tained **3** and were blue. UV: λ_{max} (CS_2) 690.5, 601 nm; λ_{max} (benzene) 667, 580, sh 318 nm; λ_{max} (benzene + TFA) 526, 407 nm. NMR: 3.843 (q, 2 H, J = 6.2 Hz), 3.42 (t, 4 H, J = 6.2 Hz).

2-Oxa-6,7-ditelluraspiro[3.4]octane (4). To a cooled solution (room temperature) of KTeCN in DMSO (50 mL),[10] which was generated from tellurium (5.1 g, 0.04 mol) and KCN (2.6 g, 0.04 mol) under nitrogen, was added 3,3-bis(chloromethyl)oxetane (3.1 g, 0.05 mol) in DMSO (25 mL). The dark mixture was stirred overnight and then heated to form a brown slurry. The mixture was diluted with water, and the dark solid was filtered. Crystallization from boiling ethanol furnished dark shiny crystals of **4** with a purplish sheen (5.1 g; yield 65%). Alternately, ditelluride **4** can also be extracted via Soxhlet extraction using CS_2 or $CHCl_3$. The yield of **4** varied from 25 to 65% depending on the quality of the bis(chloromethyl)oxetane, the duration of heating, etc. Compound **4**: mp >165 °C dec. UV: λ_{max} (CS_2) 697 (ϵ 308), 602 (279), 580 sh (223), 381 nm (2347). Raman: Te–Te bands at 181, 191 cm^{-1} (overtones at 363, 376 cm^{-1}). MS (^{130}Te): 344 (M^+, 40). NMR: ^1H 4.39 (s, 4 H), 3.65 (2, 4 H); ^{13}C 83.36, 57.6, 18.00; ^{125}Te (uncoupled) 57.07 (J_{Te-H} = 27.5 Hz). Anal. Calcd for $C_5H_8OTe_2$: C, 17.69; H, 2.36; Te, 75.23. Found: C, 17.3; H, 2.4; Te, 74.9.

6,7-Ditelluraspiro[3.4]octane (5). To a cooled solution of KTeCN in DMSO (30 mL) under nitrogen, which was generated from tellurium (1.30 g, 0.01 mol) and KCN (0.69 g, 0.011 mol), was added a solution of 1,1-bis[(tosyloxy)methyl]cyclobutane (**10**; 1.50 g, 0.0035 mol). The mixture was heated overnight at 90–100 °C under nitrogen and then stirred at room temperature for 1 day. The dark suspension was poured into dilute aqueous NaOH solution (100 mL, 1.5%). The precipitate was filtered, washed, dried, and extracted into CH_2Cl_2 using a Soxhlet extractor, until no more blue color was extracted. Concentration of the blue extract followed by addition of cyclohexane yielded ditellurolane derivative **5** (0.21 g; 21% yield) in two crops: mp 98 °C dec. UV: λ_{max} (CS_2) 696 (ϵ 308), 603 nm (270). MS (^{130}Te): *m/e* 342 (M^+, 28), 260 (M^+ − 82, 67). NMR: ^1H 3.46 (s, 4 H), 2.0–1.8 (m, 6 H); ^{13}C 56.42, 34.38, 23.45, 12.84; ^{125}Te (uncoupled) 50.01 (t, J_{Te-H} = 29 Hz). Anal. Calcd for $C_6H_{10}Te_2$: 339.888 943. Found: 339.887 131.

Action of Triflic Acid on 5. A suspension of **5** (40 mg) in CH_2Cl_2 (10 mL) was cautiously treated with a dilute solution of triflic acid in CH_2Cl_2 under sonification until a red precipitate resulted and the supernatant ceased to be blue. The salt was filtered, washed with more CH_2Cl_2 and hexane, and dried. A weighed quantity (0.054 g) of the salt was vibrated with distilled water when it reverted to **5**. This was filtered and washed with more distilled water. The aqueous filtrate containing triflic acid was titrated against standard NaOH solution (0.025 N) using phenolphthalein as the indicator, and it consumed 4.6 mL, leading to a H^+:**5** ratio of 1.045:1.0.

Acknowledgment. We thank the National Science Foundation (Grant CHE-9001714) for support of this work.

Supplementary Material Available: One figure, showing the unit-cell packing in **4**, and three tables, listing final fractional coordinates, bond distances and angles, and anisotropic thermal parameters for **4** (2 pages); a table of observed and calculated structure factors for **4** (8 pages). Ordering information is given on any current masthead page.

A Mechanistic Study of the Electrochemical Oxidation of 2,5-Bis(2-thienyl)pyrroles

Renée E. Niziurski-Mann, Chariclea Scordilis-Kelley, Tea-Lane Liu, Michael P. Cava,* and Richard T. Carlin*,†

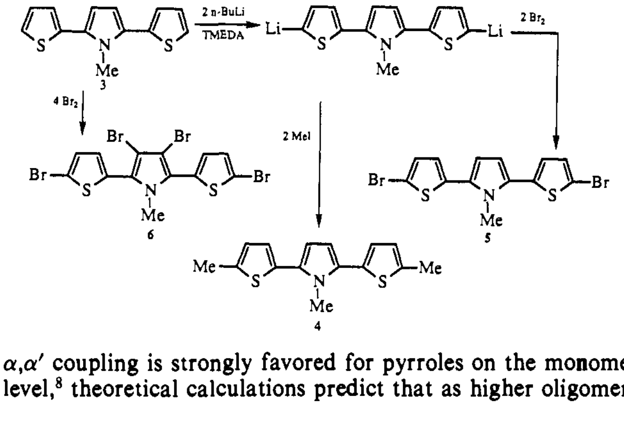
Contribution from the Department of Chemistry, Box 870336, The University of Alabama, Tuscaloosa, Alabama 35487-0336. *Received August 17, 1992*

