JOC Article

Dinitro and Quinodimethane Derivatives of Terthiophene That Can Be Both Oxidized and Reduced. Crystal Structures, Spectra, and a Method for Analyzing Quinoid Contributions to Structure[§]

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Two new oligothiophenes, the dinitro compound 3′,4′-dibutyl-5,5″-dinitro-2,2′:5′,2″-terthiophene (**1**) and the quinodimethane 3′,4′-dibutyl-5,5″-bis(dicyanomethylene)-5,5″-dihydro-2,2′:5′,2″-terthiophene (**2**), have been synthesized and studied with electrochemistry, UV−vis−NIR−IR spectroscopy, ESR, and X-ray crystallography. These compounds, designed to be both electron and hole carriers, show redox properties that are unusual for oligothiophenes. Cyclic voltammetry and spectroelectrochemistry demonstrated that each compound could be oxidized to a cation radical and reduced to an anion radical and dianion. The spectra of **2** and its three redox partners were analyzed in terms of a limiting structure in which the neutral **2** has orbitals corresponding to those of a substituted-terthiophene dication. Compound **1** crystallizes with the thiophene rings held in an unusual nonplanar, cisoid configuration in face-to-face π-stacks, with a spacing between molecules of 3.65 Å. The C−C bond lengths of the outer nitro-substituted rings have quinoid character. Compound **2** crystallizes with the thiophene rings in a planar, transoid configuration. The molecules are held in π-stacks formed from π-dimers with a spacing between molecules of 3.47 and 3.63 Å. The C−C bond distances of the thiophene rings of **1** and **2** and other oligomers were analyzed by a principal component analysis. The analysis found that 93% of the structural variance resided in one principal component related to the quinoid structure of the oligothiophene moiety. The analysis reliably demonstrated a quinoid contribution to the structure of **1**. This method should be applicable to understanding the structure of other conjugated molecules in which quinoid structures contribute.

Introduction

Oligothiophenes continue to present interesting fundamental and applied research opportunities.[1−12] As part of a program directed toward material applications,[13−15] we have prepared several new terthiophenes with electron-withdrawing groups on the terminal positions. The goal was to make crystalline compounds that would be both easily oxidized and reduced. Such compounds could then be tested as materials that could conduct both holes and electrons. Of interest here are the dinitro compound 3′,4′-

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[§] Dedicated to the memory of Baruch Zinger.

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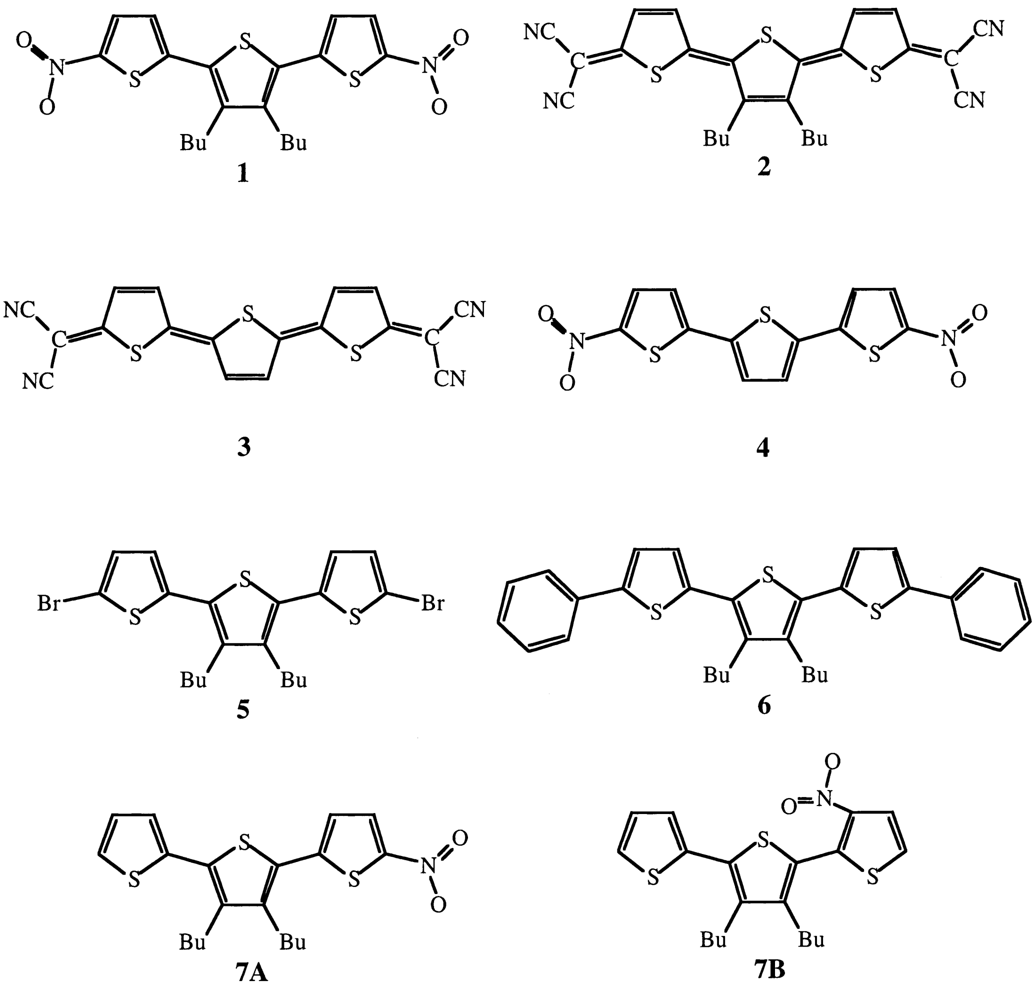
SCHEME 1. Structures and Abbreviations



