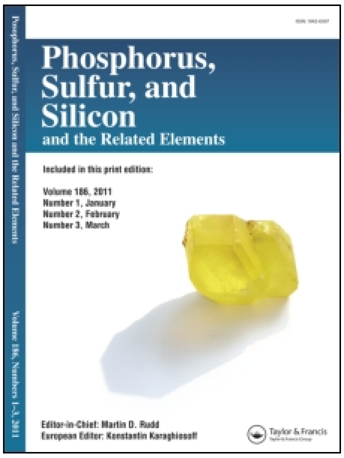

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STUDIES OF SOME HINDERED 2,2'-BITHIENYLS AND 3,3'-BRIDGED 2,2'-BITHIENYLS WITH SPECIAL REFERENCE TO THEIR UV SPECTRA AND OXIDATION POTENTIALS

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STUDIES OF SOME HINDERED 2,2'-BITHIENYLS AND 3,3'-BRIDGED 2,2'-BITHIENYLS WITH SPECIAL REFERENCE TO THEIR UV SPECTRA AND OXIDATION POTENTIALS

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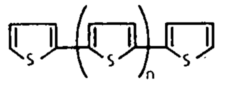
Some hindered bithienyl derivatives have been synthesized by cross-coupling reaction of Grignard reagents using $NiCl_2(dppp)(dppp = Ph_2PCH_2CH_2CH_2PPh_2)$ or by reductive dimerization in the presence of $Zn/NiCl_2(PPh_3)_2$. Their UV spectra and oxidation potentials are discussed in terms of their coplanarity and of the inductive effect of the substituent.

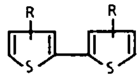
Key words: 2,2'-Bithienyls; 3,3'-Bridged Bithienyls; UV Spectra; Oxidation Potentials; Sonochemical Grignard Reactions

INTRODUCTION

As one aspect of our continuing research on the synthesis, spectra and electrical properties of oligomeric thiophenes,[1] we predicted and showed that in the unsubstituted series **1** the λ_{max} of the UV spectra should show a bathochromic shift with increasing *n*, whereas the values of the oxidation potential (E_{ox}) should exhibit a decrease. As a reason for this behavior we were discussing coplanarity of the oligomer and electron delocalization in the cation radical, which result from the electro-oxidation of the oligomer. If, due to substitution in the 3- and/or 3'-position of the bithienyl species coplanarity would be partially impeded, in agreement with this assumption, the λ_{max} of the UV spectra should show a hypsochromic shift and the E_{ox} value should increase. These predictions, again, were confirmed by the experimental results.[1]



1

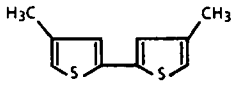
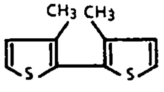


2

n = 1, 2, 3, 4
R = R' = H, CH_3 in various positions

Shortly after our results were published a paper appeared reporting on the oxidation potentials of four 2,2'-bithienyls.[2] Three of the investigated compounds were identical with ours. The E_{ox} values of them found by us and by the Swedish group are listed in Table I. Comparing the data one notices that for 2,2'-bithienyl **4a** and 4,4'-dimethyl-2,2'-bithienyl practically identical values were reported by both groups. However, for the 3,3'-dimethyl-2,2'-bithienyl **4c** a large discrepancy

