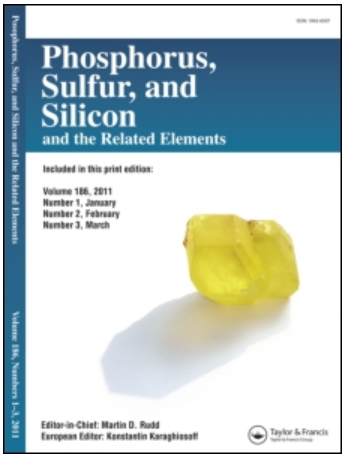

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SYNTHESIS OF MIXED OLIGOMERIC HETEROARYLENES CONTAINING UNSUBSTITUTED FURAN, THIOPHENE, AND SELENOPHENE RINGS; THEIR UV SPECTRA AND OXIDATION POTENTIALS

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SYNTHESIS OF MIXED OLIGOMERIC HETEROARYLENES CONTAINING UNSUBSTITUTED FURAN, THIOPHENE, AND SELENOPHENE RINGS; THEIR UV SPECTRA AND OXIDATION POTENTIALS

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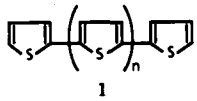
Mixed oligomeric 2,2'- and 2,2'-5',2"-unsubstituted five-membered heteroarylenes containing furan, thiophene, and selenophene rings **2a–f** and **3a–i** have been synthesized. Their UV spectra and oxidation potentials are discussed.

Key words: Mixed oligomeric heteroarylenes; furan; thiophene; selenophene; conducting polymers; UV spectra; oxidation potentials.

INTRODUCTION

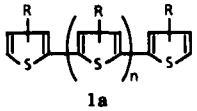
In a series of papers we described the synthesis of a number of oligomeric five-membered heteroarylenes and discussed their UV spectra and oxidation potentials. We found that in unsubstituted oligomeric thiophenes **1** with increas-



1

n = 0, 1, 2, 3

ing n the λ_{max} of the long wavelengths absorption shows a bathochromic shift, while the oxidation potentials E_{ox} decrease. Such a clear cut relationship, however, was not evident when the oligomers contained substituents[2–4] as in **1a**.



1a

n = 0, 1, 2

R = H, Me, Et

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Absence of such relationship was explained by impediment of coplanarity by steric hindrance caused by the substituents. More recently in our efforts to synthesize better conducting organic polymers derived from mixed oligomeric five-membered heteroarylenes containing methyl substituted thiophene rings and unsubstituted selenophene and/or furan rings we found that besides the substituent also the element of the heteroring had a significant influence on both the position of the λ_{max} and the E_{ox} of the compounds. However, we were not able to detect any obvious relationship between these parameters and the element of the five-membered rings.[5] Since, as we have shown earlier,[2] substitution and the so caused impediment of coplanarity influences profoundly the position of λ_{max} and E_{ox}, we hoped that by investigating unsubstituted mixed oligomers the role of the heteroatom on the position and magnitude of these two parameters could be revealed. In the present communication we report the results of this study.

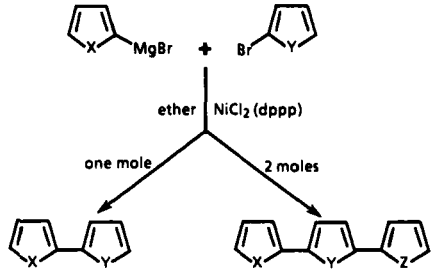
RESULTS AND DISCUSSION

Compounds **2a–f**, **3a–f** and **3h** have been prepared by a cross-coupling reaction of the Grignard reagent derived from the appropriate 2-haloheteroarylene with either one or two moles of 2-haloheteroarylenes in the presence of $NiCl_2$ (dppp).[2,6]

Compounds **3g** and **3i** were prepared by coupling of 2-selenopheneboronic acid with 2,5-dibromoselenophene or 2,5-dibromofuran in dimethoxyethane in presence of tetrakis(triphenylphosphine)palladium(0) as catalyst,[7] as given in Scheme 1.