dibutyl-5,5″-dinitro-2,2′:5′,2″-terthiophene (**1**) and the dicyanoquinodimethane 3′,4′-dibutyl-5,5″-bis(dicyanomethylene)-5,5″-dihydro-2,2′:5′,2″-terthiophene (**2**) (please see Scheme 1 for compound structures and abbreviations). Cyclic voltammetry demonstrated that, indeed, **1** and **2** could be both oxidized and reduced. Spectroscopically characterized cation radicals, anion radicals, and dianions were formed. Compounds **1** and **2** could also be crystallized, and single-crystal X-ray diffraction showed that the molecules were arranged in cofacial π-stacks instead of the herringbone stacks found for most other oligothiophenes. We applied principal component analysis (PCA) as a new method for analyzing the bond lengths in these structures. PCA provided the quinoid contributions to the structures in these conjugated molecules and allowed an understanding of the complex spectroscopy of **2** and its redox partners.The redox behavior and the solid-state structures prompted us to use these compounds for the active layer in field effect transistors (FETs). As reported elsewhere,[16] the use of **2** led to a device that performed as an n-type transistor with electron mobilities as high as 0.005 cm^2/Vs. The device results give significance to the study reported here in which we thoroughly examined the structure, spectroscopy, and electrochemistry of the two compounds. There is much knowledge of the structure, spectroscopy, and electrochemistry of oligothiophenes, and quinoid forms are often invoked as structural models for oligothiophene cation radicals and dications.[1,3a,6a,17] There is, however, little information available concerning neutral quinoid forms of oligothiophenes. Two examples of bis(dicyano-

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methylene) oligothiophenes, terthiophene **3** (**2** without the butyls) and a quaterthiophene analogue, have been prepared.[18−21] Oxidative, but not reductive, cyclic voltammetry was reported for **3**. Similarly, unbutylated dinitroterthiophene (**4**) has been prepared and oxidized,[22] but its electrochemistry is substantially different from that of the butylated **1**. Neither crystal structures of the neutral compounds nor spectroscopic studies of redoxed species have been reported for any analogue of **1** or **2**. Compound **2** provides the first example of a crystallographically determined structure for a quinoidal oligothiophene.[23]

Experimental Section

General Considerations. Synthetic procedures were carried out under an inert atmosphere of argon, and oven-dried glassware was used for the synthesis of **2**. 1,2-Dimethoxyethane was distilled from Na/benzophenone under a nitrogen atmosphere. 3′,4′-Dibutyl-2,2′:5′,2″-terthiophene was synthesized in a manner similar to a previously reported procedure.[24] $Pd(PPh_3)_4$ and malononitrile were purchased and used as received. ^1H NMR were recorded on a Varian VXR-300 MHz instrument. The chemical shifts are reported in ppm and referenced to the residual chloroform peak (7.26 ppm). Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer. Elemental analysis were performed by Quantitative Technologies, Inc., Whitehouse, NJ. The UV−vis−NIR spectra (230−2000 nm) were recorded with a computer-controlled Cary 17 spectrometer. Electrochemical experiments were performed with a BAS 100B electrochemical analyzer using methods previously described.[4b] Potentials are reported vs aqueous Ag/AgCl and are not corrected for the junction potential. The $E^{o\prime}$ values for the ferrocenium/ferrocene couple for concentrations similar to those used in this study were +0.46 for dichloromethane solutions at a glassy carbon electrode. Spectroelectrochemical studies were performed in a specular reflectance cell. Spectra in the UV−vis region (300−850 nm) were obtained with an Ocean Optics spectrometer equipped with a silicon detector. Spectra in the IR region (900−7000 cm^{-1}) were obtained with a Nicolet 550 IR spectrometer equipped with a MCD detector. Electrolyses were controlled by a BAS-100 bulk electrolysis program. EPR spectra were obtained on an X-band IBM-Bruker ESP-300 spectrometer.

3′,4′-Dibutyl-5-nitro-2,2′:5′,2″-terthiophene (7A) and 3′,4′-Dibutyl-3-nitro-2,2′:5′,2″-terthiophene (7B). To a 50 mL round-bottom flask were added 0.578 g (1.60 mmol) of 3′,4′-Dibutyl-2,2′:5′,2″-terthiophene and 16 mL of a 1:1 acetic acid: dichloromethane mixture. The system was purged with argon and cooled to 0 °C while stirring. A 3.68 M solution of nitric acid was prepared in acetic acid. An aliquot of this solution (0.46 mL, 1.7 mmol) was added dropwise over 40 min to the reaction flask. The reaction was allowed to warm to room temperature overnight, at which time 10 mL of water was added. The organic layers were separated, washed with water and a $NaHCO_3$ solution, and finally dried with $MgSO_4$. The crude oil was purified by silica gel flash chromatography (25% dichloromethane in hexanes) to provide 0.40 g (62%) of a 70:30 mixture of the 5- and 3-nitro isomers respectively based on integration of the NMR data. 3′,4′-Dibutyl-5-nitro-2,2′:5′,2″-terthiophene (**7A**): ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, 1H, $J_{4,3} = 4.5$ Hz), 7.37 (dd, 1H, $J_{5'',4''} = 5.2$ Hz, $J_{5'',3''} = 1.2$ Hz), 7.18 (dd, 1H, $J_{3'',4''} = 3.6$ Hz, $J_{3'',5''} = 1.2$ Hz), 7.09 (dd, 1H, $J_{4'',5''} = 5.2$ Hz, $J_{4'',3''} = 3.6$ Hz), 7.07 (d, 1H, $J_{3,4} = 4.5$ Hz), 2.74 (m, 4H), 1.50 (m, 8H), 0.96 (m, 6H). 3′,4′-Dibutyl-3-nitro-2,2′:5′,2″-terthiophene (**7B**): ^1H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, 1H, $J_{5,4} = 5.7$ Hz), 7.35 (d, 1H, $J_{4,5} = 5.4$ Hz), 7.34 (dd, 1H, $J_{5'',4''} = 5.3$ Hz, $J_{5'',3''} = 1.2$ Hz), 7.15 (dd, 1H, $J_{3'',4''} = 3.6$ Hz, $J_{3'',5''} = 1.2$ Hz), 7.08 (dd, 1H, $J_{4'',5''} = 5.1$ Hz, $J_{4'',3''} = 3.6$ Hz), 2.48 (m, 4H), 1.25 (m, 8H), 0.81 (m, 6H); HREIMS calcd 405.0891, found 405.0911 (M^+).

