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SYNTHESIS, UV-SPECTRA, AND SOME ELECTROCHEMICAL PROPERTIES OF NOVEL 3,3'-BRIDGED-2,2'-BITHIENYLS*

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A convenient synthesis of a number of 3,3'-bridged-bis-2,2'-thienyls as potential building blocks for novel conducting polymers is reported. The UV-spectra and oxidation potentials of these novel compounds are given.

Although the UV-spectra correlated to the degree of coplanarity of these species, the oxidation potentials did not correlate, and no tendency to polymerize was observed for the N-bridged thienyls, **Ia-1d**, **2a-2c**. This behavior is in contrast to results found for other 2,2'-bithienyls. These findings are explained by nitrogen and sulfur adsorption orientation of the N-bridged biethienyl molecules on the electrode surface prior to electron transfer

Keywords: 3,3'-bridged–2,2'-bithienyls; UV-spectra; oxidation potentials; cyclic voltammetry; electrode adsorption orientation.

INTRODUCTION

In a number of papers Zimmer and coworkers reported on the synthesis of novel 2,5-thiophene based oligomers¹. They also examined the UV-spectra and oxidation potentials of a number of 3,3'-substituted-2,2'-bithienyls and related oligomers.¹⁻³. Included in these investigations were also methylene- and ethylene-3,3'-bridged-2,2'- bithienyls.² These studies revealed a correlation between steric hindrance due to substitution at the 3- and 3,3'- positions with concomitant loss of coplanatity position of the electron transfer band of the UV-spectra of these compounds. The same trend was observed on their oxidation potential. To further investigate these correlations a number of novel nitrogen containing 3,3'-bridged-2,2'-thienyls were synthetized and studied with respect to these

^{*} Taken in part from M.S. Thesis of Mike Wehmeier, Univ. of Cincinnati, 1995 Dedicated to Professor Robert Wolf on the occasion of his 70th birthday

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spectroscopic and electrochemical properties. Specifically, compounds **1a–1d**, and **2a–2c** were synthetized and investigated. (Scheme 1)



2a, $R = CH_3CH_2$; **2b**, $R = C_8H_3$; **2c**, R = 4-BrC₆H₅CH₂ SCHEME 1

SYNTHESIS

The azepine derivatives 1a-1d were all prepared in analogy to a procedure developed by W.Wenner⁴ for the synthesis of dihydrodibenz [c,e]azepines (eq.1).



The thirteen membered nitrogen containing crow ethers 2a, 2b and 2c were synthesized by reacting the appropriately N-substituted diethanolamine with 3,3'-bis (bromomethyl)–2,2'-bithienyl in the presence of sodium hybride and tetrahydrofuran as solvent (eq.2).



SPECTROPHOTOMETRIC STUDIES

As a result of our previous examinations of the UV-spectral characteristics and oxidation potentials of a fairly large number of 3,3'-substitued–2,2'-bithienyl monomers and derived oligomers it was found that in all cases the hypsochromic shifts of the electron transfer band and the positive shift of the oxidation potentials correlated directly with the increase of steric hindrance due to the substitution at the 3–and 3'-positions, and thus, loss of coplanarity of the thiophene rings as expected.^{3,5-7} Furthermore, all of these species electropolymerized to form conducting polymers films, also as expected.¹ The bithienyls of the present study exhibited the expected UV-characteristics but their oxidation potentials and electropolymerization behavior are contradictory to our expectation (Table I). For comparison the UV-spectra of the previously examined 2,2'-bithienyls are briefly discussed. They exhibited the following features:

- a. a band of moderate intensity at 247-253mm (local excitation band). The position, as expected, of this band was almost independent of the substituents.
- b. A band of high intensity at longer wavelength (electron transfer band), which exhibited a hypsochromic shift and a significant decrease in intensity with increasing steric hindrance between the substituents in the 3- and 3'-positions.