The structures of these compounds have been established by UV, ^1H NMR, MS spectroscopy and elemental analyses.

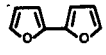
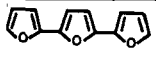
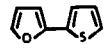
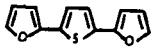
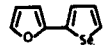
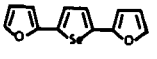
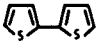
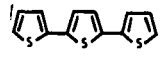
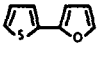
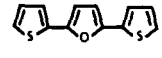
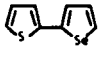
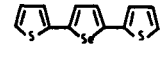
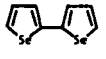
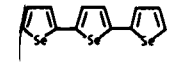
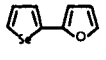
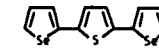
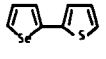
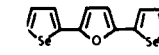
Qualitative analyses of these data for the UV spectra for the "unmixed" dimers and trimers of furan, thiophene, and selenophene reveal that the λ_{max} increases



SCHEME 1.

TABLE I

UV spectra and oxidation potentials

Type 2 compounds	λ_{max} ($CHCl_3$)	E_{ox} V (vs. Ag/AgCl)	Type 3 compounds	λ_{max} ($CHCl_3$)	E_{ox} V (vs. Ag/AgCl)
	278	1.47		331	—
	268	1.60		312	0.96
	305	1.25		362	0.96
	302	1.3		355	1.05
	268	1.6		315	1.00
	311	1.52		363	1.14
	321	1.20		376	0.96
	305	1.24		372	0.96
	311	1.52		367	0.89

with increasing atomic number of the heteroatom, a trend which also occurs in the monomeric species.[8] It also can be seen that in every dimer and trimer the furan containing species also, regardless of the position in the "mixed" trimeric oligomers, exhibits the lowest λ_{max} position. The data for the oxidation potentials do not show any regular trend. The data are presented in Table I.

ELECTROCHEMISTRY

E_{ox} values are reported in reference to a Ag/AgCl electrode as the potential of the peak oxidation current of the cyclic voltammograms (scan rate 50 m Vs^{-1}). The solvent was acetonitrile with $[(n\text{-}C_4H_9)_4]^{\oplus}BF_4^{\ominus}$ as the supporting electrolyte. The concentration of the oligomer was 50 mmol.[9]

EXPERIMENTAL

Melting points were determined with a Mel Temp apparatus and are uncorrected, as are the boiling points. UV spectra were run in $CHCl_3$ on a Perkin–Elmer Lambda 5 UV/VIS spectrophotometer. ^1H NMR spectra were recorded at 80 MHz on an IBM FTQ NMR spectrometer. Chemical shifts are expressed in δ (ppm) relative to tetramethylsilane as internal standard and $CDCl_3$ as solvent.

Elemental analyses were performed at M-H-W Laboratories, Phoenix, Arizona. All reactions were performed under N_2. Silica gel 60 (Merck) was used for column chromatography and petroleum ether (b.p. 37–59°C) was used as an eluent. The reported yields refer to pure isolated materials.

STARTING MATERIALS

The following halides were prepared according to methods reported earlier: 2-bromofuran,[10] 2,5-dibromofuran,[10] 2-bromoselenophene,[11] 2,5-dibromoselenophene.[12] 2-Bromothiophene and 2,5-dibromothiophene are commercially available and were used without further purification. Nickel(II) [1,3-bis(diphenylphosphino)propane]chloride, $NiCl_2$ (dppp)[13] was used as a catalyst in the coupling reaction.

The following mixed oligomers have been prepared according to known methods: 2a,[14]2b,[14]2d,[2]2e,[5]3a,[15]3b,[14]3d,[2]3e,[14]3f[5].