3′,4′-Dibutyl-5,5″-dinitro-2,2′:5′,2″-terthiophene (4). Further elution of the column from the above procedure using 40−50% dichloromethane in hexanes yielded 0.14 g (19%) of **4** as a bright orange solid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, 2 H, $J_{4,3} = 4.5$ Hz), 7.11 (d, 2H, $J_{3,4} = 4.5$ Hz), 2.77 (t, 4H), 1.52 (m, 8H), 0.99 (t, 6H); HREIMS calcd 450.0742, found 450.0727 (M^+). Anal. Calcd for $C_{20}H_{22}N_2O_4S_3$: C, 53.31; H, 4.92; N, 6.22. Found: C, 53.25; H, 4.81; N, 6.10.

3′,4′-Dibutyl-5,5″-dibromo-2,2′:5′,2″-terthiophene (5). To a 100 mL round-bottom flask equipped with an addition funnel were added 3′,4′-Dibutyl-2,2′:5′,2″-terthiophene (1.00 g, 2.77 mmol), 0.695 g of $NaHCO_3$ (8.27 mmol), and 15 mL of $CHCl_3$. Bromine (0.88 g, 5.51 mmol) was added to 10 mL of $CHCl_3$ in the addition funnel. The flask was cooled to 0 °C, and the bromine solution was added dropwise with stirring such that the red color had dissipated between drops (about 1 drop/3 s; total time = 45 min). A bubbler was added to the system to monitor the release of CO_2. After complete addition of the Br_2 solution, 20 mL of water was added, and the organic layer was dried with $MgSO_4$ and concentrated to provide a light brownish-yellow oil. The resulting crude oil was purified by column chromatography (silica gel/100% hexanes) to provide a yellow oil which solidified over time to provide 1.36 g (95%) of a light yellow solid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.06 (d, 2H, $J_{3,4} =$ 3.6 Hz), 6.87 (d, 2H, $J_{3,4} = 3.6$ Hz), 2.64 (t, 4H), 1.48 (m, 8H), 0.95 (t, 6H); HREIMS calcd 515.9251, found 515.9250 (M^+). Anal. Calcd for $C_{20}H_{22}Br_2S_3$: C, 46.34; H, 4.28. Found: C, 46.65; H, 4.23.

3′,4′-Dibutyl-5,5″-bis(dicyanomethylene)-5,5″-dihydro-2,2′:5′,2″-terthiophene (2). Malononitrile (0.153 g, 2.32 mmol) was added to a suspension of sodium hydride (0.185 g, 4.63 mmol) in 12 mL of dimethoxyethane at 0 °C under argon. The reaction was removed from the ice bath and stirred for 30 min. To this mixture was added **5** (0.500 g, 0.96 mmol) and $Pd(PPh_3)_4$ (0.111 g, 0.096 mmol). The system was evacuated and back-filled with argon three times and then heated to reflux. Over time, the solution became deep orange, indicating the formation of the dianion intermediate. After 4 h, the mixture was cooled to 0 °C and 20 mL of a saturated Br_2/H_2O solution was added. The solution initially turned blue, followed by the formation of a greenish-olive precipitate. This suspension was transferred to a flask containing 30 mL of water and stirred at 0 °Cfor 10 min. The resulting solid was filtered and washed with water (4 × 5 mL). The solid was purified using column chromatography (alumina/dichloromethane) to provide 0.190 g (41%) of **2** as a deep olive-green solid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, 2H, $J_{4,3} = 5.4$ Hz), 7.32 (d, 2H, $J_{3,4} =$ 5.4 Hz), 2.80 (br, 4H), 1.55 (br, 8H), 1.03 (t, 6H); HREIMS calcd 486.1007, found 486.1002 (M^+). Anal. Calcd for $C_{26}H_{22}N_4S_3$: C, 64.17; H, 4.56; N, 11.51. Found: C, 63.93; H, 4.57; N, 11.26.

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Single-Crystal X-ray Studies. Data for compound **2** were reported as Supporting Information in ref 16. The analysis closely resembled that described here for compound **1**. Supporting Information (Table S1) contains additional crystal and refinement information. Single crystals of **1** were grown by slow evaporation of a chloroform solution. A crystal was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Siemens SMART Platform CCD diffractometer for data collection at 173(2) K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrixes determined from 139 reflections. The data collection was carried out using Mo Kα radiation (graphite monochromator) with a frame time of 15 s. A randomly oriented region of reciprocal space was surveyed to the extent of 1.5 hemispheres and to a resolution of 0.84 Å. Three major sections of frames were collected with 0.30° steps in ω at three different ϕ settings and a detector position of $-28°$ in 2θ. The intensity data were corrected for absorption and decay (SADABS).[25] Final cell constants were calculated from the *xyz* centroids of 5671 strong reflections from the actual data collection after integration.[26] The structure was solved using SHELXS-86[27] and refined using SHELXL-97.[27] The space group $P1$ was determined on the basis of systematic absences and intensity statistics. A direct-methods solution was calculated that provided most non-hydrogen atoms from the E-map. All non-hydrogen atoms were refined with anisotropic displacement parameters, unless stated otherwise. All hydrogen atoms were found via least squares Fourier refinement and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0396$ and $wR2 = 0.0958$ (F^2, all data).

