Bandgap control through reduction of bond length alternation in bridged poly(diethienylethylene)s

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X-Ray structure analysis of a new rigid dithienylethylene shows that the observed reduction of the HOMO–LUMO gap results from a relaxation of bond length alternation.

In recent years, the control of the bandgap (*E*g) of linearly π-conjugated systems has become one of the main challenges for synthetic chemists involved in the field of organic conductors. Since *E*g governs the intrinsic electronic properties of the π-conjugated system, progress in this area constitutes the key to many fundamental and technological problems and in the longer term to the possible achievement of intrinsic metallic conductivity.

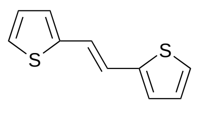
In addition to the degree of coplanarity of the π-conjugated backbone, the degree of bond length alternation (BLA) related to the difference between the average length of single and double bonds (δr) represents the main contribution to the existence of a finite bandgap in π-conjugated polymers.[1]

Poly(isothianaphthene) was one of the earliest and most successful attempts at reducing *E*g in poly(heterocyclic) conjugated polymers.[2] The fusion of the benzene and thiophene rings leads to an increase in the quinoid character of the poly(thiophene) backbone, to the detriment of its aromaticity. This results in a relaxation of BLA accompanied with a reduction of *E*g from 2.0–2.2 eV for poly(thiophene)[3] to 1.1 eV.[4] While this approach is still widely used,[5] recent years have witnessed the emergence of other strategies, such as the introduction of electron-withdrawing groups at selected positions of the π-conjugated backbone[6] or the rigidification of the π-conjugated system.[7]

Recently, we have shown that the covalent bridging of the thiophene rings with the central double bond of dithienylethylene **1** leads to a reduction of the bandgap of the corresponding electrogenerated polymer from 1.80 to 1.40 eV.[8] However, the origin of this decrease in *E*g was not clearly identified.

We report here the synthesis and X-ray structural characterization of a new substituted bridged DTE **2**.† Experimental and theoretical data show unequivocally that the observed narrowing of the HOMO–LUMO gap results from a reduction of BLA induced by the rigidification of the DTE molecule.

The synthesis of 6,6′-bis(4-butyl-4,5-dihydro-6*H*-cyclopenta-[*b*]thienylidene) **2** is depicted in Scheme 1. 3-Pentanoylthiophene **6** was obtained by reaction of butylmagnesium bromide with thiophene-3-carbaldehyde **7** followed by oxidation of the resulting secondary alcohol with chromium trioxide. Wittig–Horner olefination of **6** with ethyl diethylphosphonoacetate gave a mixture of *Z* and *E* isomers of the α-unsaturated ester **5**. Saponification of **5** followed by reduction of the double bond with sodium amalgam and acidification gave carboxylic acid **4**.



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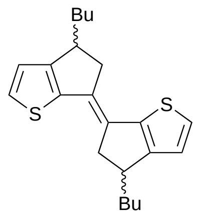
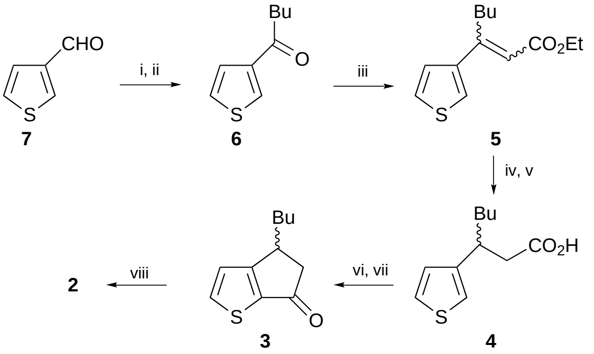


2

Conversion of **4** into the corresponding acid chloride and intramolecular Friedel–Crafts acylation yielded cyclic ketone **3** as a racemic mixture. The target compound **2** was then obtained as a mixture of diastereomers by McMurry dimerization of **3**.‡

Fig. 1 shows the ORTEP view of the *meso* form of 2.§ Molecules **1**[9] and **2** belong to the C_i molecular point group. In both cases the thiophene ring is almost planar and there is a dihedral angle value of 3° between the thiophene ring average plane and the C1–C1′ double bond. The invariance of this angle shows that the reduction of *E*g observed for the polymers derived from bridged precursors[8] is not related to an enhancement of the planarity of the DTE moiety.