2-(2-*Selenyl*)*furan* (**2c**). To a solution of 15.7 ml of 1.6 *n*-butyllithium (25 mm) in 20 ml THF at −25°C was added 1.7 g of furan (25 mm). The reaction mixture was stirred at room temperature for 30 min (15°C) and syringed to another flask containing 6.5 g (25 mm) of $MgBr_2$ etherate in 20 ml THF. After stirring for one hr at room temperature the mixture was added to another flask containing 2.1 g (10 mm) of 2-bromoselenophene and 200 mg of $NiCl_2$ (dppp) in 25 ml THF. The coupling reaction was done at room temperature followed by a reflux period of one hr and left overnight at room temperature. It was worked up by adding 2 N aqu. HCl and extracted by ether and dried over anhydrous $MgSO_4$. Final purification was achieved by column chromatography using silica gel and petroleum ether as eluent to give 0.6 g of the title compound as an oil (yield 30%). Anal. Calcd. for C_8H_6OSe: C, 48.75; H, 3.07. Found: C, 49.00; H, 3.29. ^1H NMR ($CDCl_3$) δ 7.85 (dd, 1 H, 5-position of Se-containing ring) 7.35 (m, 2 H, 3 and 4 position in selenophene ring), 7.25 (dd, 1 H, 5 position in furan ring), 6.45 (m, 2 H, 3 and 4 position in furan ring).

2,2′-*Biselenyl* (**2f**). A mixture of 2.1 g (10 mm) of 2-bromoselenophene, 0.65 g (1 mm) of $NiCl_2(PPh_3)_2$, 0.98 g (15 mm) Zn and 3.69 g (10 mm) of $[t\text{-}Bu_4N]I$ in 30 ml THF was heated for 2 hrs at 50°C and worked up by adding on 2 N aqu. HCl and extraction by ether. Final purification was achieved by column chromatography on silica gel using petroleum ether as eluent to give 0.25 g of **2f**, m.p. 50°C (lit. 49°C),[16] ^1H NMR ($CDCl_3$) δ 7.9 (dd, 2 H, H's in 5 and 5′-positions of selenophene rings), 7.2 (m, 4 H, 3 and 3′, and 4 and 4′-positions of selenophene rings).

2,5-*Bis*-(2-*Furyl*)*selenophene* (**3c**). To 25 ml of 1.6 molar butyllithium (40 mm) in THF (at −25°C) were added 2.72 g (40 mm) of furan. The reaction mixture was stirred for 30 min at 15°C and syringed into a solution of 10.33 g (40 mm) of $MgBr_2$ etherate in 40 ml THF and stirred for one hr at room temperature, and then 2.89 g (10 mm) of 2,5-dibromoselenophene were added. After stirring for 4 hrs at room temperature it was worked up as described for compound **1** giving 0.26 g of yellow needles (10%) of the title compound; m.p. 83°C. ^1H NMR ($CDCl_3$) δ 7.4 (2H, s, protons in 3 and 4 position of selenophene ring), 7.30 (2 H, protons in 5 and 5′-position of furan rings), 6.45 (m, 4 H, protons in 3 and 3′-position of furan rings). Anal. Calcd. for $C_{12}H_8O_2Se$: C, 54.77; H, 3.06. Found: C, 54.63; H, 3.18.

2-*Selenopheneboronic acid.*[17] To a solution of 26.2 g (0.2 mole) selenophene in 100 ml dry ether under nitrogen were added 155 ml of 1.42 N *n*-butyllithium in hexane at such a rate that gentle reflux was maintained. When the addition was complete, the reaction mixture was refluxed for 20 min, whereupon it was cooled to −70°C when 65 g of *n*-butyl borate in 200 ml of dry ether were added dropwise. After three hrs at −70°C the reaction mixture was allowed to obtain 0°C, whereupon it was poured into 2 N aqu. HCl and ice. The phases were separated and the water phase extracted twice with ether. The combined ether phases were extracted with cold 2 N aqu. sodium hydroxide solution. The alkaline phases were immediately poured into 2 N aqu. sulphuric acid and ice. The precipitated boronic acid was taken up in ether, washed with water and dried over anhydrous sodium sulphate. Evaporation of the ether gave 28.0 g (80%) of 2-selenopheneboronic acid.