Results and Discussion

Oligomer Synthesis. Compound **1** was prepared by treating 3′,4′-dibutyl-2,2′:5′,2″-terthiophene with nitric acid in an acetic acid/dichloromethane mixture.[28] The mononitration products (**7A/7B**) were easily separated from **1** by column chromatography to provide 62% of a 70:30 mixture of the 5- and 3-nitro isomers, respectively, based on integration of the NMR data. Compound **1** was isolated in 19% yield.

Compound **2** was synthesized using procedures for similar molecules.[18,19] Treatment of 3′,4′-dibutyl-2,2′:5′,2″-terthiophene with bromine in a $NaHCO_3$/chloroform suspension resulted in dibromoterthiophene **5** in 95% yield. The sodium salt of malononitrile was coupled to **5** using a palladium catalyst. Deprotonation of the product with NaH afforded the sodium salt of the dianion intermediate. Oxidation of the dianion with bromine/water afforded **2** in 41% yield.

Electrochemical Properties. Cyclic voltammograms (CV) of the oligomers **1**, **2**, and **5** were measured in 0.1 M $TBAPF_6/CH_2Cl_2$ solution. The CV of **1** (Table 1, Figure 1a) exhibited a reversible one-electron oxidation process, with $E°' = 1.64$ V, and a reversible two-electron reduction at $E°' = -0.84$ V. The reductive process corresponds to one-electron reduction of each nitro group. The oxidative process generates a stable cation radical. This process occurs 0.75 V more positive than that for the diphenyl-substituted analogue,[4] as a consequence of the destabilizing effect of the electron-withdrawing nitro groups. A previous electrochemical study of the unsubstituted dinitroterthiophene (**4**) displayed no reversibility of the oxidative process, even at high scan rates.[22] Clearly, the dibutyl substitution of **1** provides a stabilizing effect for the radical cation. No reductive processes were reported in the previous work. This compound represents an unusual example of an oligothiophene that can be easily reduced. This quality can be useful for materials chemistry applications if the solid-state structure can allow electron transport. Usually, oligothiophenes are hole transporters.

TABLE 1. Electrochemical Data for Terthiophene Oligomers[a]

	oxidation processes		reduction process
compd	$E°_1$ (V)	$E°_2$ (V)	$E°'$ (V)
1	1.64		−0.84
2	1.27	1.96[b]	−0.15
5	1.15	1.68[c]	
6[d]	0.89	1.29	

[a] Measured at room temperature with a scan rate of 100 mV/s in 0.1 M $TBA^+PF_6^-$. [b] Partially reversible process; E_{pa} value provided. [c] Irreversible process; E_{pa} value provided. [d] Values from ref 4.

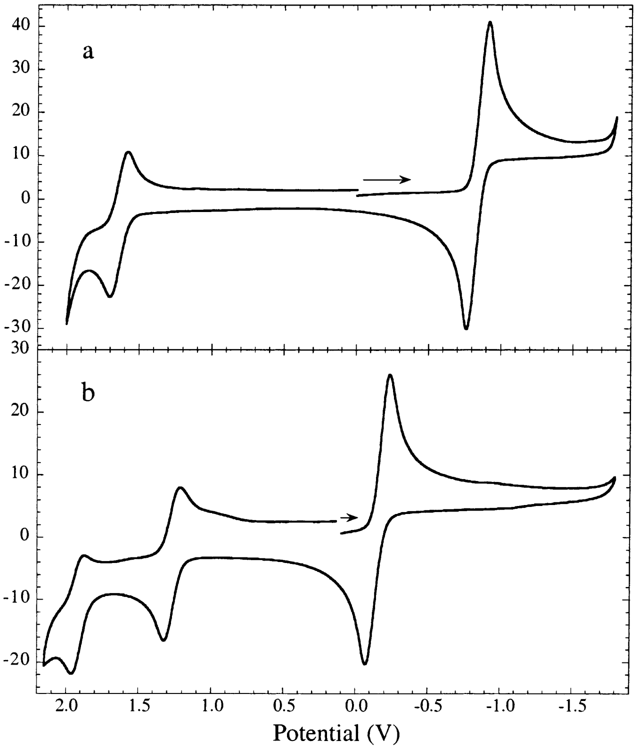

FIGURE 1. Cyclic voltammograms of **1** (a) and **2** (b) in 0.1M $TBAPF_6/CH_2Cl_2$, $\nu = 100$ mV/s.

The CV of **2** (Table 1, Figure 1b) exhibits a reversible one-electron oxidation process with $E°' = 1.27$ V, a less-reversible second oxidation at $E_{pa} = 1.96$, and a two-electron reduction at $E°' = -0.15$ V. The two-electron reduction process was not resolved into a pair of one-electron processes at lower scan rates or in different

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[26] SAINT V6.10, Bruker Analytical X-ray Systems, Madison, WI.

[27] SHELXTL-Plus V5.10, Bruker Analytical X-ray Systems, Madison, WI.

[28] Similar results have been reported for the nitration of α-terthiophene: Leitch, L. C.; Arnason, T.; Morand, P. *J. Heterocyclic Chem.* **1991**, *28*, 411−416.

