NaCl) 1691 cm^{-1} (C=O); UV−vis (CH_2Cl_2) λ_{max} nm (log ϵ) 265 (4.21). Anal. Calcd for C_8H_8OS: C, 63.13; H, 5.30; S, 21.06. Found: C, 63.41; H, 5.55; S, 20.68.

4-Butyl-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-6-one (6b). This compound was obtained using the procedure already described for the preparation of **6a** from **8b** (8.56 g, 0.036 mol): yellow oil; 2.63 g (38%); ^{1}H NMR ($CDCl_3$) δ 0.91 (t, 3H, $^3J = 7.0$ Hz), 1.28−1.43 (m, 4H), 1.43−1.62 (m, 1H), 1.72−1.85 (m, 1H), 2.61 (dd, 1H, $^2J_{gem} = 18.3$ Hz and $^3J = 2.4$ Hz), 3.12 (dd, 1H, $^2J_{gem} = 18.3$ Hz and $^3J = 6.7$ Hz), 3.23−3.33 (m, 1H), 7.06 (d, 1H, $^3J = 4.9$ Hz), 7.87 (d, 1H, $^3J = 4.9$ Hz); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.6, 29.7, 35.2, 36.9, 47.9, 123.4, 140.3, 140.5, 172.9, 196.7; MS (EI) 194 ($M^{\bullet+}$); IR (KBr) 1697 cm^{-1} (C=O); UV−vis (CH_2Cl_2) λ_{max} nm (log ϵ) 266 (4.15). Anal. Calcd for $C_{11}H_{14}OS$: C, 68.00; H, 7.26; S, 16.50. Found: C 68.42; H, 7.35; S, 16.09.

General Procedure for the McMurry Reaction. After dropwise addition of $TiCl_4$ (4−7 mmol) to 20−30 mL of anhydrous THF at 0 °C under N_2 atmosphere, zinc dust (16−28 mmol) was added portionwise. The mixture was then refluxed for 0.5 h and cooled to 0 °C. A solution of ketone (4−7 mmol) in THF was added dropwise, and the mixture was refluxed again for 4 h. After being cooled to rt and addition of water, the mixture was extracted with CH_2Cl_2. The combined organic phases were washed with water, dried ($MgSO_4$), and evaporated *in vacuo*.

6,6′-Bis(4,5-dihydro-6H-cyclopenta[*b*]thienylidene) (2): yield 86%; yellow solid: mp 205 °C; ^{1}H NMR ($CDCl_3$) δ 3.00 (m, 4H), 3.27 (m, 2H), 6.92 (d, 2H, $^3J = 4.9$ Hz), 7.02 d, 2H, $^3J = 4.9$ Hz); ^{13}C NMR ($CDCl_3$) δ 27.23, 35.2, 122.5, 123.0, 128.3, 129.3, 150.1; UV−vis (CH_2Cl_2) λ_{max} nm (log ϵ) 331 (4.23), 348 (4.42), 367 (4.37); MS (EI) 244 ($M^{\bullet+}$); HRMS calcd 244.3080, found 244.3082. Anal. Calcd for $C_{14}H_{12}S_2$: C, 68.84; H, 4.96; S, 26.20. Found: C, 68.75; H, 4.95; S, 25.80.

6,6′-Bis(4,5-dihydro-5-methyl-6*H*-cyclopenta[b]thienylidene) (3): chromatographed on silica gel (petroleum ether/CH_2Cl_2 9:1): yield 0.20 g (37%) of yellow powder containing a mixture of diastereomers; mp 180 °C; ^{1}H NMR ($CDCl_3$) δ 1.30 (d, 6H, $^3J = 6.8$ Hz), 2.49 (dd, 2H, $^2J = 16$ Hz), 3.18 (dq, 2H, $^3J = 6.8, 7.05$ Hz), 3.62 (dd, 2H, $^2J = 16$ Hz, $^3J = 7.05$ Hz), 6.89 (d, 2H, $^3J = 4.9$ Hz), 7.30 (d,2H, $^3J = 4.9$ Hz); ^{13}C NMR ($CDCl_3$) δ 21.5, 22.9, 36.28, 36.4, 42.9, 43.2, 123.0, 123.1, 128.5, 129.3, 133.1, 141.1, 141.2, 148.2, 148.9; UV−vis (CH_2Cl_2) λ_{max} nm (log ϵ) 333, (4.41) 349 (4.50), 368 (4.33). MS (EI) 272 ($M^{\bullet+}$). HRMS calcd for $C_{16}H_{16}S_2$ 272.0693, found 272.0703.

6,6′-Bis(4-methyl-4,5-dihydro-6*H*-cyclopenta[*b*]thienylidene) (4): chromatographed on silica gel (petroleum ether/CH_2Cl_2 9:1). Yield 0.52 g (83%) of a mixture of two diastereomers; beige solid; mp 68−90 °C. ^{1}H NMR ($CDCl_3$) δ 1.32−1.37 (m, 6H), 2.73−2.84 (m, 2H), 3.30−3.56 (m, 4H), 6.92 (d, 2H, $^3J = 4.9$ Hz), 7.32 (d, 2H, $^3J = 4.9$ Hz); ^{13}C NMR ($CDCl_3$) δ 22.0, 34.9, 44.3, 122.2, 125.4, 129.4, 142.8, 155.4; MS (EI) 272 ($M^{\bullet+}$); HRMS calcd for $C_{16}H_{16}S_2$ 272.069 344, found 272.069 690; UV−vis (CH_2Cl_2) λ_{max} nm (log ϵ) 367 (4.43), 348 (4.47), 331 (4.27). Anal. Calcd for $C_{16}H_{16}S_2$: C, 70.54; H, 5.92. Found: C, 70.02; H, 5.41.

6,6′-Bis(4-butyl-4,5-dihydro-6*H*-cyclopenta[b]thienylidene) (5): chromatographed on silica gel (petroleum ether/CH_2Cl_2 9:1). Yield 0.29 g of the first eluted diastereomer as pale yellow solid (mp 57−61°C) and 0.07 g of the second one as yellow oil, final yield 50%; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, 6H, $J = 6.8$ Hz), 1.30−1.80 (m, 12 H), 2.80−2.90 (m, 2H), 3.25−3.35 (m, 2H), 3.35−3.50 (m, 2H), 6.93 (d, 2H, $^3J = 4.9$ Hz), 7.31 (d, 2H, $^3J = 4.9$ Hz); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.9, 29.7, 36.5, 40.4, 42.4, 122.7, 125.4, 129.1, 143.2, 154.2; MS (EI) 356 ($M^{\bullet+}$); HRMS calcd 356.163 245, found: 356.163 784. UV−vis (CH_2Cl_2) λ_{max} nm (log ϵ) 369 (4.54), 349 (4.58), 332 (4.36). Anal. Calcd for $C_{22}H_{28}S_2$: C, 74.10; H, 7.91; S, 17.98. Found: C, 73.79; H, 7.85; S, 18.11.

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