Table I Oxidation Potentials of Bithienylenes

 **4a**		
1.27[a] 1.28[b]	1.15 1.16	1.19 1.58

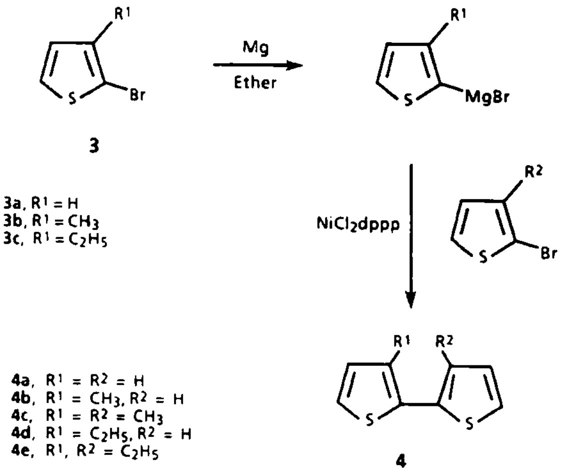
a) Values from ref. 2.
b) Our values

in the values for E_{ox} exists. Therefore, and also in the light of our interest in studying the behavior of thiophene oligomers on electropolymerization[3-5] it was decided to reinvestigate the oxidation potential value of **4c**. In addition, to further clarify the role of steric hindrance in this area, a number of related thiophene dimers of type **4** compounds were included to test our hypothesis that partial inhibition of coplanarity of the thiophene moieties in the oligomers influences the position of λ_{max} of the UV spectra and E_{ox} of the oxidation potentials. To further corroborate this hypothesis two tricyclic fused thiophenes, dithieno[2,3-b;3′,2′-d]cyclopentadiene **5** and dithieno[2,3-a;3′,2′-c]cyclohexa-1,3-diene **6**, were included in the present investigation. In these compounds, coplanarity is structurally enforced. The position of the two studied parameters in these tricyclic heterocycles should give a good indication of the soundness of our hypothesis. Finally, in order to make sure that the method of preparation has no influence on the values of E_{ox} we synthesized **4c** (where the discrepancy with the Swedish authors occurred) as well as an additional analog 3,3′-diethyl-2,2′-bithienyl **4e** by our method and the method used by the Swedish authors.[2] The result of our experiments will be reported here.

RESULTS AND DISCUSSION

The bithienyls which were needed to study in more detail the effect of substituents in the 3- and/or 3′-positions on the oxidation potential and the position of the long wavelength absorption of their UV spectra were anticipated to be obtainable by the Kumada coupling reactions[6] between a Grignard compound and a thienyl bromide[7] catalyzed by $NiCl_2$ (dppp). However, we were unable to start the reaction between 2-bromo-3-ethylthiophene and magnesium by any of the usual methods. Neither iodine nor 1,2-dibromoethane activation of the metal gave the desired result. Finally, we found that ultrasound irradiation started the Grignard reaction immediately,[8] and the coupling procedure gave high yields of pure product (Scheme 1).

As stated already according to our hypothesis the oxidation potential and the position of λ_{max} should depend to a large degree on the coplanarity of these molecules. The influence of the inductive effect of the alkyl groups on these parameters is less clear than the degree of steric hindrance they impose on the molecule. The measured value for E_{ox} and λ_{max} of compounds **4b–e** as well as **5**

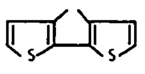


Scheme 1 Synthesis of 3- and 3,3′-Substituted 2,2′ Bithienyls by the $NiCl_2(dppp)$ promoted Coupling Reaction.

and 6 are listed in Table II. The values for E_{ox} and λ_{max} of 2,2′-bithienyl **4a** are reported as reference for this investigation.

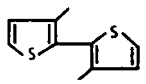
Inspection of these data presented in Table II seem to corroborate our hypothesis.

Alkyl groups, which by virtue of their +I effect should cause a bathochromic shift of the position of λ_{max} do this only if they are not in the 3 position of the bithienyls. Thus, 4,4′-dimethyl-2,2′-bithienyl has a λ_{max} of 312 nm, while the 3,3′-dimethyl isomer exhibits its λ_{max} at 270 nm. An analogous effect was observed with the position of the E_{ox} where values of 1.16 V and 1.58 V were recorded.[1] We hypothesized that the reason for this behavior is steric hindrance and the concomitant partial inhibition of coplanarity. We cannot decide as yet, however, whether the compounds occur in the s-cis or s-trans conformation.



s-cis-conformation

and



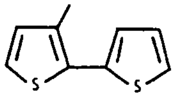
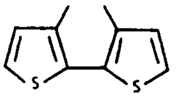
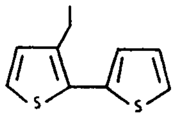
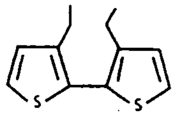
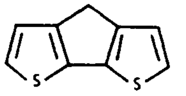
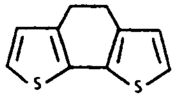
s-trans-conformation

To further test our hypothesis that the positions of λ_{max} and E_{ox} are at least partially dependent on steric hindrance and its impeding of coplanarity, we included compounds **5** and **6** in this research. These two compounds because of the bridge between the 3- and 3′-positions are virtually coplanar. As expected the data show the most rigid compound **5** to have its λ_{max} at the longest wavelength and possesses by far the lowest oxidation potential. The less rigid analog **6** still exhibits its λ_{max} at a rather long wavelength position and as expected, on the basis of our hypothesis, has a somewhat higher E_{ox}. The synthesis of compounds **5** and **6** is outlined in schemes 2 and 3.