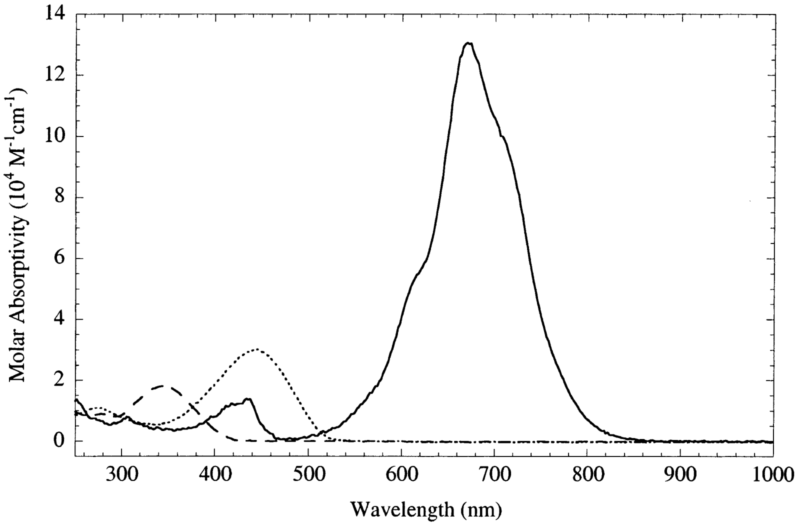

FIGURE 2. Electronic spectra of **1** (---), **5** (— — —), and **2** (—) in CH_2Cl_2.

solvents such as acetonitrile or tetrahydrofuran. The previous study[18] of the unbutylated **3** also showed a single two-electron reduction process, but no oxidation. Oxidation of a dicyanoquinodimethane is unprecedented to our knowledge and illustrates the usefulness of combining an easily oxidized oligothiophene unit with easily reduced dicyanomethylene groups in one π-system.

Electronic Spectra. Dramatic differences are seen in the electronic spectra of the neutral oligomers **1**, **2**, and **5** (Figure 2). Each molecule exhibits an intense band attributed to the $\pi-\pi^*$ transition of the conjugated thiophene system.[29] **1** has a peak ($\lambda_{max} = 444$ nm, $\epsilon = 3.0 \times 10^4$ M^{-1} cm^{-1}) that is at a slightly lower energy than that observed for the nonbutyl-substituted analogue ($\lambda_{max} = 438$ nm).[30] **5** has a peak ($\lambda_{max} = 346$ nm, $\epsilon = 1.8 \times 10^4$ M^{-1} cm^{-1}) at substantially higher energy than that of **1**. The band for compound **2** is at much longer wavelength ($\lambda_{max} = 670$ nm, $\epsilon = 1.3 \times 10^5$ M^{-1} cm^{-1}); for comparison the nonbutyl substituted **3** has $\lambda_{max} = 643$ nm.[18]

UV–Vis Spectroelectrochemical Studies. Constant potential spectroelectrochemical studies of **2** in 0.1 M $TBAPF_6/CH_2Cl_2$ solution revealed four distinct redox processes (Figure 3, Table 2). Removal of the first electron at $E_{app} = 1.40$ V caused an isosbestic change characterized by the appearance of an intense band at 688 nm (Figure 3a). Reversal of this process (reduction at $E_{app} = 0.50$ V) resulted in greater than 97% regeneration of the neutral molecule. Removal of a second electron at $E_{app} = 2.10$ V resulted in a sharp decrease of the band at 688 nm as a new band isosbestically grew in at 603 nm with shoulders at 562 and 647 nm (Figure 3b). The oxidized species that resulted from this second process could not be reduced and is not the dication.

In contrast to the result obtained in the CV experiment, two distinct reduction processes were resolved under the spectroelectrochemical conditions. When the applied potential was -0.20 V, the 670 nm band of the neutral molecule decreased as a less intense band and two shoulders grew in at 779, 681, and 608 nm respectively; an additional band at 442 nm also grew in to the spectrum (Figure 3c). Holding the potential at this value for extended periods of time resulted in no additional spectral changes. Further reduction at $E_{app} = -0.70$ V resulted in a second set of spectral changes. The band and shoulders at 779, 681, and 608 nm disappeared as a large band with a shoulder at 451 and an additional band at 381 nm (Figure 3d) grew in intensity. Reversal of both reduction processes was accomplished by oxidation at $E_{app} = 0.30$ V and resulted in greater than 95% regeneration of the neutral molecule.

IR Spectroelectrochemical Studies. In addition to the UV–vis studies of **2** we also investigated the changes that occur in the near and mid-IR spectral regions (900–7000 cm^{-1}). As in the case of the UV–vis experiments, we observed spectral changes that resulted from two sequential reduction processes and two sequential oxidation processes.

Addition of an electron to **2** (Figure 4a) caused an intense band from an electronic transition to appear at 6330 cm^{-1} (1580 nm) and an isosbestic change in the CN stretching region as the 2211 cm^{-1} band of neutral **2** decreased with the increase of a band at 2173 cm^{-1}. Further reduction to the dianion resulted in the growth of two bands at 2166 and 2114 cm^{-1}. In addition, the intense electronic transition at 6330 cm^{-1} decreased as the dianion formed (Figure 4b). Removal of the first electron from **2** caused a small shift to higher energy from 2211 to 2215 cm^{-1}. A summary of the IR spectroelectrochemical results for the various redox states of **2** can be found in Table 2.

Chemical Redox Properties. Compound **2** was chemically oxidized to the cation radical in dichloromethane by the addition of a stoichiometric amount of nitrosonium tetrafluoroborate. The spectrum of the oxidized species produced was nearly identical to the cation radical generated in the spectroelectrochemical experiment. The formulation of this species as the odd electron cation radical is confirmed by the observation of a strong EPR signal ($g = 2.00355$) without fine structure.

The spectroelectrochemical reduction of **2** was also confirmed by sequentially producing both reduced species

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[29] Murrell, J. N. *J. Chem. Soc.* **1956**, 3779.

[30] Zhao, M. T.; Samoc, M.; Singh, B. P.; Prasad, P. N. *J. Phys. Chem.* **1989**, *93*, 7916–7920.

