

Synthesis of Mixed Oligomeric Heteroarylenes containing Thiophene and Selenophene Rings; their U.V. Spectra and Oxidation Potentials

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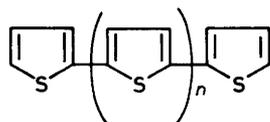
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Mixed oligomers containing thiophene and selenophene rings have been synthesized; their u.v. spectra and oxidation potentials determined and discussed in terms of coplanarity of the rings and the +*I*-effect of the methyl substituent.

In our investigations directed towards synthesis, spectroscopic, and electrochemical behaviour of thiophene based polymers^{1,2,3} it became desirable to use oligomeric 2,5-thiophylenes as starting materials for such polymers. By starting the polymerization with larger monomeric blocks, we hoped to obtain polymers with superior electrochemical properties. Thus, after developing an unambiguous synthesis of such oligomers we reported on some electrochemical and spectroscopic properties of these compounds.⁴ We also found that in the series of unsubstituted oligomeric 2,5-thienylenes (**1**) the position of λ_{\max} of the u.v. spectrum shows a bathochromic shift with increasing *n*, whereas the oxidation potentials of the corresponding compounds decrease. Thus, there exists at least a qualitative relationship between the oxidation potentials and the λ_{\max} of these compounds.⁴ A similar trend was not found in Me-substituted type (**1**) compounds. We explained these facts by assuming that, due to steric hindrance caused by the methyl groups, coplanarity of these type (**1**) compounds is impeded.⁴ To further explore electrochemical properties of oligomeric group vi five-membered heteroarylenes we started a program to synthesize and measure u.v. spectra, oxidation potentials, polymerization, and conductivity of mixed thiophene and selenophene containing oligomers. A recent publication⁵ on the synthesis of 3-methylselenophene stating the intent to prepare polymers from this type of heteroarylenes prompts us to publish our first results in this area.

To synthesize the mixed heteroarylenes we used the NiCl₂(dppp) (dppp = Ph₂PCH₂CH₂CH₂PPh₂), catalyzed cross-coupling reaction^{4,6} between 2-bromoselenophene, 2-bromo-3-methylselenophene, or 2,5-dibromoselenophene⁷



(1) $n = 0, 1, 2, 3, 4$

Table 1

Compound ^a	λ_{\max}/nm , CHCl ₃	E_{ox}/V (M) ^b
(3)	311	1.50
(4)	308	1.45
(5)	306	1.63
(6)	316	1.55
(7)	363	1.14
(8)	352	1.43
(9)	370	1.53

^a All compounds gave checking elemental analysis within 0.4% of theory and ¹H n.m.r. spectra are in agreement with the assigned structures; ^b M = monomer, vs. Ag/AgCl.

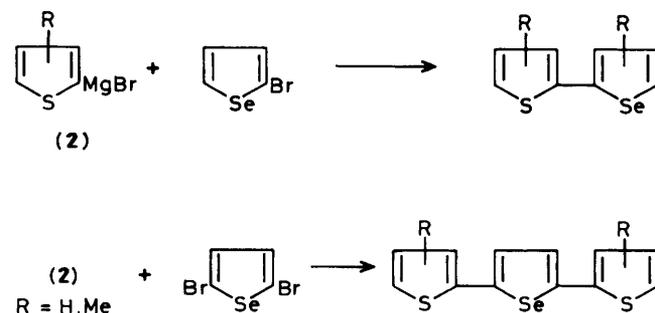
and the Grignard compounds derived of the appropriate bromothiophene, Scheme 1.

The obtained mixed oligomeric heteroarylenes along with their λ_{\max} , and E_{ox} values are listed in Table 1.