Compound	λ _{max} (mm) L.E. Band E.T. Band	$\varepsilon (M^{-1}cm^{-1})$
1 a	245.0	3820
1 b	248.4	4840
1 c	255.7	8920 7840 7880
1 d	260.2 321.4	10300
2 a	242 260 sh	-
2 c	243 260 sh	-

TABLE I UV-Spectra of N-Containing Bridged Bithienyls

These results were interpreted in terms of coplanarity of the compounds. Increasing steric hindrance should twist the molecule out of this position, resulting in a decreased intensity and a hypsochromic shift of the electron transfer

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band because of diminished conjugation in the heteroaromatic ring system. The UV-spectra of these compounds are reported in Table II.

	Compound Structure	λ _{max} (nm)	E _{ox} V vs Ag/AgCl Monomer
1)		302	1.28
2)	C _s C _s	299	1.22
3)		270	1.57
4)	<u> </u>	311	0.97
5)		305	1.20

TABLE II

It is evident that the L.E. bands for compounds **1a** - **1d** vary between 245 nm and 260 nm, a feature that was rather unexpected and cannot at present be adequately explained. For compounds **2a** and **2c** the value for this band varies not at all and is as anticipated. The position of the E.T. bands for compounds **1a** - **1d** falls between 316.4 and 321.4 nm and is nearly the same for all four compounds. This can be explained by assuming that in these azepines the two thiophene moieties are virtually coplanar. Thus, the C-N-C bridge causes the seven-membered ring to be rigid and therefore does not interfere with the coplanarity of the chromophore. This statement is corroborated by the results of our above mentioned investigation in which we included two $3,3'(CH_2)_n$ -bridged-2,2'-bithienyls (n = 1,2),²; namely entries 4 and 5 of Table II. Because in these

two compounds, the two thienyl moieties are coplanar or nearly so, and thus are useful in correlating the degree of rigidity with the λ_{max} value of the bithienyls. It is noteworthy that the λ_{max} value of entry 5 is lower than that of entry 4, indicating that the -CH₂CH₂-bridge decreases the rigidity and therefore the coplanarity of this compound. Comparing now the λ_{max} values of the N-containing bridged compounds **1a-1d**, it seems to be obvious that the positions of the reported λ_{max} values can be explained by a high degree of coplanarity of the two thienyl units, and thus a large degree of rigidity of the 7-membered rings of these species seems to be certain. A comparison of the λ_{max} values of compounds **2a** and **2c**, which are 13-membered-ring species, with shoulders at around λ_{max} of 260–265 nm, lends further support of our argument that **1a-1d** are basically planar compounds whereas **2a** and **2c** are, due to the much larger ring size, less rigid and bent out of coplonarity. Similar arguments for the correlation of UV-spectra between steric hindrance and coplanarity in diphenyls have been published extensively earlier.^{8,9}

ELECTROANALYTICAL STUDIES

Previously we have obtained a good correlation of the electro-oxidation peak potentials for various substituted thiophene monomers and oligomers with their UV-VIS spectra.^{3,5-7} In order to determine if a similar correlation exists here, the electro-oxidation potentials of the following 2,2'-bithienyl monomers (Table III) were determined by cyclic voltammetry.

The resulting cyclic voltammograms of compounds 1a, 1c, 1d, 2a, and 2c are shown in Figs. 1–5, respectively and the peak oxidation potentials (Ep_{ox}) are listed in Table III.

COMPOUND	CONCENTRATION	EP _{ox}
1 a	25 mM	+ 1.48 V
1 c	saturated solution	+ 1.22 V
1 d	3 mM	+ 1.45 V
2 a	15 mM	+ 1.20 V
2 c	5 mM	+ 1.45 V

TABLE III Peak Oxidation Potentials

All of the cyclo voltammograms obtained have the following characteristics in common: (i) oxidation peaks at rather high positive potentials (1.2-1.5V); (ii) no



FIGURE 1 Cyclic Voltammograms of Compound 1a

FIGURE 2 Cyclic Voltammograms of Compound 1c





FIGURE 3 Cyclic Voltammograms of Compound 1d

FIGURE 4 Cyclic Voltammograms of Compound 2a



FIGURE 5 Cyclic Voltammograms of Compound 2c

reduction peak on the reverse negative potential scan; (iii) almost constant peak currents on subsequent cycles; (iv) no visible polymer films on the Pt working electrode.