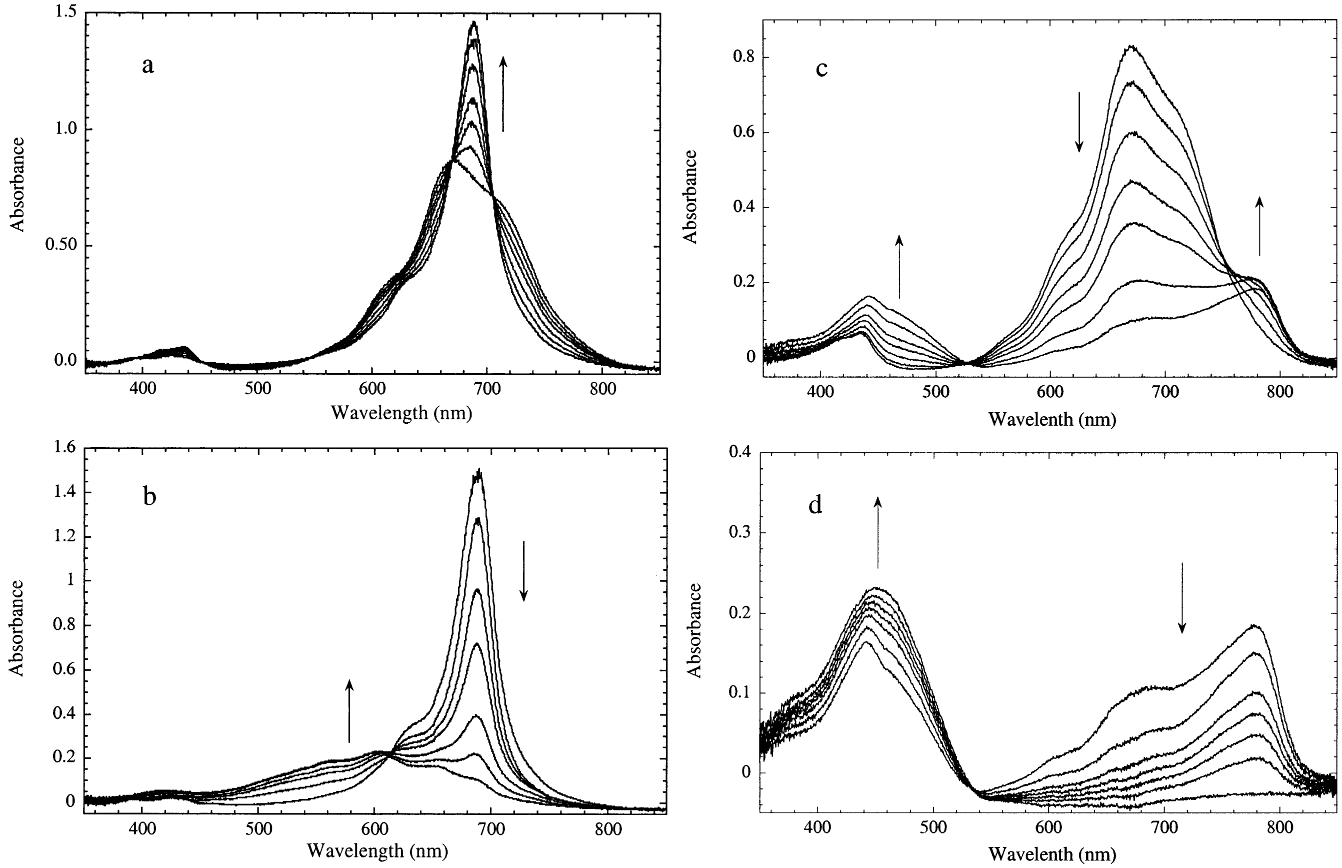

FIGURE 3. UV−vis−NIR spectroelectrochemical data for **2**: removal of first (a) and second (b) electrons. Arrows indicate the direction of changes. UV−vis−NIR spectroelectrochemical data for **2**: addition of first (c) and second (d) electrons. Arrows indicate the direction of changes.

TABLE 2. Electronic and Vibrational Spectral Values

species	electronic transition(s) (nm)	ν(CN) stretch (cm^{-1})
$Bu_2(DCM)_2Tth$	670	2211
$[Bu_2(DCM)_2Tth]^-$	608(sh), 681 (sh), 779, 1301 (sh), 1580	2173
$[Bu_2(DCM)_2Tth]^{2-}$	381 (sh), 451	2166, 2114
$[Bu_2(DCM)_2Tth]^+$	688, 1019 (w), 1194 (w), 1420 (w)	2215
$[Bu_2(DCM)_2Tth]^{2+}$	562 (sh), 603, 647 (sh)	2226

with a chemical reducing agent. Tetrabutylammonium borohydride ($TBABH_4$) was selected on the basis of its ability to act as a one-electron reducing agent in nonpolar organic solvents.[31,32] The addition of 1 equiv of $TBABH_4$ to $Bu_2(DCM)_2Tth$ in dichloromethane generated the one-electron reduced species with a UV−vis spectrum nearly identical to the spectrum observed in the spectroelectrochemical experiment. As in the case of the cation radical, the anion radical was further characterized as a radical with an intense EPR signal ($g = 2.00265$) without fine structure. Further reduction to the two-electron reduced species was accomplished by adding an additional equivalent of $TBABH_4$ to a solution of the anion radical. The spectrum of the dianion is nearly identical to the spectroelectrochemical spectra. The dianion gave no observable EPR signal.