2,5-(2-*Selenienyl*)*selenophene* (**3g**). A mixture consisting of 4.81 g (0.017 mole) of 2,5-dibromoselenophene, 133 ml dimethoxyethane and 1.18 g (1.2 mmole) tetrakis(triphenylphosphine)palladium(0) was stirred at room temperature under N_2 for 10 min, whereupon 7.0 g (0.04 mole) selenopheneboronic acid and 100 ml 1 N aqu. sodium hydrogen carbonate were added. The reaction mixture was refluxed with vigorous stirring for four hrs and cooled to room temperature. The catalyst was filtered off and the dimethoxyethane was evaporated. The residue was extracted several times with methylene

chloride. The combined methylene chloride phases were washed with water and sodium chloride solution and dried over anhydrous magnesium sulfate. The methylene chloride was evaporated and the crude product was solved in ethyl acetate and flash chromatographed on silica 60 using heptane/methylene chloride (90:10) as eluent. 1.48 g (22%) of the title compound were obtained, m.p. 174–176°C (lit. 175.5–177.5°C).[18] ^{1}H NMR (acetone-d6): δ 8.08 (5 H), δ 7.37 (3 H), 7.28 (4 H), 7.28 (3 H = 4 H). J_{34} = 3.80 Hz, J_{35} = 1.08 Hz, J_{45} = 5.59 Hz. MS: molecular ion centered at 390.

2,5-*Bis*(2-*Selenienyl*)*thiophene* (**3h**). To 2.1 g (10 mmole) of 2-bromoselenophene in dry ether (15 ml) were added 5 ml of 2.0 M solution of isopropylmagnesium chloride (10 mmole) in diethyl ether at −25°C and stirred for 2 hrs. The 2-selenophene magnesium chloride was then syringed into a mixture of 1.2 g (5 mmole) of 2,5-dibromothiophene and 100 mg of $NiCl_2$ (dppp) in 25 ml dry diethyl ether and left overnight at room temperature. The reaction mixture was poured in 2 N aqu. HCl and extracted with ether. After evaporation of the ether the residue was purified using column chromatography and silica gel with petroleum ether as eluent to give 70 mg (5%) of a yellow product m.p. 128°C. Anal. Calcd. for $C_{12}H_8SSe_2$. C, 42.12; H, 2.36. Found: C, 42.03; H, 2.17. ^{1}H NMR ($CDCl_3$) δ 7.90 (dd, 2 H, ortho to selenophene ring), 7.30 (m, 6H, meta protons in both selenophene rings and the central thiophene ring).

2,5-*Bis*(2-*Selenienyl*)*furan* (**3i**). A mixture consisting of 2.26 (0.010 mole) of 2,5-dibromofuran, 80 ml of dimethoxyethane and 0.69 g (0.6 mmole) of tetrakis(triphenylphosphine)palladium(0) was stirred at room temperature under N_2 for 10 min, whereupon 4.2 g of 2-selenopheneboronic acid and 60 ml of sodium hydrogen carbonate were added. The reaction mixture was refluxed with vigorous stirring for 4 hrs. After cooling to room temperature the catalyst was filtered off and the dimethoxyethane evaporated. The residue was extracted several times with ether; the combined ether phases were washed with water and sodium chloride solution and dried over anhydrous magnesium sulfate. After evaporating the ether the crude product was flash chromatographed on silica 60 using heptane/methylene chloride (90:10) as eluent to give 1.2 g (37%) of the title compound, m.p. 92–97°C. ^{1}H NMR ($CDCl_3$): δ 7.19 (5 H − Se), 7.46 (3 H − Se), 7.29 (4 H − Se), 6.55 (3 H, 4 H − O). J_{34} = 3.85 Hz, J_{35} = 1.10 Hz, J_{45} = 5.55 Hz. Anal. calcd. for $C_{12}H_8OSe_2$: C, 44.20; H, 2.47. Found: C, 44.31; H, 2.49. MS: Molecular ion centered at 326. Calculated M wt. 325.16.

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