Abstract: A series of 2,5-bis(2-thienyl)pyrroles has been synthesized in which the α-thiophene protons and/or the β-pyrrole protons have been replaced by Me or Br substituents. A systematic electrochemical investigation of these compounds has yielded rate constants of 36 000 $M^{-1}\ s^{-1}$ for linear coupling of the electrochemically generated cation radicals and 14 000–17 000 $M^{-1}\ s^{-1}$ for branched coupling reactions of the cation radicals. These results constitute the first kinetic evidence for appreciable branched coupling of the electrochemical radical cations of an oligomer precursor of a conducting polymer.

Introduction

The chemistry of organic conducting polymers has been the subject of intensive worldwide investigation in recent years. With the exception of polyaniline, the polythiophenes and polypyrroles have received the most attention.[1] Hybrid polymers containing varying proportions of thiophene and pyrrole units are logical second generation materials of related structure. These have been produced not only by oxidative polymerization of simple mixtures of thiophene and pyrrole[2] but also from 2-(2-thienyl)pyrrole (**1**)[3] as well as the triheterocyclic precursor 2,5-bis(2-thienyl)pyrrole (**2**) and its *N*-alkyl derivatives.[4-6] Our interest has focused on the latter system for several reasons. First, polymers in this series have been reported to have conductivities which vary from 10^{-3} to 280 S/cm, depending on the dopant and the method of preparation. Second, the symmetrical nature of the tricyclic monomer **2** would be expected to lead to polymers of greater linearity and symmetry than that derived from the biheterocycle **1**, in which, as Pelter has noted, "...the order of the units is unknown, as well as the positions of linkage, the degree of branching, and the extent of crosslinking".[7] Such a view seems well justified since, while α,α' coupling is strongly favored for pyrroles on the monomer level,[8] theoretical calculations predict that as higher oligomers

Scheme I



[†] Frank J. Seiler Research Laboratory/NE, USAF Academy, Fort Collins, CO 80840.

(1) Skotheim, T. A., Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986; Vol. 1.

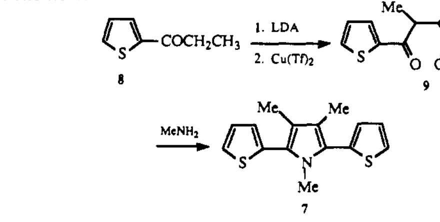
(2) Kawabata, S.; Ito, S.; Yoneyama, H. *J. Electrochem. Soc.* **1988**, *135*, 1691.

(3) Naitoh, S. *Synth. Met.* **1987**, *18*, 237.

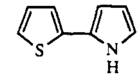
(4) Ferraris, J. P.; Skiles, G. D. *Polymer* **1987**, *28*, 179.

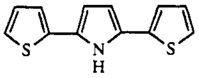
0002-7863/93/1515-887$04.00/0

Scheme II



form the unpaired electron density of a radical intermediate can be almost as high in the β-positions as in the α-positions.[9]


1


2

In the present study, a number of ring-substituted dithienylpyrroles have been synthesized and subjected to a systematic electrochemical investigation with the objective of obtaining kinetic evidence concerning the extent of branched coupling in the course of electrochemical oxidation.

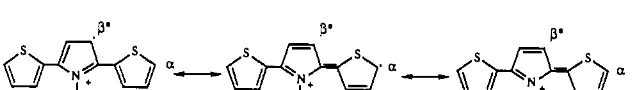
Results and Discussion

Synthesis. The compounds chosen for this study were 2,5-bis(2-thienyl)pyrrole (**2**),[10] its *N*-methyl derivative (**3**),[4] and four substitution products of **3** in which the α-thiophene protons or the β-pyrrole protons were replaced by methyls or bromines (i.e., **4**–**7**). The synthesis of three of these compounds from **3** is outlined in Scheme I.

The fourth substrate **7** was obtained in two steps from the commercially available 1-(2-thienyl)-1-propanone (**8**) by copper triflate coupling[11] of its enolate to dione **9** and reaction of the latter with methylamine as shown in Scheme II.

Electrochemical Polymerization Kinetics. Polymerization of the triheterocyclic precursors is accomplished by electrochemical or chemical oxidation and proceeds by coupling of cation radicals.[1] Electrochemical polymerization is particularly useful because it offers control over the polymerization potential and provides an analytical method for monitoring and evaluating the polymerization process. Most importantly, electroanalytical techniques can provide quantitation of the stability and coupling rates of the cation radicals generated by one-electron oxidation of the triheterocyclic precursors.

The three likely resonance structures for the cation radical of the *N*-alkyl-substituted 2,5-bis(2-thienyl)pyrroles are shown below; the positive charge is localized on the pyrrole unit, and the unpaired radical electron is placed on three different carbon atoms. Radical coupling of these structures will lead to a linear structure (α-α coupling) or to various branched structures (α-β', α-β'', β'-β', β-β'', β''-β'' couplings). The degree of linear versus branched structure will influence the properties of the final polymer.