Crystal Structures of 1 and 2. In the crystal (Figure 5) **1** adopts a cis-orientation of the sulfur atoms in adjacent thiophene rings. Each terthiophene unit is nonplanar, due to twisting of adjacent rings. The twist angles for the rings are 21.5° for rings containing S3 and S2 and 3.6° for rings containing S2 and S1. Most interesting are the bond lengths in the outer thiophene rings substituted with a nitro group (Supporting Information Table 2). Comparison of these bond lengths with those of the corresponding bonds in **6** reveals that the outer rings of **1** have some quinoidal character. For example, the average C═C and C−C bond distances of the outer rings in **6** are 1.352(7) and 1.412(7) Å respectively, compared to 1.370(3) and 1.403(3) Å for **1**. Although the changes are small, nitro substitution gives longer 2,5-C═C bond lengths and shorter 3,4-C−C bond lengths, reflecting the quinoid character in **1**.

The nonplanar **1** molecules form slipped columnar stacks (Figure 6) similar to those found at high temperature for the **6** cation radical (**6**$^+$). The average distance between the molecules (3.65 Å) is, however, much larger than the interplanar distance of 3.47 Å in **6**$^+$. This difference offers an interesting opportunity for materials chemistry in that either electron or hole mobility should be dependent on the extent of intermolecular interaction. Examination of the packing diagram also shows an additional intermolecular interaction, namely a hydrogen

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(31) (a) Lucarini, M.; Pedulli, G. F.; Alberti, A.; Paradisi, C.; Roffia, S. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2083−2087. (b) Lucarini, M.; Pedulli, G. F. *J. Organomet. Chem.* **1995**, *494*, 123−131.

(32) Boyd, D. C.; Connelly, N. G.; Herbosa, G. G.; Hill, M. G.; Mann, K. R.; Mealli, C.; Orpen, A. G.; Richardson, K. E. Rieger, P. H. *Inorg. Chem.* **1994**, *33*, 960−971.

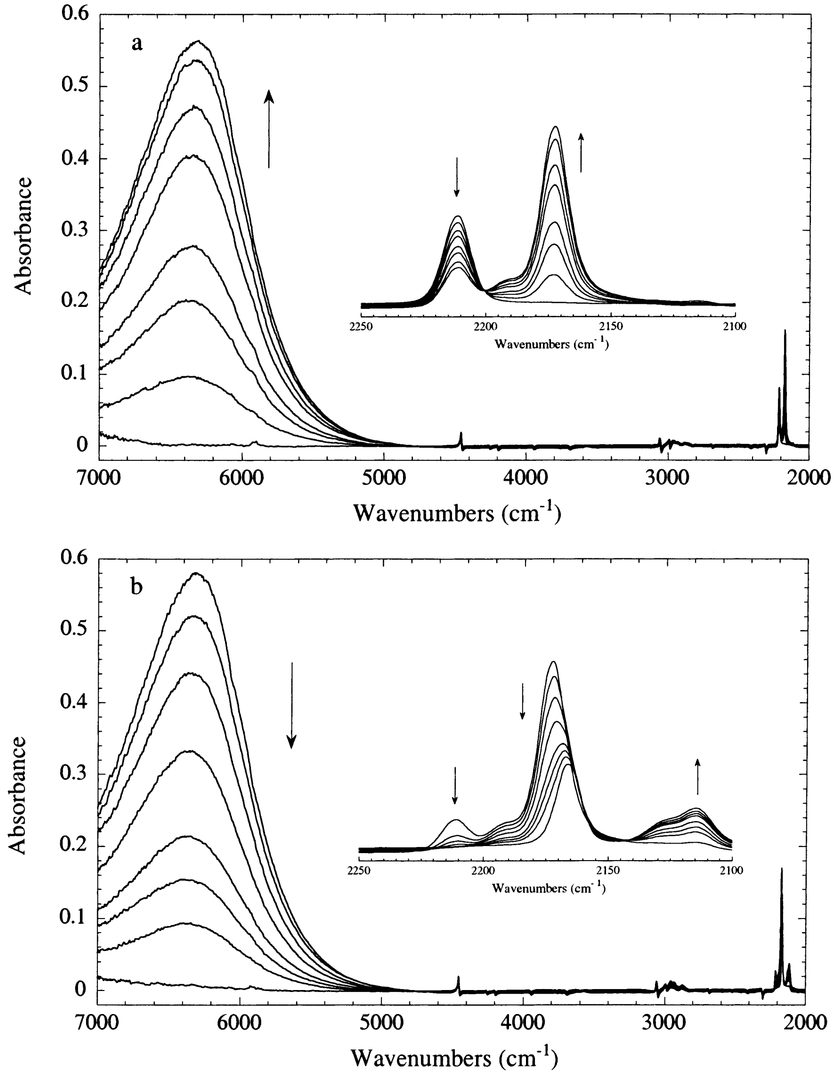

FIGURE 4. NIR−IR spectroelectrochemical data for **2**: Addition of first (a) and second (b) electrons. Arrows indicate the direction of changes. Insets show the ν(CN) region (2250−2100cm^{-1}).

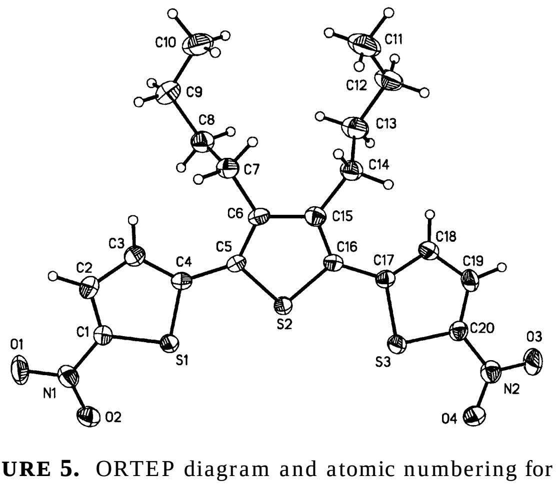

FIGURE 5. ORTEP diagram and atomic numbering for **1**.

bond of 2.522 Å between the hydrogen of C19 and the oxygen of the nitro group (O2) of **1**.