Comparison of the bond distances along the conjugated path for **1** and **2** (Table 1) shows that the bridging of the DTE molecule induces a deformation of the thiophene ring with a 0.031 and 0.044 Å shortening of the C5–C6 and C3–C6 bonds,



Scheme 1 *Reagents*: i, BuMgBr; ii, CrO_3; iii, $(EtO)_2P(O)CH_2CO_2Et$, BuLi; iv, NaOH–EtOH; v, Na/Hg then HCl; vi, $SOCl_2$; vii $AlCl_3$; viii, $TiCl_4$–Zn

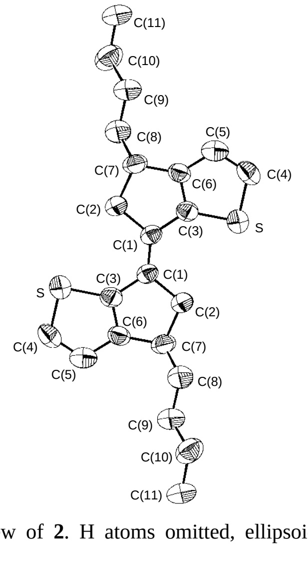


Fig. 1 ORTEP view of **2**. H atoms omitted, ellipsoids drawn at 2.5% probability level

Table 1 Selected bond lengths for compounds **1** and **2** along the conjugated path

	Length/Å	
Bond	**1**	**2**
C4–C5	1.351(8)	1.350(1)
C5–C6	1.44(1)	1.409(8)
C6–C3	1.40(1)	1.356(8)
C3–C1	1.457(7)	1.440(7)
C1–C1′	1.309(8)	1.335(6)
δr/Å	0.095	0.078

Table 2 Anodic peak potentials[a] and computed HOMO–LUMO gaps for **1** and **2**

Compound	Epa/V	E_{HOMO}/eV	E_{LUMO}/eV
1	1.10	−8.58	−0.63
2	0.72	−8.16	−0.59

[a] Substrate (10^{-3} m) in Bu_4NPF_6–MeCN (0.1 m), scan rate 100 mV s^{-1}, Pt electrodes, saturated calomel electrode.

respectively. On the other hand, the length of the C3–C1 single bond in the linker group decreases by 0.017 Å while that of the C1–C1′ central double bond increases by 0.026 Å. These various bond length modifications lead to a decrease of δr from 0.095 Å for **1** to 0.078 Å for **2**.

Table 2 lists the values of the anodic peak potentials (Epa) for **1** and **2** together with the computed values of the HOMO and LUMO energies.¶ As for the parent unsubstituted analogue of **2**, the bridging of the DTE molecule leads to a *ca.* 0.40 V negative shift of Epa.[8] This difference, which nicely agrees with the 0.42 eV increase in E_{HOMO}, shows that the smaller HOMO–LUMO gap of bridged DTEs is related to an increase in E_{HOMO}.

These results, which confirm the efficiency of the rigidification approach for controlling Eg, provide the first conclusive evidence that the bandgap of conjugated polymers is adjustable *via* bond length control.

Footnotes

† The synthesis and characterization of poly(**2**) and other small bandgap polymers derived from substituted bridged DTEs will be published elsewhere.

‡ Satisfactory analytical and spectroscopic data were obtained.

§ *Crystal data* for **2**: $C_{22}H_{28}S_2$, M_W = 356.58, monoclinic, $P21/n$, $Z = 2$, $a = 11.891(7)$, $b = 5.284(15)$, $c = 15.89(2)$ Å, $\beta = 100.98(7)°$, $V = 980(3)$ Å^3, $\lambda = 0.71069$ Å. Data collection: Data collection was carried out by zig-zag ω scan technique ($2.5 \geqslant \theta \geqslant 30°$) 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%). 3182 Independent reflections were collected from which 1071 correspond to $I > 3\sigma(I)$. Structure refinement: After Lorentz and polarisation 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-square 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 $w = 1/\sigma(F_0)^2 = 4F_0{}^2/[\sigma(I)^2 + (0.04\ F_0{}^2)^2]\cdot$ with the resulting $R = 0.078$, Rw = 0.090}. All calculations were performed using the MolEN package.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/362.

¶ AM1 (ref. 10) calculations 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 using VAMP 5.51, (Oxford Molecular Ltd. England).

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