Further inspection of the data of Table II reveal that by comparing the methyl substitued compounds **4b** and **4c** the former has a higher λ_{max} and a lower E_{ox} than the 3,3′-dimethyl substituted **4c**. The same trend is observed in the ethyl

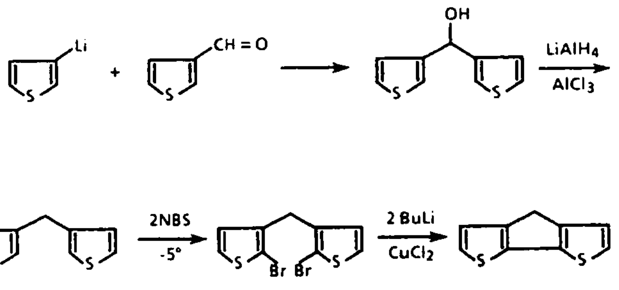
TABLE II

UV Spectra and Oxidation Potential for 2,2'-Bithienyls and 3,3'-Bridged 2,2'-Bithienyls

Compound	λ_{max} (nm)	E_{ox}V vs Ag/AgCl (Monomer)
4a 	302	1.28
4b 	299	1.22[a]
4c 	270 270	1.57[a] 1.51[b]
4d 	295	1.75[a]
4e 	279 279	1.87[a] 1.90[b]
5 	311	0.97
6 	305	1.20

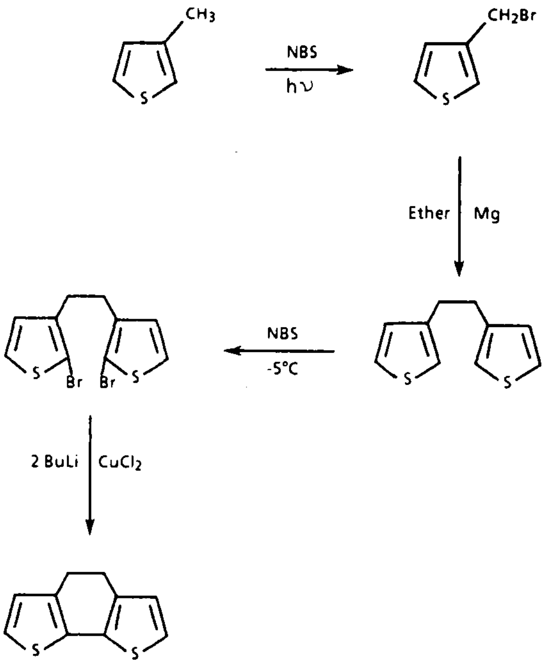
[a] Prepared by $NiCl_2(dppp)$ coupling.

[b] Prepared by $Zn/NiCl_2(PPh_3)_2$ coupling



5

Scheme 2 Synthesis of Dithieno[2,3-b; 3',2'-d]cyclopentadiene 5.



6

Scheme 3 Synthesis of Dithieno[2,3-a;3′,2′-c]cyclohexa-1,3-diene **6**.

substituted species **4d** and **4e**. Again the monosubstituted one has the longer wavelength position for λ_{max} and a lower oxidation potential than the 3,3′-disubstituted analog.

In summary then, one trend seems to exist. Generally, when comparing the ethyl with the corresponding methyl substituted 2,2′-bithienyls, the latter always have the lower oxidation potentials. However, the trend of the position of the λ_{max} is reversed and cannot be satisfactorily explained at this time.

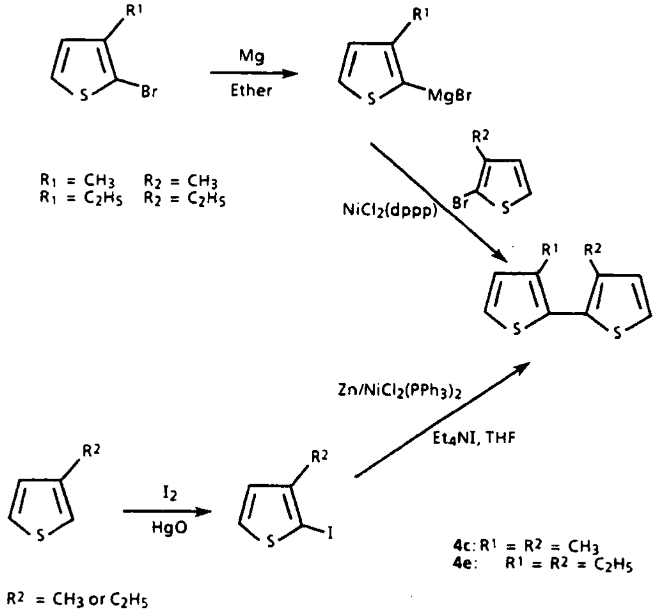
Finally the method of preparation apparantly has no influence on these parameters. The value for E_{ox} of **4c** (measured on three different samples) is 1.5 V as reported earlier by us[1] and not 1.2 V as reported by the Swedish group[2] (Scheme 4).