The total irreversibility of the electro-oxidation and the fact that these species do not undergo electropolymerization (except for compound 2a, which will be discussed later), is completely opposite to the previously reported 3,3'-substituted 2,2'-bithienyl compounds.⁵⁻⁷ Even more surprising is the fact that the peak oxidation potentials of compounds (1a,1c,1d, 2a, 2b) are significantly more positive than the oxidation potential of the methylene bridged bithienyl (entry 4 in Table II, +0.97 V) even though the UV spectra indicate that in these compounds all the thienyl rings are nearly planar due to the rigid ring bridge systems. One would expect that the redox electron transfer potential, based on the electron transfer peaks of the UV-spectra, should have the same or nearly the same oxidation potentials.⁵⁻⁷ Examination of the cyclic voltammogram of triethylamine (Fig. 6) indicates that it is very close, $E_{ox} + 1.32V$, to that of compound 1c. Thus, leading to the conclusion that the oxidation of compound 1c is taking place at the nitrogen atom which indicates that the thiophene system is not undergoing oxidation. This fact explains why no polymerization of 1c occurs. The same can be concluded for compounds 1a, 1d, and 2c. This behavior of these species is very difficult to understand as the oxidation potentials of all bithienyls occur at potentials less positive than that of the investigated amine bridged bithienvls, thus one would not expect the nitrogen atom of the bridge to exact an inductive effect on the thiophene rings. One can speculate that these compounds get absorbed via the nitrogen atom on the Pt-surface prior to the electron transfer.¹⁰ The absorption orientation therefore is such that the bithienyl system projects into the solvent phase and is too far from the electrode to undergo oxidation.



FIGURE 6 Cyclic Voltammograms of triethylamine, 25 mM

For compound **2a**, the decreasing peak current on successive CV's indicates that a thin non-visible insulating film is probably formed on the electrode. In order to avoid the influence of the nitrogen atom compound of **2a**, compound **4** was synthesized and electro-oxidized (Fig. 7).



FIGURE 7 Cyclic Voltammograms of Compound 4

Here, the current decreases more rapidly only after few repetitive cycles than in compound **2a**; and again no visible polymer film was obtained. In this case a thin non-conducting film formed and totally passivates the electrode ; and thus inhibiting further electropolymerizations. This type of behavior is quite common in organic electrooxidation ; for example the cyclic voltammograms of o-phenylenediamine are very similar to those of compounds **2a** and **4**.¹¹ In these cases, the polymers can not attain planarity of the rings and are non-conducting.

EXPERIMENTAL

Synthesis

Melting points were determined with a Mel Tempapparatus and are uncorrected. The ¹H NMR spectra were recorded on a Varian T-60 and/or an IBM 80 (80 mHz) spectrometer. Chemical shifts are expressed in δ relative to tetramethylsilane as internal standard. MS data were obtained on a gas chromatograph/mass spectrometer HP 5995. UV-Vis spectra were recorded on Perkin-Elmer Lambda 5, UV-Vis spectrometer. Elemental analyses were per-

formed at M-H-W Laboratories, Phoenix, Arizona. All reactions were performed under a blanket or argon. The reported yields refer to pure isolated materials.

