Semi-empirical Evaluation of Substituted Terthiophenes as Polythiophene Precursors.

Stephen P. Stanforth

Department of Chemical and Life Sciences, University of Northumbria at Newcastle,
Newcastle upon Tyne, NE1 8ST UK.

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PM3 Semi-empirical molecular orbital calculations have been performed on terthiophene derivatives which are also heteropentalene mesomeric betaines. The ionization potentials and band-gaps have been determined in order to identify systems which might provide suitable monomers for conducting polythiophene derivatives.

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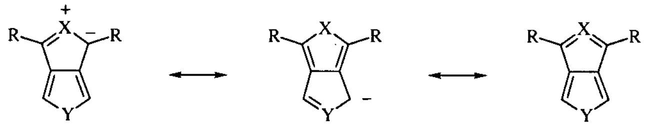
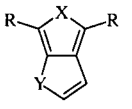
Introduction.

The preparation of polythiophene and substituted polythiophenes as conducting materials with potentially low band-gaps (E_g's) and ionization potentials has been the subject of great interest for many years [1-4]. Two related objectives in the field of polythiophene conducting materials are: (a) reducing the E_g in polythiophenes which might enable the development of true 'organic' metals exhibiting intrinsic conductivity and (b) reducing the ionization potential of polythiophenes which would stabilize the corresponding oxidatively doped state. One particularly interesting strategy to achieve these two objectives is to prepare and subsequently polymerise derivatives of 2,2':5',2"-terthiophene (α-terthiophene) which are substituted at the central ring with an additional fused, conjugated ring system. Within this strategy, we are especially interested in a theoretical evaluation of substituted α-terthiophenes which are also derivatives of heteropentalene mesomeric betaines [5] in order to identify trends in E_g's and ionization potentials which might be useful in designing novel conducting polythiophene derivatives. One class of heteropentalene mesomeric betaines includes the general structure **1** in which the heteroatoms X and Y are normally chosen from oxygen, appropriately substituted nitrogen and sulphur. Structure **1** can only be represented as a dipolar structure in the singlet ground state (with the exception of when X or Y is sulphur then tetravalent sulphur can be invoked) and molecules which are derivatives of structure **1** have the interesting property that their highest occupied molecular orbital (HOMO) has characteristics of a non-bonding molecular orbital (NBMO) [5]. The HOMO of heteropentalene mesomeric betaines **1** are therefore of significantly higher energy than their covalent isomers such as structure **3**. As a consequence of their relatively high energy HOMO's, polymerisation of α-terthiophene derivatives such as heteropentalene mesomeric betaines **2** (X = S) are expected to provide polythiophenes **5** with relatively low E_g's and

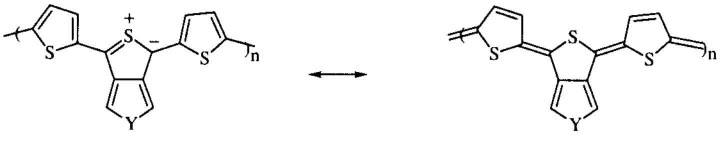


1 R = H
2 R = 2-thienyl

(X = S)

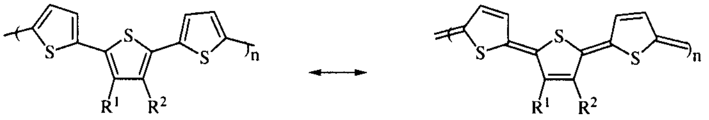


3 R = H
4 R = 2-thienyl



5a

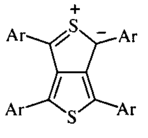
5b



6a $R^1 = R^2 = H$
7a $R^1 + R^2$ = benzo

6b $R^1 = R^2 = H$
7b $R^1 + R^2$ = benzo

ionization potentials compared to polythiophene **6** (E_g = 2.0 eV [6]).