The cyclic voltammograms for **4c** prepared by cross-coupling reaction of Grignard reagent using $NiCl_2(dppp)$, and that prepared by the reductive dimerization[9] in the presence of $Zn/NiCl_2(PPh_3)_2$, are shown in Figure 1(a) and 1(b), and Table I respectively. It can be concluded from these voltammograms that:

(i) The shape of the cyclic voltammogram in both figures is generally the same, however,

(ii) A difference of 60 mV between the oxidation peak potential values (vs. Ag/AgCl) of compound **4c**, prepared by both methods, was noted. (cf. Table II).

(iii) A second oxidation peak potential appears at around 2.0 V (*vs.* Ag/AgCl),



Scheme 4 Synthesis of 2,2'-Bithienyls **4c** and **4e** by the Zn/$NiCl_2(PPh_3)_2$ Reductive Coupling Method and the $NiCl_2$(dppp) Coupling Reactions.

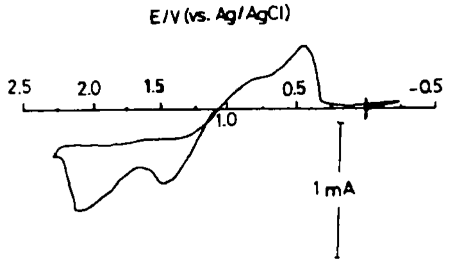


FIGURE 1a Cyclic Voltammogram of **4c**: Synthesized by the $NiCl_2$(dppp) Coupling Method.

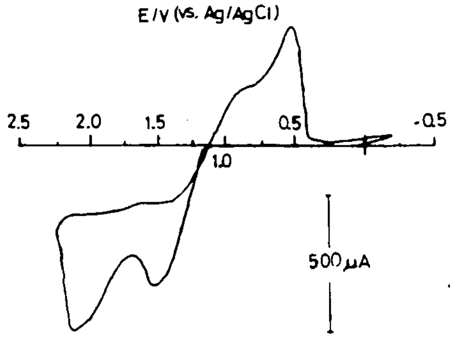


FIGURE 1b Cyclic Voltammogram of **4c**: Synthesized by the Zn/$NiCl_2(PPh_3)_2$ Coupling Method.

which could be attributed to further polymer film formation along with its concurrent oxidation.

(iv) The reduction process, in spite of its complex character, probably could be explained on the basis of two steps, the first being a radical cation reduction, as suggested by the appearance of a cathodic shoulder near 0.75 V (*vs.* Ag/AgCl). The second peak could be attributed to the reduction of the partially oxidized polymer film formed during the anodic cycle; this is evidenced by the appearance of a well defined cathodic peak at 0.5 V (*vs.* Ag/AgCl).

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on an IBM NR-80 spectrometer. Chemical shifts are recorded on the δ scale in parts per million downfield from internal tetramethylsilane (Me_4Si) standard. Elemental analyses were obtained from M. L. W. Laboratories, Phoenix, AZ.

3-Methyl-2,2′-bithienyl **4b.** A solution of 8.85 g (0.05 mole) of 2-bromo-3-methylthiophene, 60 mg of $NiCl_2$ (dppp), and the Grignard reagent derived from 9.78 g (0.06 mole) of 2-bromothiophene in dry ether was refluxed for 2 hr. The reaction mixture was then poured on crushed ice and diluted hydrochloric acid (2N). The organic layer was separated and dried over anhydrous magnesium sulfate. After removal of the solvent, the remaining oil was purified by column chromatography using silica gel and petroleum ether (b.p. 37–59°C) as eluent. Yield 6.5 g (72%), b.p. 2.2 mm Hg 107°C; ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3H, CH_3); 6.82–7.36 (m, aromat, 5H). Anal. Calcd. for $C_9H_8C_2$. Calcd. C, 59.96; H, 4.47. Found C, 59.81; H, 4.36.