Materials

2,5-Dibromothiophene and 3-methylthiophene were purchased from Fairfield Chemical Co., Inc. All solvents used were reagent grade. Tetrahydrofuran (THF) was purified by continuous distillation under argon from benzophenone-potassium. Nickel(II)[1,3-bis(diphenylphosphino)propane] chloride, NiCl₂(dppp), was prepared as reported earlier.¹

Benzyl-2,7-dihydrothieno[c,e]azepine(1a)

To 1g of 3,3'-bis(bromomethyl-2,2'-bithienyl (3) and 0.3g of benzylamine dissolved in 300 ml tetrahydrofuran (THF) 2g of anhydrous potassium carbonate was added and refluxed for 24 h. The obtained brownish precipitate was filtered off, washed with water and extracted several times with 1N HCI. The acidic solution was brought with aqueous NaOH to pH-10 when a colorless solid formed. It was taken up in diethyl ether and dried over anhydrous magnesium sulfate. The ether was distilled off to leave a colorless solid; m.p. 116– 117° (ethanol). Anal. Calcd. for $C_{17}H_{15}NS_2$: C, 68.65; H, 5.08. Found: C, 68.46; H, 5.14. ¹H-NMR (DCCl₃): δ (3.66, 2, 2H), (4.19, s, 4H), (6.66, d, 2H), (7.04, d, 2H), (7.20–7.30, 5H).

N-Phenyl-2,7-dihydrodithieno[c,e]azepine(1b)

It was obtained analogously by reacting 1g of 3 with .26g of aniline, 2g of anhydrous potassium carbonate in 30 ml of THF for 24 h at room temperature; m.p. 136–137°C (ethanol); yield 20 %. Anal. Calcd. for $C_{16}H_{13}NS_2$: C, 67.81; H, 4.62. Found: C, 67.71; H, 4.60. ¹H-NMR (DCCl₃): δ (4.85, s, 4H), (6.67, t, 1H), (6.79, d, 2H), (6.90, d, 2H), (7.02, d, 2H), (7.12, dd, 2H).

N-tert-Butyl-2,7-dihydrodithieno[c,e]azepine(1c)

Compound 1c was synthesized essentially as 1a and 1b, except that due to the low boiling point of tert-butylamine the reaction was run in a pressure bottle. The azepine obtained as an oil solidified after keeping it overnight at -10° C, m.p. 81–82°C (ethanol). Anal. Calcd. for C₂₀H₁₇NS₂: C, 63.84; H, 6.50. Found: C, 64.09;

H, 6.43. ¹H-NMR (DCCl₃). δ (1.11, s, 9H), (4.00, s, 4H), (6.73, d, 2H), (6.96, d, 2H).

N-(p-Bromophenyl)-2,7-dihydrodithieno[c,e]azepine (1d)

It was obtained essentially as the above compounds, m.p. $184-185^{\circ}C$ (toluene). Anal. Calcd. for $C_{16}H_{12}BrNS_2$: C, 53.04; H, 3.34. Found: C, 53.19; H, 3.50. ¹H-NMR (DCCl₃). δ (4.81 ppm, s, 4H), (6.65, 3, 2H), (6.89, d, 2H), (7.03, d, 2H), (7.17, d, 2H). MS: (FW 362.18g/mole), M⁺(m/z)[⁷⁹Br] 361; M⁺(m/z)[⁸¹Br] 363.

N-Ethyl-2,3,5,6,8,13-hexahydro-9,10,11,12-dithieno-1,7-dioxa-4azacyclotridecatine (2a)

To 0.16g of sodium hydride (as 0.27g of a 60 % suspension in mineral oil) in 10ml of anhydrous THF, 0.38g of N-ethyldiethanolamine in 30ml of dry THF was added, stirred and refluxed for 1 h. When a colorless solid precipitated a solution of 1.0g of **3** in 150ml of dry THF was added and the mixture was refluxed for 24 h. After cooling to room temperature water was added and the solvents were subsequently removed under reduced pressure and the remainder extracted several times with diethyl ether. The combined ether solutions were distilled off until an orange oil was obtained. It was dissolved into a mixture of 10ml of chloroform and 20ml of water to remove remaining N-ethyldiethanolamine. The two layers were separated, and the chloroform was removed under reduced pressure. The resulting oil was purified by silica gel column chromatography using ethyl acetate as eluent to give a colorless solid, m.p. 75°C (diethyl ether). Anal. Calcd. for $C_{16}H_{21}NO_2S_2$: C, 59.41; H, 6.54. Found: C, 59.25; H, 6.62. ¹H-NMR (DCCl₃): δ (0.99, t, 3H), (2.55, q, 2H), (2.65, t, 4H), (3.55, t, 4H), (4.39, s, 4H), (7.16, d, 2H), (7.34, 3, 2H).