Because of their selective site substitutions, compounds **2**–**7** offer a unique opportunity to explore the competition between linear and branched coupling processes through an electrochemical evaluation of the cation radical coupling kinetics. Compounds **2** and **3** possess no site substitution, other than *N*-methyl substitution for **3** and so are expected to undergo geometrically unrestrained coupling processes. The methyl and bromo substitutions at the α-positions in **4** and **5**, respectively, are expected to hinder linear (α-α) coupling, leading to predominantly branched β''-β'' coupling. Although β'-β' coupling is possible with **4** and **5**, this is unlikely on the basis of the observation that nucleophilic attack on α-substituted triheterocyclic monomers occurs almost exclusively at the β''-position. In **7**, the methyl substitution at the β''-sites on the pyrrole unit will lead to predominantly linear (α-α) coupling; β'-β' coupling should not occur for the same reasons given above. Finally, the tetrabromo compound **6** is substituted at all α- and β''-sites, thus hindering both α-α and β''-β'' couplings; therefore, the cation radical of **6** is expected to be the most stable. The hexaheterocyclic products expected from α-α and β''-β'' couplings of the cation radicals of **4**, **5**, and **7** are shown prior to proton elimination (vide infra).

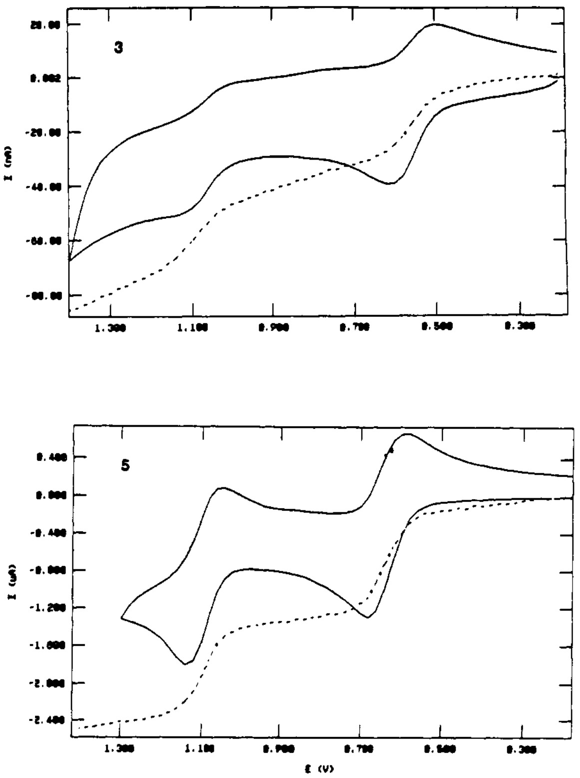
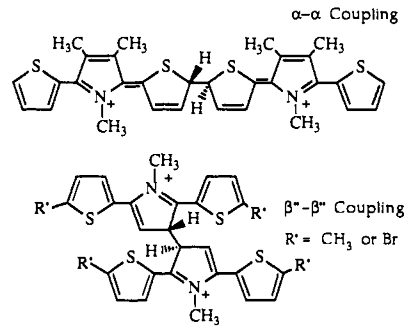


Figure 1. Fast-scan cyclic voltammograms and normal pulse voltammograms for compounds **3** (1 mM, 25-μm Pt electrode, ν = 100 V/s, t_p = 2 ms) and **5** (1.2 mM, 130-μm Pt electrode, ν = 50 V/s, t_p = 2 ms). Potential is versus the Ag^+(0.01 M in CH_3CN)/Ag reference electrode.



Using Pt disk working electrodes having diameters of 1.6 mm, 130 μm, and 25 μm, the homogeneous electrochemical kinetics of **2**–**7** were investigated in acetonitrile (0.1 M NBu_4PF_6) using staircase cyclic voltammetry at scan rates from 10 mV/s to 100 V/s and normal pulse voltammetry at pulse widths from 0.2 to 20 ms. The 1.6-mm Pt electrode was used for scan rates ≤1 V/s, while the microelectrodes were employed for fast-scan cyclic voltammetry (1–100 V/s) and for normal pulse voltammetry.

---

(5) Ferraris, J. P.; Andrus, R. G.; Hrncir, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1318.

(6) Ferraris, J. P.; Hanlon, T. R. *Polymer* **1989**, 1319.

(7) Pelter, A.; Rowlands, M.; Jenkins, I. H. *Tetrahedron Lett.* **1987**, *28*, 5213.

(8) Jackson, A. H. In *Reactivity of the 1H-Pyrrole Ring System, The Chemistry of Heterocyclic Compounds: Pyrroles, Part I*; Jones, R. A., Ed.; John Wiley & Sons: New York, 1990, Vol. 48, pp 295–303.

(9) Waltman, R. J.; Bargon, J. *Tetrahedron* **1984**, *40*, 3963.

(10) Wynberg, H.; Metselaar, J. *Synth. Commun.* **1984**, *14*, 1.

(11) Kobayashi, Y.; Taguchi, T.; Tokuno, E. *Tetrahedron Lett.* **1977**, 3741.

Table I. Half-Wave Potentials, $E_{1/2}$, for Substituted 2,5-Bis(2-thienyl)pyrroles[a]

compd	$E_{1/2}(1)$, V	$E_{1/2}(2)$, V	compd	$E_{1/2}(1)$, V	$E_{1/2}(2)$, V
2	0.303	0.899	**5**	0.463	0.927
3	0.374	0.919	**6**	0.760	1.080
4	0.261	0.706	**7**	0.341	1.015

[a] Measured in acetonitrile with 0.1 M NBu_4PF_6 as the support electrolyte. Potentials are referenced to the ferrocene/ferrocenium couple.