3,3′-Dimethyl-2,2′-bithienyl **4c** was obtained analogously to **4b**, yield 86%; b.p. 2.3 mm Hg 112°C (b.p. 11 mm Hg 131°C[10]). ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 6H); 6.90 (d, 2H aromat. J = 5.6 Hz); 7.23 (d, 2H, aromat. J = 5.6 Hz).

2-Bromo-3-ethylthiophene **3c** was obtained by treating under cooling 11 g (0.1 mol) 3-ethylthiophene in a mixture of chloroform (40 ml) and glacial acetic acid (40 ml) with 19 g (0.1 mol) N-bromosuccinimide which was added in small portions over a 4 hr. period. When the mixture reached room temperature 100 ml of water was added, the organic layer was separated, and washed several times with water. The collected water phases were extracted with ether and dried over anhydrous magnesium sulfate. Now the ether was evaporated and the remainder was distilled *in vacuo* using a Vigreux column to yield 15.9 g (78% of theory) of the desired compound; b.p. 6 mm Hg 55°C. ^{1}H NMR ($CDCl_3$) δ 1.18 (t, 3H, -CH_3, J = 8 Hz); 2.58 (q, 2H, -CH_2-; J = 8 Hz); 6.78 (d, 1H, aromat. J = 7 Hz); 7.13 (d, 1H, aromat. J = 7 Hz).

3-Ethyl-2,2′-dithienyl **4d.** To a solution of **3c** in anhydrous ether in the presence of 100 mmNiCl$_2$(dppp) catalyst[11] was added by syringe the Grignard reagent made of 1.21 (0.05 mol) magnesium turnings and 8.15 g 2-bromothiophene (0.05 mol) in 50 ml ether. The mixture was refluxed for two hr. and worked up as usual. The obtained oily residue was distilled *in vacuo* using a Vigreux column; yield 6.93 g (89% of theory) b.p. 50 mm Hg 78°C. ^{1}H NMR ($CDCl_3$) δ 1.22 (t, 3H, CH_3, J = 7 Hz); 2.76 (q, 4H, -CH_2-, J = 7 Hz); 7.15 (m, 5H, aromat.) ^{13}C-NMR ($CDCl_3$) 15.0, 22.4, 123.7, 124.1, 125, 127.1, 127.5, 129.2, 130.2, 136.1, 140.6 UV ($CHCl_3$) λ_{max} 295 nm (ε = 8900) MS 196 (M + 2, 5.70), 195 (M + 1, 7.57), 194 (M, 58.20), 180 (M − CH_3 + 1, 11.52), 179 (M-CH_3, 100). Calcd. C 61.81; H, 5.19. Found: C 61.68; H, 4.95.

3,3′-Diethyl-2,2′-bithienyl **4e.** To a suspension of 0.60 g of magnesium turnings (0.025 mol) in 40 ml of anhydrous diethyl ether was added slowly with stirring a solution of 4.78 g of **3c** (0.025 mol) in 50 ml of anhydrous diethyl ether. The Grignard reaction did not start until the reaction flask was exposed to ultrasonic radiation in a 125-W ultrasonic bath. After 30 min., when the magnesium had completely disappeared, a solution of 4.2 g of **3c** (0.022 mol) in 40 ml of anhydrous diethyl ether was added to the reaction mixture, followed by 150 mg of the NiCl$_2$(dppp) catalyst which caused the reaction mixture to reflux, which was continued overnight. The reaction was terminated by pouring the mixture on crushed ice and HCl (2N). The organic layer was separated and the aqueous layer extracted three times with 35 ml portions of diethyl ether. The combined organic layers were dried over anhydrous magnesium sulfate and the solvent distilled under vacuum. Purification was achieved by chromatography on a silica gel column using hexanes as eluant. The yield was 3.94 g (79% of theory) of a slightly yellow liquid. On a smaller scale (2g), the yield could be improved to 88% of theory. ^{1}H NMR ($CDCl_3$) δ 1.13 (t, 6H, CH_3, J = 7 Hz); 2.52 (q, 4H, -CH_2-, J = 7 Hz); 6.95 (d, 2H, aromat. J = 5 Hz); 7.25 (d, 2H, aromat. J = 5.5 Hz). ^{13}C-NMR ($CDCl_3$) δ 15.1, 22.05, 125.24, 128.0, 128.3, 143.4. UV ($CHCl_3$) λ_{max} 279 nm ($\varepsilon = 5100$). MS 224(M + 2, 8.07), 223(M + 1, 11.83), 222 (M^+, 100), 209 (M-CH_3 + 2, 8.55) 208 (M-CH_3 + 1, 11.90), 207 (M-CH_3, 97.70), 194 (M-C_2H_5 + 1, 8.55), 193 (M-C_2H_5, 56.50). Anal. Calcd for: $C_{12}H_{14}S_2$, Calcd. C, 64.81; H, 6.35. Found: C, 64.61; H, 6.21.