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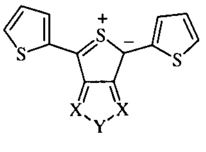
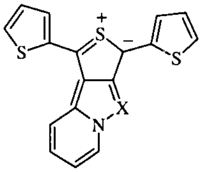
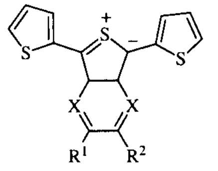


	X	Y
9	C-H	S
10	C-CN	S
11	N	S
12	C-H	NH
13	C-CN	NH
14	N	NH



15 X = C-CN
16 X = N



	X	R^1	R^2
17	C-H	H	H
18	C-H	benzo	
19	N	H	H

The aim of this paper is to investigate semi-empirically trends in the E_g's and ionization potentials of a number of heteropentalene mesomeric betaine monomers which are derivatives of structure **2** (X = S; Y = S or NH) with the objective of identifying potential monomer precursors of low E_g and ionization potential polythiophene derivatives **5**. Additionally, derivatives of structures **2** (X = S; Y = S or NH) have been identified which are expected to have reasonable stability in view of the known stability of related heteropentalene mesomeric betaines. Thus, calculations on derivatives of thieno[3,4-*c*]furans **1** (X = S; Y = O) have not been attempted in view of the known reactivity of these systems [5].

There has been considerable theoretical debate relating to the nature of the ground state of polythiophene **6** and its derivatives [7-11]. Both non-degenerate aromatic or quinoid structures (as depicted in formulae **6a** and **6b** respectively for polythiophene) can be drawn, each of which is associated with a different E_g. In polythiophene, the aromatic structure **6a** is preferred. In contrast, the quinoid structure **7b** of poly-**17** is preferred over the corresponding aromatic structure **7a** and this is not suprising in view of the aromatic benzene moiety in structure **7b** compared to the *ortho* quinomethide fragment in structure **7a**.

Although we are not calculating properties of polymers in this paper, but seeking to identify trends in a related series of monomers, it is interesting to briefly consider the question of aromatic versus quinoid ground states in heteropentalene mesomeric betaine containing polymers **5** and to make comparisons with polythiophene **6**. Thus, charge neutralisation between adjacent monomer units in the dipolar resonance form **5a** enables the covalent structure **5b** to be drawn. Structure **5b** however is not directly related to the quinoid polythiophene structure **6b** because it does not possess a continuous polyacetylene moiety: the heteroatom Y in structure **5b** precludes this. The quinoid structure **7b** is also a true polyacetylene derivative in contrast to the covalent representation **5b** of the heteropentalene mesomeric betaine polymers **5**.

EXPERIMENTAL

Calculations were performed using 'HyperChem' software [12] as follows. An initial geometry optimization was carried out using the MM^+ molecular mechanics program keeping the two exocyclic thiophene rings antiparallel to the central ring system. The resulting structure was then geometry optimised using the semi-empirical PM3 RHF method (in all cases the central ring system and exocyclic thiophene rings were essentially coplanar)

Table

Ionization Potentials, HOMO-LUMO Energy Separations and Band-Gaps (E_g's)

Structure	Calculated Ionization Potential (eV)	HOMO-LUMO separation (eV)	Calculated E_g (eV)	Experimental E_g (eV)	Experimental Polymer E_g (eV)
α-terthiophene	8.7	7.3	3.5	3.5 [13]	2.0 [6]
4	8.2	6.5	3.0		
9	7.6	5.3	2.4		
10	8.1	5.2	2.3		
11	8.0	5.4	2.4	2.0 [19]	0.9 [19]
12	7.3	5.7	2.5		
13	8.0	5.7	2.6		
14	8.1	6.1	2.7		
15	7.7	5.8	2.6		
16	7.8	6.0	2.7		
17	8.0	6.2	2.9	2.9 [13]	1.6 [13]
18	7.7	5.6	2.5	2.3 [21]	0.7 [21]
19	8.4	6.4	2.9	2.3 [22]	1.0 [22]

and the molecular orbital energies were then determined by a single point calculation on this optimised geometry. The energy of the HOMO is approximately equivalent in magnitude to the first ionization potential (Koopmans' theorem). E_g's (defined as the lowest energy allowed $\pi \rightarrow \pi$ * transition) were determined using configurational interaction (CI) and the four highest energy occupied and four lowest energy unoccupied molecular orbitals were included in the CI calculations. Only singly excited states were considered. The results of our calculations on heterocycles **9** - **16** together with α-terthiophene (E_g = 3.5 eV [13]) for reference purposes are given in the Table. The electronic properties of the benzo[*c*]thiophene derivative **17** and the related heterocycles **18** and **19** have also been determined and are also included in the Table.

Discussion.