Figures 1 shows voltammograms for **3** and **5** which are also representative of the electrochemical behavior observed for all six compounds investigated. Using fast-scan cyclic voltammetry, two oxidation waves are observed for all compounds. In each case, the ratio of the normal pulse-limiting currents (i_{lim}) for the two oxidations is equal to 1, and the slope of E versus log $[(i_{\mathrm{lim}} - i)/i]$ for the first oxidation is approximately 70 mV (one-electron theoretical value = 59 mV).[12] Therefore, both oxidations for each of the compounds are one-electron transfers. The first oxidation corresponds to formation of the cation radical, while the subsequent oxidation results in generation of the dication. More importantly, at fast scan rates (>10 V/s), scan reversal reveals a well-defined reduction wave associated with the first oxidation wave for all six compounds, indicating an approach to chemical reversibility. As expected for less stable dication species, the second redox process is not as chemically reversible as the first, and so its associated reduction wave is not as obvious. However, the second redox process does approach chemical reversibility at 100 V/s for the α-substituted compounds **4** and **5**.

The half-wave potentials, $E_{1/2}(1)$ and $E_{1/2}(2)$, for the two redox processes determined from the normal pulse oxidation waves are presented in Table I. As observed by Ferraris and co-workers, the first oxidation of the *N*-methyl derivative **3** is found at +60 mV from the first oxidation of **2**.[6] This shift has been attributed to the steric constraints imparted by the *N*-alkyl group which hinder the ability of the triheterocyclic molecule to achieve coplanarity.[6] Aside from this discrepancy, the $E_{1/2}(1)$ values vary according to the electronic properties of the substituents in that methyl groups shift $E_{1/2}(1)$ to less positive values while the bromo groups produce a positive shift in $E_{1/2}(1)$. Although the $E_{1/2}(2)$ values show similar trends, the shifts are not consistent and will not be elaborated upon further here.

A detailed homogeneous kinetic analysis of the first oxidation process was performed using staircase cyclic voltammetry at scan rates, ν, from 10 mV/s to 100 V/s and triheterocyclic concentrations from 0.5 to 10 mM. By reversing the scan direction at ca. 150 mV positive of $E_{1/2}(1)$, the first redox process was isolated and analyzed. At scan rates ≥10 V/s, scan reversal gives a well-defined reduction peak corresponding to reduction of the cation radical back to the neutral compound. The ratio of the cathodic peak to the anodic peak, $i_{\mathrm{pc}}/i_{\mathrm{pa}}$, increases with increasing scan rate as expected for an EC mechanism.[13] At scan rates ≤1 V/s, the reduction peak is absent for all of the compounds except **6** (α- and β''-substituted), which retains a reduction peak down to 50 mV/s. Importantly, at scan rates >1 V/s, the value of $i_{\mathrm{pa}}/\nu^{1/2}$ remains constant, indicating that the first oxidation process remains a one-electron process at these scan rates and so can be analyzed as an EC process.

For the EC analysis, staircase cyclic voltammograms for each compound were obtained at the 0.13-mm Pt electrode at scan rates from 10 to 100 V/s and triheterocyclic concentrations from 0.5 to 10 mM. These data were fit to a simple EC mechanism (reversible electron transfer followed by a first-order irreversible chemical reaction) using the COOL algorithm.[14] Examination of all of the data revealed that the first-order kinetic rate constant obtained from the COOL program systematically increased with scan rate and was also proportional to the concentration of the triheterocyclic compound when comparing data obtained at the same scan rate. These observations are indicative of a second-order process involving coupling of the cation radicals and has been addressed in an earlier study of anthracene.[15] Because the present version of the COOL program does not allow for fitting of voltammograms to an EC mechanism in which the following chemical step is a dimerization, the pseudo-first-order rate constants obtained from the COOL program were converted to second-order rate constants using the equation

Table II. Kinetic Rate Constants for Oxidation of Substituted 2,5-Bis(2-thienyl)pyrroles Proceeding by an ECCE Mechanism

compd	k_1, $M^{-1}\,s^{-1}$	$t_{1/2}$, ms[a]	k_2, s^{-1}	$t_{1/2}$, ms[b]
2	$(7.6 \pm 1.1) \times 10^4$	13	0.46 (±0.05)	1500
3	$(1.2 \pm 0.6) \times 10^5$	8	0.45 (±0.12)	1500
4	$(1.4 \pm 0.5) \times 10^4$	71	1.4 (±0.6)	500
5	$(1.7 \pm 0.6) \times 10^4$	59	2.4 (±0.5)	290
6	$\sim(3 \pm 1) \times 10^2$	3000		
7	$(3.6 \pm 1.2) \times 10^4$	28	0.11 (±0.02)	6300

[a] Half-life of the cation radical calculated for [heterocyclic] = 1 mM using $t_{1/2} = (k_1[\mathrm{heterocyclic}])^{-1}$. [b] Half-life for the protonated radical coupling product calculated using $t_{1/2} = 0.693/k_2$.

$$k_1 = (1/t)\ \ln\ (A_0 k_2 t + 1)$$

where k_1 is the pseudo-first-order rate constant, k_2 is the second-order rate constant, A_0 is the concentration of the analyte, and t is the time from $E_{1/2}(1)$ to the switching potential (i.e., the characteristic time of the cyclic voltammogram).[15] These second-order rate constants are given as k_1 in Table II and correspond to the cation radical coupling rates associated with the first oxidation at $E_{1/2}(1)$.