3,3′-Dithienylmethane was obtained in 77% yield by $AlCl_3/LiAlH_4$ reduction of 3,3′-dithienylcarbinol in a yield of 77%; m.p. 30–32°C (m.p. 31.5–32°C[12]). ^{1}H NMR ($CDCl_3$) δ 3.9(s, 2H, CH_2) 7.1(m, 6H, aromat.).

2,2′-Dibromo-*3,3′*-dithienylmethane was obtained from the above compound by NBS bromination in THF; yield 79%, m.p. 41–43°C (m.p. 42°C[12]). ^{1}H NMR ($CDCl_3$) δ 6.6 (d, 2H, aromat.), 7.2 (d, 2H, aromat.), 3.9 (s, 2H, CH_2).

Dithieno[2,3-b;3′,2′-d]cyclopentadiene **5** was obtained by a $CuCl_2$ induced coupling from the above dibromo compound in a yield of 40%; m.p. 75–76°C (m.p. 74–75°C[12]). ^{1}H NMR ($CDCl_3$) δ 3.4 (s, 2H, -CH_2-); 6.9(d, 2H, aromat.) 7.1 (d, 2H, aromat.).

1,2-bis(3-Thienyl)ethane was obtained from 2.03 g (5.82 mmol) 3-bromomethylthiophene by refluxing with an equivalent amount of magnesium shavings and typical Grignard reaction work-up; yield 0.9 g (73%); m.p. 67–69°C (m.p. 64–66°C[13]). ^{1}H NMR ($CDCl_3$) δ 2.92 (s, 4H); 6.8–7.3 (m, 6H).

1,2-bis(2-Bromo-3-dithienyl)ethane was obtained by NBS bromination of the above compound; yield 80%, m.p. 48–50°C (m.p. 50.5°C[13]). ^{1}H NMR ($CDCl_3$) δ 2.85 (s, 4H); 6.7 (d, 2H), 7.2 (d, 2H).

Dithieno[2,3-a; 3′,2′-*c*-]*cyclohexa-1,3-diene* **6**. To a stirred solution of 1.66 g (4.71 mmoles) of 1,2-bis(2-bromo-3-thienyl)ethane in 40 ml of anhydrous ether, 6.3 ml of a 1.5M n-BuLi (9.45 mmole) solution in hexane was added and stirred for 1 hr. The mixture was transferred to an ice cooled solution of 1.2 g (9.5 mmole) of anhydrous $CuCl_2$ in 10 ml absolute ether. The mixture was stirred at 0°C for 2 hr, and allowed to warm to room temperature and stirred overnight. It was then poured into 50 ml 2N HCl and filtered. The ether layer was washed with water, aqueous $NaHCO_3$ and then with water again and dried over anhydrous $MgSO_4$ before the ether was evaporated. The product was purified by column chromatography using basic alumina with hexane as eluent. Evaporation of the solvent left a solid residue, which on recrystallization from methanol yielded 0.41 g (45%); m.p. 83–84°C; ^{1}H NMR ($CDCl_3$) two doublets centered at δ 6.9 (d, 2H), 7.05 (d, 2H), 2.88 (d, 4H). Anal. Calcd. for $C_{10}H_8S_2$: Calcd. C, 62.50; H, 4.16. Found: C, 62.37; H, 4.14.

ELECTROCHEMISTRY

All oxidation potentials, E_{ox} values are reported in reference to an Ag/AgCl electrode and represent the potential at the first oxidation current peak observed on the first oxidation scan. Scan rate was 50 mVs^{-1}. All experiments were conducted in argon deaerated acetonitrile containing 50 mM monomer and 50 mM TBAFB (tetrabutyl ammonium tetrafluoroborate) supporting electrolyte. The reproducibility of E_{ox} values reported in Table II was ±5 mV. A platinum disc working electrode was used and all other experimental details have been previously reported.[1,2]

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