Although both the ionization potential and E_g of 1,3-di(2-thienyl)thieno[3,4-*c*]thiophene **9** are suitably low, thieno[3,4-*c*]thiophene derivatives **1** (X = Y = S) which are unsubstituted in one of the thiophene rings are extremely reactive and consequently have only been prepared *in situ* [5]. Stable derivatives of this heterocyclic ring system, and also of other related heteropentalene mesomeric betaines, generally have sterically demanding (usually phenyl substituents) or electron withdrawing groups (such as nitrile substituents [14]) at each of the available positions of the parent ring system. The tetraphenyl derivative **8** (Ar = Ph) is a highly stable compound [15,16] but an X-ray structure reveals that the phenyl rings are not coplanar with the central ring system [17]. The tetrathiophene derivative **8** (Ar = 2-thienyl) has also been prepared [18], and although there is no X-ray structure available for this compound, it is expected that the exocyclic thiophene rings similarly would not be coplanar with the central ring system. Calculations on compound **8** (Ar = 2-thienyl) were not therefore performed and calculations on compound **9** were carried out only for comparative purposes. Similarly, calculations on the thieno[3,4-*c*]pyrrole derivative **12** have only been made for comparative purposes.

The ionization potential and E_g of heterocycle **10** which has sterically undemanding nitrile substituents as stabilizing groups was therefore determined. The relative ionization potential increases (0.5 eV) in going from compound **9** to compound **10** as expected for the addition of electron-withdrawing substituents, but the E_g and HOMO-lowest unoccupied molecular orbital (LUMO) energy difference are almost unaltered.

It is interesting to compare the calculated ionization potentials and E_g's of dipolar and covalent isomers **9** and **4** (X = Y = S) respectively. The heteropentalene mesomeric betaine derivative **9** has a significantly lower ionization potential (0.4 eV) and E_g (0.6 eV) than its covalent counterpart **4** (X = Y = S) and this is a consequence of the relatively high energy HOMO of heteropentalene mesomeric betaines described above.

Aza-substitution provides an additional method of stabilizing heteropentalene mesomeric betaines and it is interesting to note that heterocycles **10** and **11** have almost identical calculated ionization potentials and E_g's showing that either aza substitution or addition of a nitrile group have similar effects upon these parameters. 4,6-Di(2-thienyl)thieno[3,4-*c*][1,2,5]thiadiazole **11** is the only α-terthiophene derivative of a bicyclic heteropentalene mesomeric betaine related to structure **1** which has been prepared and polymerised [19]. The X-ray structure of heterocycle **11** reveals nearly coplanar rings and the experimental E_g for this monomer is 2.0 eV; this E_g is 0.4 eV lower than the PM3 calculated value and possible reasons for this are discussed below. The E_g of the resulting polymer has been determined as 0.9 eV from both its absorption spectrum and cyclic voltrammogram indicating the potential for other low E_g polymers derived from heteropentalene mesomeric betaines.

We have also performed calculations on 1,3-di(2-thienyl)thieno[3,4-*c*]pyrrole **12**, the related aza and cyano substituted heterocycles **13** and **14** as well as the fused pyrido derivatives **15** and **16**. When the two heterocycles **10** and **11** are compared with their counterparts **13** and **14**, there is very little variation in the calculated ionization potentials for each pair of compounds and the calculated E_g's in the thieno[3,4-*c*]pyrrole series are only slightly higher (0.2-0.4 eV). The extended conjugation in the pyrido analogues **15** and **16** of the heterocycles **13** and **14** respectively did not significantly alter their ionization potential's and E_g's.

PM3 calculations on the known heterocycles **17-19** have been carried out in order to compare calculated and experimentally determined E_g's. There is good correlation between the calculated and experimentally determined E_g's in compounds **17** [13, 20] and **18** [21] but for the diaza compound **19** [22] the correlation is not particularly good, with a much higher calculated value (0.6 eV) being obtained. This suggests that the E_g's for the aza substituted heteropentalene mesomeric betaines may well be over estimated as already noted for heterocycle **11**, although we realise that this direct comparison of different types of ring systems may not be valid.

Conclusion.

In conclusion, we have identified a number of heteropentalene mesomeric betaine monomers (i) with low calculated E_g's and ionization potentials, (ii) which are essentially planar structures and (iii) which might be sufficiently unreactive to enable their synthesis, isolation and subsequent polymerisation. The relatively low E_g's and ionization potentials of these monomers are expected to be carried over into their resulting polymers.

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