The k_1 results lead to a quantitation of the cation radical coupling rates for various heterocyclic sites if it is assumed that (1) methyl and bromo substituents block, or significantly slow, the coupling process at the substitution sites and (2) the electronic difference between methyl and bromo groups does not significantly alter the coupling rate as borne out by the near equivalency of coupling rates for **4** and **5**. With these two assumptions, the first observation made from the k_1 results is that the tetrabromo compound **6** displays the slowest coupling rate (300 $M^{-1}\,s^{-1}$), thus confirming the statement above that β'-β' coupling is negligible in these systems. Compound **6**, may undergo slow, hindered α-α coupling with subsequent elimination of Br^+. Next, the cation radical coupling rates for **4** and **5** are nearly identical, and so the β''-β'' coupling rate is taken as 14 000–17 000 $M^{-1}\,s^{-1}$. Finally, analysis of data for **7** yields a k_1 value of 36 000 $M^{-1}\,s^{-1}$ for the linear (α-α) cation radical coupling process.

Importantly, although the linear coupling rate is twice the branched coupling rate, both processes will significantly influence the product distribution obtained from the cation radical coupling of unsubstituted compounds. Therefore, the coupling rates for **2** and **3** should be the sum of the coupling rates for the individual pathways since they possess no site-hindering substitutions. By summing $\{k_1(\alpha\text{-}\alpha) + k_1(\beta''\text{-}\beta'') + [2k_1(\alpha\text{-}\beta'')]\}$, where $k_1(\alpha\text{-}\beta'')$ is taken to be $[k_1(\alpha\text{-}\alpha) + k_1(\beta''\text{-}\beta'')]/2$ and is twice as likely to occur as α-α or β''-β'' alone, a k_1 value of 100 000 $M^{-1}\,s^{-1}$ is obtained, in good agreement with the values of 76 000 and 120 000 $M^{-1}\,s^{-1}$ found for **2** and **3**, respectively. It is worth noting that the coupling rates for the triheterocyclic compounds are considerably slower than the values of 2.2×10^5 to 1.8×10^6 $M^{-1}\,s^{-1}$ measured by Savéant and co-workers for monoheterocyclic derivatives of pyrrole using fast double potential step chronoamperometry.[16] In the substituted-pyrrole investigation, only α-α coupling was assumed to occur.[16] The slower coupling rates observed in the extended aromatic systems may be explained by the greater electronic delocalization in the triheterocyclic compounds versus the monoheterocyclic, which relieves some of the

---

(12) Parry, E. P.; Osteryoung, R. A. *Anal. Chem.* **1965**, *37*, 1654.

(13) Bard, A. J.; Faulkner, L. *Electrochemical Methods*; Wiley: New York, 1980.

(14) O'Dea, J. J.; Osteryoung, J.; Lane, T. P. *J. Phys. Chem.* **1986**, *90*, 2761.

(15) Carlin, R. T.; Trulove, P. C.; Osteryoung, R. A. *Electrochim. Acta*, in press.

(16) Andrieux, C. P.; Audebert, P.; Hapiot, P.; Savéant, J.-M. *J. Phys. Chem.* **1991**, *95*, 10158.

reorganizational energy encountered during the coupling step.[16]

Although the k_1 values lend valuable insight into the coupling processes leading to polymer formation, they do not provide a complete picture, because for continued polymer growth, it is necessary for each coupled dication, represented as $(SNS)_2^{2+}$, to eliminate two protons and repeat the oxidative coupling process.[1] Because this second chemical step is much slower than the cation radical coupling step for all of the compounds except **6**, the rate constant for this following first-order process, k_2, can be evaluated using staircase cyclic voltammetry performed at slower scan rates. Examination of slow-scan voltammograms at the 1.6-mm Pt electrode revealed that the value of $i_{pa}/\nu^{1/2}$ increases as the scan rate is decreased below 1 V/s, indicating that the first oxidation process behaves as an ECE process when a longer experimental time frame is employed. The complete electrochemical mechanism is actually ECCE and is represented for **2–5** and **7** by the reaction sequence

$$\mathrm{SNS} \xrightarrow{-1e} \mathrm{SNS}^{\bullet+}$$

$$\mathrm{SNS}^{+} \xrightarrow{k_1\,(\mathrm{fast})} \tfrac{1}{2}(\mathrm{SNS})_2^{2+}$$

$$(\mathrm{SNS})_2^{2+} \xrightarrow{k_2\,(\mathrm{slow})} (\mathrm{SNS(2H)})_2 + 2\mathrm{H}^+$$

$$(\mathrm{SNS(2H)})_2 \xrightarrow{-2e} (\mathrm{SNS(2H)})_2^{2+}$$

For **6**, the coupling and elimination steps occur at similar rates, and Br^+ may be eliminated instead of H^+. The second electron transfer is expected to involve two electrons per hexaheterocyclic molecule (one electron per SNS unit) since this will regenerate a positive charge on both pyrrole nitrogens.

The slow-scan data was analyzed using the method of Nicholson and Shain by assigning i_{pa} at 1 V/s to the diffusion-controlled peak current, i_d, in the absence of kinetics, dividing all of the slow-scan anodic peak currents (10 mV/s to 1 V/s) by $\nu^{1/2}$ to obtain the normalized peak currents, i_k, in the presence of ECE kinetics, and finally applying the equation $i_k/i_d = (0.4 + k_2/a)/(0.396 + 0.469k_2/a)$, where $a = nF\nu/RT$.[17,18] The k_2 values obtained in this manner are summarized in Table II. The half-lives for each cation radical and its corresponding coupled dication, $(SNS)_2^{2+}$, are also listed to emphasize the large difference in stability of these two species, which is a prerequisite for deconvoluting the k_1 and k_2 kinetic steps. In the case of **6**, only k_1 is reported because the overlap of the two kinetic steps is too great to allow proper evaluation of k_2. Although k_1 values determine the site of the first cation radical coupling process, it is important to note that both k_1 and k_2 must be used in any calculation which aims to predict the degree of linear and branched structural units found in the completed polymer.