N-Benzyl-2,3,5,6,8,13-hexahydro-9,10,11,12-dithieno-1,7-dioxa-4-azacyclotridecane (2b)

It was obtained essentially as described for **2a** from 0.72g of N-benzyldiethanolamine, 0.35g of sodium hydride (as a 60 % suspension in mineral oil) and 1.3g of **3** in THF. The resulting yellowish oil was purified *via* silica gel column chromatography using petrolether-ether (5:1) as eluent to give a clear yellow oil. ¹H-NMR (DCCl₃): δ (2.70, t, 4H), (3.55, t, 4H), (3.63, s, 2H), (4.42, s, 4H), (7.18, d, 2H), (7.21–2.29, m, 5H), (7.36, d, 2H).

N-4-Bromobenzyl-2,3,5,5,8-hexahydro-9,10,11,12-dithieno-1,7-dioxa-4-azacyclotridecane (2c)

This compound was prepared as described above from 1g of N-(4-bromobenzyl) diethanolamine, 0.35g of sodium hydride (as a 60 % suspension in mineral oil) and 1.28g of **3** in THF. The resulting orange oil was purified *via* silica gel column chromatography using diethyl ether-petrol ether (1:1) as eluents to give a clear yellow oil. Anal. Calcd. for $C_{21}H_{22}BrNO_2S_2$: C, 54.31; H, 4.77. Found: C, 54.14; H, 4.80. ¹H-NMR (DCCl₃): δ (2.67, t, 4H), (3.54, t, 4H), (3.56, s, 2H), (4.41, s, 4H), (7.15–7.38, 8H), MS: (FW 464.02g/mole), M⁺(m/z)[⁷⁹Br] 463, M⁺(m/z)[⁸¹Br] 465.

2,3,5,10-Tetrahydro 6,7,8,9-dithieno-1,4-dixoacyclodecane (4)

It was synthesized essentially as the above compounds from 0.22g sodium hydride (as a 60 % suspension in mineral oil), 0.14g ethylene glycol and 0.8g 3 in THF. It was purified by silica gel column chromatography with petrol ether-ether (6:1) as eluent, colorless crystals, m.p. 152°C. Ana. Calcd. for $C_{12}H_{12}O_2S_2$: C, 57.11; H, 4.79. Found: C, 56.98; H, 5.00. ¹H-NMR (OCCl₃). δ (3.45, s, 4H), (4.42, s, 4H), (7.11, d, 2H), (7.33, d, 2H).

Electrochemistry

The experiments were performed in acetonitrile containing 0.01 M tetrabutylammonium fluoroborate (TBABF). The concentration of the monomers differ due to amounts of material available, however, since oxidation potentials are relatively independent of concentration, this fact should not invalidate our conclusions. All of the electrochemical studies were performed in a one-compartment cell consisting of a Ag/AgCl reference electrode (BAS MF–2012), a 3mm Pt working electrode and a Pt wire auxiliary electrode. Electrochemical data were made by using a Bioanalytical Systems (BAS) potentiostat Model CV–1A and a Hewlett Packard Model 7015 X-Y recorder. The solutions were deaerated by bubbling argon through them for 10 minutes before electrolysis. They were kept under an argon atmosphere during the entire experiment. The Pt working electrode was cleaned and kept in an ultrasonic bath for 15 minutes before each experiment. The current-potential oxidation profile of each monomer was recorded between 0.0V and 1.7V at a scan rate of 100mV/s. Each time 5 cycles were taken.

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