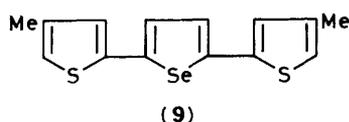
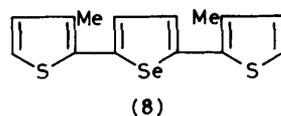
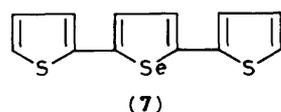
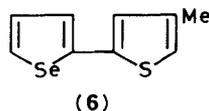
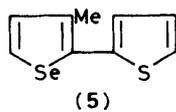
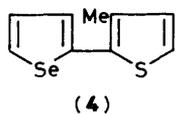
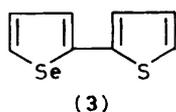
$E_{\text{ox}}(M)$ is taken as the potential of the peak oxidation current of the cyclic voltammograms (scan rate 50 mV s⁻¹). The working electrode was a Pt disc of an apparent area of 0.03 cm²; the electrolyte was n-butylammonium tetrafluoroborate in anhydrous acetonitrile as solvent. Although the electro-oxidation is irreversible, the mechanism and rate constants could eventually be the same for all the oligomers. Hence, the potential of the peak oxidation currents obtained from the cyclic voltammograms should correlate directly with the formal potential, E^{01} , for the redox reaction.⁸

Inspection of the measured λ_{\max} and $E_{\text{ox}}/V(M)$ values shows that the same trend for the mixed oligomers is followed as earlier reported^{4,9} for a number of oligomeric 2,5-thienylenes. The unsubstituted compounds (**3**) and (**7**) in which there is no steric hindrance and, thus maximum coplanarity, show an *n*-dependent increase in λ_{\max} with a concomitant decrease of $E_{\text{ox}}/V(M)$. In the methyl substituted compounds (**4**), (**5**), and (**6**), however, no such clear cut relationship exists.

Comparing the u.v. spectra of these compounds with the spectrum of (**3**) one finds that (**4**) and (**5**) show a hypsochromic shift whereas (**6**) exhibits a shift to longer wavelengths. Moreover, since steric hindrance in compounds (**4**) and (**5**) should be practically identical one would expect that both compounds should show nearly the same position for the λ_{\max} and the same values for the oxidation potentials. While this is the case for the u.v. data the corresponding values for the oxidation potentials, however, show a rather significant difference. Comparing the corresponding parameters of the trimeric compounds (**7**), (**8**), and (**9**) the trend observed for the position of the λ_{\max} can still be rationalized on the basis of steric hindrance and the +*I*-effect of the methyl groups. Most severe steric hindrance should be in compound (**8**) whereas no difference of steric hindrance exists between compounds (**7**) and (**9**). Therefore, one would expect compound (**8**) to have the lowest λ_{\max} (the least coplanar species among these three compounds) and compound (**9**) a slightly higher λ_{\max} than (**7**)



Scheme 1



due to the $+I$ -effect of the methyl groups. Inspecting the measured values of the oxidation potentials one observes however, that this parameter increases from (7) via (8) to (9), which is not in agreement with the above argument. A possible explanation for this observation might be a contribution by the Se atom of the selenophene rings to these parameters. Further studies to clarify this problem by including furan, pyrrole, and tellurophene containing mixed oligomers are under way in this laboratory.

The polymer derived by electro-oxidation of (8) when pressed into a pellet shows the remarkable high conductivity value of at least $500\text{--}700\text{ S cm}^{-1}$. Thus, its conductivity is in the upper range of conducting organic materials.¹⁰ This is a rather unexpected observation since it was earlier reported that films obtained similarly by electro-oxidation of selenophene

showed only a rather poor conductivity in the range of $10^{-4}\text{--}10^{-3}\text{ S cm}^{-1}$.¹¹

In summary, we have synthesized for the first time mixed oligomeric five-membered heteroarylenes containing substituted and unsubstituted thiophene and selenophene units. We also show that there exists a relationship between the position of the long-wavelength u.v. absorption and the oxidation potential of the unsubstituted compounds. Observed deviation from this relationship in the substituted species is explained by a barrier to assumed coplanarity caused by steric hindrance imposed by the methyl group. The $+I$ -effect of the methyl groups exerts a rather unpredictable influence on the λ_{max} and the oxidation potentials of the compounds. Also, it is suspected that the Se atom of the selenophene moieties exerts an influence on the position of the λ_{max} and the oxidation potentials. The films obtained by electro-oxidation of the thiophene and selenophene containing oligomers show a remarkable conductivity.

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