One might expect k_2 to correlate with the acidity of the protonated coupling product which will be, in part, a function of (1) the steric constraints at the coupling ring site (i.e., greater strain will promote proton loss) and (2) the electron-withdrawing properties of the ring substituents. From factor 1, coupling at β'' (as well as β and β') is expected to be more strained than coupling at the α-position; therefore, $k_2(\mathbf{4}) > k_2(\mathbf{7})$. From factor 2, bromo substituents will enhance acidity, while methyl groups will reduce the acidity; therefore, $k_2(\mathbf{5}) > k_2(\mathbf{4})$. The k_2 value for **2** and **3** will be an average value between $k_2(\mathbf{4})$ and $k_2(\mathbf{7})$ because it is an average of proton loss rates from a mixture of α and β'' coupling sites. The k_2 value for **6**, which was not determined, is expected to be slow since it may involve loss of Br^+ instead of H^+ if the coupling occurs at a brominated site. Therefore, the ordering is expected to be $k_2(\mathbf{5}) > k_2(\mathbf{4}) > k_2(\mathbf{2}) \approx k_2(\mathbf{3}) > k_2(\mathbf{7}) > k_2(\mathbf{6})$, and this ordering is observed.

Conclusions

The results provide the first direct evidence for the importance of branched coupling in the electropolymerization of heterocyclic precursors to conducting polymers. In addition, these studies have shown that for the triheterocyclic precursors (1) fast-scan voltammetry allows observation of the cation radical and the two-electron-oxidized dication; (2) the oxidation potential can be altered by changing the electronic properties of the ring substituents; (3) both linear and branched cation radical coupling reactions can occur at significant rates during their polymerization; and (4) the complete electrochemical mechanism for the first oxidation process is ECCE.

Experimental Section

Syntheses. Infrared spectra were recorded on a Perkin-Elmer 781 spectrophotometer as Nujol mulls. NMR spectra were determined on a Nicolet 200 or a Bruker 260 spectrometer in $CDCl_3$. Mass spectra were obtained on a VG Auto Spec.

***N*-Methyl-2,5-bis(5-bromo-2-thienyl)pyrrole (5).** To a cold (0 °C) solution of *N*-methyl-2,5-bis(2-thienyl)pyrrole (**3**) (0.25 g, 1.02 mmol) and TMEDA (0.30 g, 2.55 mmol) in dry THF (8 mL) under nitrogen atmosphere was added *n*-butyllithium (1.02 mL of a 2.5 M solution in hexanes, 2.55 mol). After being stirred at 0 °C for 45 min, the reaction mixture was further cooled to −78 °C before bromine (0.13 mL, 2.55 mmol) was added via syringe. The mixture was stirred at −78 °C for 30 min and warmed slightly, and a solution of saturated aqueous sodium bisulfite was added. The mixture was extracted with diethyl ether (2 × 15 mL), and the combined extracts were washed with saturated aqueous $NaHCO_3$ and water and dried (Na_2SO_4). Removal of the solvent under reduced pressure afforded a red solid (0.44 g). Recrystallization from CH_2Cl_2/hexanes gave *N*-methyl-2,5-bis(5-bromo-2-thienyl)pyrrole (**5**) (0.20 g, 48.8%) as white needles: mp 109–110 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 3.68 (s, 3 H), 6.30 (s, 2 H), 6.81 (d, 2 H, J = 4.0 Hz), 7.04 (d, 2 H, J = 4.0 Hz); IR (Nujol) 1413, 1035, 924, 790 cm^{-1}; UV–vis ($CHCl_3$) 332.2, 242.2 nm; MS (EI) *m/e* (relative intensity) 405 (M + 2, 88.7), 404 (M + 1, 56.5), 403 (M^+, 100), 401 (83.8), 388 (32.1), 324 (28.0), 280 (59.6), 278 (56.6), 267 (39.2), 243 (23.0), 201 (44.5), 186 (24.8), 154 (31.5), 142 (33.9), 121 (30.6); exact mass calcd for $C_{13}H_9Br_2NS_2$ (M^+) 400.8543, found 400.8550.

***N*-Methyl-2,5-bis(5-methyl-2-thienyl)pyrrole (4).** To a cold (0 °C) solution of *N*-methyl-2,5-bis(2-thienyl)pyrrole (**3**) (0.25 g, 1.20 mmol) and TMEDA (0.30 g, 2.55 mmol) in dry THF (5 mL) was added *n*-butyllithium (1.02 mL of a 2.5 M solution in hexanes, 2.55 mmol). After stirring at 0 °C for 2 h, the reaction mixture was cooled to −50 °C and methyl iodide (0.50 mL, 8.03 mmol) was added. The cooling bath was removed and stirring continued at room temperature for 1 h before the mixture was poured into water (25 mL) and extracted with ether (3 × 20 mL). The solvent was removed under reduced pressure, and the residue was redissolved in CH_2Cl_2 (30 mL), washed with 10% HCl (15 mL), water (15 mL), and brine (15 mL), and dried (Na_2SO_4). After concentration in vacuo, the residue was purified by column chromatography on silica (hexanes) and crystallized from benzene/hexanes to give *N*-methyl-2,5-bis(5-methyl-2-thienyl)pyrrole (**4**) (0.24 g, 86%) as white crystals, which were again crystallized from CH_2Cl_2/hexanes: mp 83–84.5 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 2.50 (s, 6 H), 3.70 (s, 3 H), 6.27 (s, 2 H), 6.72 (dd, 2 H, J = 1.08, 3.4 Hz), 6.84 (d, 2 H, J = 3.4 Hz); ^{13}C NMR (360 MHz, $CDCl_3$) δ 15.25, 33.46, 109.52, 125.48, 125.51, 129.24, 132.71, 139.54; UV–vis ($CHCl_3$) 327.2, 242.8 nm; MS (EI) *m/e* (relative intensity) 275 (M + 2, 11.1), 274 (M + 1, 19.9), 273 (M^+, 100), 259 (4.0), 258 (19.3), 136 (9.0), 128 (3.7). Anal. Calcd for $C_{15}H_{15}NS_2$: C, 65.88; H, 5.54; N, 5.12. Found: C, 65.80; H, 5.56; N, 5.14.

Tetrabromination of 3 to Tetrabromide 6. To a well-stirred cold (0 °C) solution of *N*-methyl-2,5-bis(2-thienyl)pyrrole (**3**) (0.050 g, 0.204 mmol) in CCl_4 (3 mL) was added bromine (0.04 mL, 0.816 mmol). The reaction mixture was stirred overnight. NMR spectra were taken 15 min and 14 h after the start of the reaction, producing nearly identical data. Evolution of HBr gas was noted throughout the reaction period. The reaction mixture was washed with saturated $NaHCO_3$ and dried (Na_2SO_4). Removal of the solvent in vacuo afforded a yellow-green solid (0.083 g, 75.5%). Column chromatography of the products on silica (5:1 hexanes/CH_2Cl_2) gave a poorly separated mixture. The first fraction gave *N*-methyl-2,5-bis(5-bromo-2-thienyl)-3,4-dibromopyrrole (**6**) (62.5 mg, 56.8%) as white crystals from CH_2Cl_2/hexanes: mp 130–132 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 3.51 (s, 3 H), 6.92 (d, 2 H, J = 3.8 Hz), 7.11 (d, 2 H, J = 3.8 Hz); UV–vis ($CHCl_3$) 311.8, 242.4 nm; MS (EI) *m/e* (relative intensity) 564 (M + 4, 21.6), 562 (M + 2, 77.1), 560 (M^+, 100), 558 (64.1), 556 (14.5), 545 (13.2), 483 (23.7), 481 (19.9), 273 (37.1), 144 (5.3). Anal. Calcd for $C_{13}H_7Br_4NS_2$: C, 27.83; H, 1.26; Br, 56.98. Found: C, 27.88; H, 1.26; Br, 56.91.

1,4-Bis(2-thienyl)-2,3-dimethyl-1,4-butanedione (9). To a cold (0 °C) solution of diisopropylamine (0.87 g, 8.56 mmol) in dry THF (40 mL)

---

(17) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1965**, *37*, 178.

(18) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1965**, *37*, 190.

under a nitrogen atmosphere was added *n*-butyllithium (3.42 mL of a 2.5 M solution in hexanes, 8.56 mmol). After the mixture was stirred for 15 min at 0 °C, 1-(2-thienyl)-1-propanone (**8**)[19] (1.00 g, 7.13 mmol) was added via syringe. The mixture was cooled further to −50 °C after 30 min of stirring at 0 °C, and a solution of copper triflate (2.85 g, 7.85 mmol) in dry isobutyronitrile (10 mL) was added. After 30 min at −50 °C, the mixture was stirred for 1 h at room temperature and then poured into water (50 mL). An insoluble precipitate was filtered under vacuum before the aqueous layer was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic extract was washed with water (2 × 30 mL) and brine (30 mL), dried (Na_2SO_4), and concentrated in vacuo to obtain a red-brown liquid (1.27 g). Column chromatography on silica (8:1 hexanes/ethyl acetate and 6:1 hexanes/ethyl acetate) afforded 1,4-bis(2-thienyl)-2,3-dimethyl-1,4-butanedione (**9**) (0.36 g, 36.4%) as white crystals recrystallized from CH_2Cl_2/hexanes: mp 113.5–115.5 °C; H NMR (200 MHz, $CDCl_3$) (major isomer) δ 1.35 (dd, 6 H, *J* = 2.1, 4.7 Hz), 3.77 (m, 2 H), 7.14 (m, 2 H), 7.62 (dd, 2 H, *J* = 1.0, 5.0 Hz), 7.81 (dd, 2 H, *J* = 1.2, 3.8 Hz), (minor isomer) δ 1.19 (dd, 6 H, *J* = 2.0, 4.5 Hz), 3.77 (m, 2 H), 7.18 (m, 2 H), 7.70 (dd, 2 H, *J* = 1.1, 5.0 Hz), 7.87 (dd, 2 H, *J* = 1.2, 3.8 Hz); IR (Nujol) 3100, 1650, 1520, 1420, 1240, 1220, 1060, 855, 745, 730 cm^{-1}; MS (EI) *m/e* (relative intensity) 279 (M + 1, 1.3), 278 (M^+, 7.0), 167 (16.0), 153 (13.3), 140 (13.8), 126 (8.2), 111 (100). Anal. Calcd for $C_{14}H_{14}O_2S_2$: C, 60.40; H, 5.08. Found: C, 59.76; H, 5.07.

***N*-Methyl-2,5-bis(2-thienyl)-3,4-dimethylpyrrole (7).** A solution of 1,4-bis(2-thienyl)-2,3-dimethyl-1,4-butanedione (**9**) (1.21 g, 4.35 mmol), methylamine (0.68 g of a 40% aqueous solution, 8.75 mmol), and glacial acetic acid (0.50 mL, 8.73 mmol) in benzene (12 mL) was refluxed under nitrogen atmosphere in a round-bottom flask equipped with a Dean–Stark trap. After 24 h, additional methylamine (0.50 mL, 5.81 mmol) was added to the reaction, and the mixture was refluxed for a total of 43 h before it was poured into water (20 mL). The volatile constituents were removed under reduced pressure and the aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic extract was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography on silica (hexanes) and recrystallized from EtOAc/hexane to afford *N*-methyl-2,5-bis(2-thienyl)-3,4-dimethylpyrrole (**7**) (0.93 g, 78.2%) as white needles: mp 100–101.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.07 (s, 6 H), 3.46 (s, 3 H), 7.01 (dd, 2 H, *J* = 1.1, 3.5 Hz), 7.13 (dd, 2 H, *J* = 3.5, 5.2 Hz), 7.39 (dd, 2 H, *J* = 1.1, 5.2 Hz); UV–vis ($CHCl_3$) 314.6, 242.6 nm; MS (EI) *m/e* (relative intensity) 275 (M + 2, 59.0), 274 (M + 1, 79.8), 273 (M^+, 200), 272 (90.8), 259 (36.4), 258 (72.2), 147 (25.1), 137 (33.4), 109 (29.7). Anal. Calcd for $C_{15}H_{15}NS_2$: C, 65.89; H, 5.54. Found: C, 65.84; H, 5.54.

Electrochemical Studies. An EG&G PARC Model 273 potentiostat/galvanostat controlled with a PC computer using the Model 270 or 271 software packages was employed for all studies. The COOL program analysis was performed on a PC computer running at 33 MHz. An Ag^+ (0.01 M in CH_3CN)/Ag reference electrode and a Pt wire counter electrode were employed during data collection; however, all potentials are reported relative to the ferrocene/ferrocenium couple measured in CH_3CN (0.1 M NBu_4PF_6). The ferrocene/ferrocenium couple was measured at appropriate intervals to give an accurate reference potential conversion. The 1.6-mm Pt working electrode was purchased from Bioanalytical Systems. The 130-μm and 25-μm Pt microelectrodes were constructed by sealing wire (Alfa) of the appropriate diameter in glass; the Pt microdisks were exposed and polished using SiC paper and 1-, 0.5-, and 0.03-μm Al_2O_3 polishing suspensions from Buehler. Acetonitrile was distilled from CaH_2 under nitrogen immediately before use. The NBu_4PF_6 supporting electrolyte was obtained from Bioanalytical Systems and used as received. All experiments were performed under a dry nitrogen atmosphere.

Acknowledgment. We wish to thank EG&G for providing us with a beta version of the COOL program and J. G. Osteryoung, R. A. Osteryoung, and J. J. O'Dea for providing us with an earlier version of the COOL program. We also thank the National Science Foundation for a grant (CHE 9001714) in support of this work.

---

[19] Kooreman, H. J.; Wynberg, H. *Recl. Trav. Chim.* **1967**, *86*, 37.

Enantiospecific Synthesis by Transformations of Chiral Pool-Derived Metal π-Complexes. A Strategy for the Introduction of Substituents on a Pyranose-Derived Lateral π-Ligand either Syn or Anti to the Coordinating Metal

Almudena Rubio and Lanny S. Liebeskind*

Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322.

Received August 10, 1992

Abstract: In order to extend the use of stoichiometric transition metal π-complexes to the stereocontrolled synthesis of organic target structures bearing substituents either cis or trans to each other on a cyclic unsaturated π-ligand, new strategies for the functionalization of π-complexes are required. A first-generation approach to the stereocontrolled introduction of substituents syn or anti relative to an η^5-CpMo(CO)$_2$ unit coordinated to a lateral π-ligand is reported. The pyranone ring was chosen as the first template upon which the strategy for stereocontrolled introduction of substituents would be studied. The stereocontrol of the process relies on (1) the ability of the CpMo(CO)$_2$ unit to direct all nucleophilic attack away from itself, (2) the observation that cationic diene complexes, CpMo(CO)$_2$(η^4-diene)$^+$, can be generated from (η^3-allyl)molybdenum species bearing an adjacent alkoxy substituent syn to the molybdenum by treatment with $Ph_3C^+PF_6^-$, and (3) the precedented introduction of nucleophiles adjacent to the oxygen atom in CpMo(CO)$_2$(2*H*-pyran) cations. Using these stereocontrol features, the pyranone carbonyl group was replaced by two different substituents, R^1 and R^2. By changing the order of substituent introduction, the stereochemistry of the substituents R^1 and R^2 relative to the molybdenum unit can be influenced. This can be translated into a method for controlling the introduction of multiple substituents either cis or trans to each other on a cyclic π-template.

Introduction

In recent years, stoichiometric metal π-complexes of various unsaturated ligands have been used to significant advantage in the stereocontrolled construction of substituted cyclic and acyclic hydrocarbons[1-29] and heterocycles.[30-38] With few exceptions,[1,22,39-45] the dominant mode of functionalization is addition of a nucleophilic reactant to an electrophilic metal π-complex.

---

[1] Pearson, A. J.; Mallik, S.; Pinkerton, A. A.; Adams, J. P.; Zheng, S. *J. Org. Chem.* **1992**, *57*, 2910.

0002-7863/93/1515-891$04.00/0 © 1993 American Chemical Society