The crystal structure of **2** (Figure 7) showed a planar ring system with deviations from the least-squares plane of less than 0.05 Å. There is a transoid orientation of the sulfur atoms in adjacent thiophene rings. Selected bond lengths are shown in the Supporting Information. In this case, the carbon−carbon bond lengths in the thiophene rings very dramatically show the quinoidal nature of this molecule. This is the first crystal structure of a quinoidal oligothiophene. Since quinoid forms are commonly invoked to explain the structure and properties of neutral and oxidized oligothiophenes, this structure should have some utility in establishing accurate bond lengths, especially for theoretical calculations.

Molecules of **2** pack along the *b*-axis in pairs that are slipped lengthwise by about one thiophene ring (Figure 8). Similar to the structure of **6**$^{+}$ at low temperature, the columns have regular variations in the intermolecular spacings and, in effect, form π-stacks of π-dimers. The variations in the stacking distances of **2** (3.47 and 3.63 Å) are much longer than those of **6**$^{+}$ at 106 K (3.36 and 3.42 Å). In addition, the stacks of **2** are packed with alternating columns that are at an angle of 39.4° from each other. Again, this π-stacked morphology is relatively unusual and of considerable interest for forming FETs.

^{1}H NMR of the Oligomers. ^{1}H NMR experiments provide valuable information concerning the quinoid

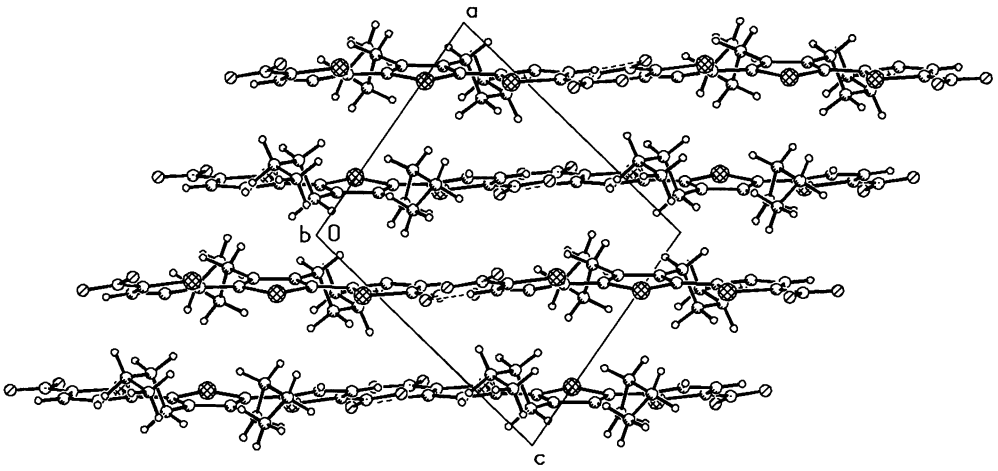

FIGURE 6. Stacking of **1** molecules viewed along the *b*-axis.

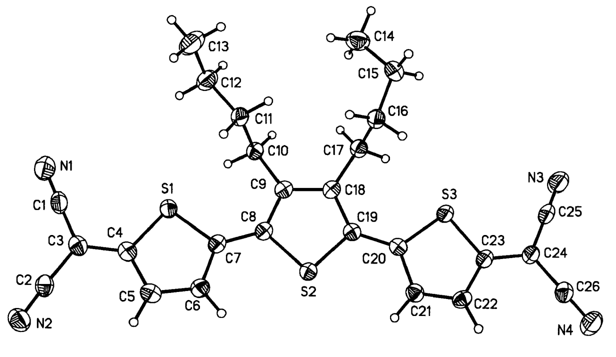

FIGURE 7. ORTEP diagram and atomic numbering for **2**.

character of the oligomers investigated, as the development of quinoid structures enhance or decrease the double bond character between specific carbon atoms and result in observable changes in proton−proton coupling constants. The butyl substitution pattern in the oligomers reported here allows for the convenient characterization of the unsubstituted protons present in all the oligomers, namely the 3- and 4-protons. Typically, the coupling constant for these protons in structures such as **5** or **6** without quinoid character is near 3.7 Hz (Table 3). As expected, compound **2** displays the highest coupling (5.4 Hz) between the 3- and 4-protons, due to the double bond between the 3- and 4-carbons. The nitro substituents on **1** give quinoid character to the molecule, as shown by the 4.5 Hz coupling of the 3- and 4-protons. It is quite interesting that the mononitro-substituted oligomer (**7A**) displays two unique coupling constants for the 3- and 4-protons of each ring, consistent with quinoid character at the nitro-substituted end and no quinoid character at the other.

Analysis of Structural Data Using Principal Component Analysis (PCA). The analysis of quinoidal character induced by variation of a substituent in a structure can, obviously, be investigated by comparisons of two or more structures in a bond-by-bond manner. Selected chemically equivalent bond lengths of **6**, $\mathbf{6}^+$, and **2** are illustrated graphically in Figure 9. Pairwise comparisons show that there are changes well beyond the errors in the bond lengths in the three molecules. In particular, the C−C bond lengths of the thiophene rings change so that the "long" and "short" bonds of **6** become the "short" and "long" bonds of **2**. Further, the analogous bonds in the one-electron oxidized form $\mathbf{6}^+$ are intermediate between the two extremes. A more careful analysis of the large number of coupled bond lengths in a series of structures such as this can be achieved using PCA.

PCA is a powerful statistical technique that has found widespread application throughout chemistry (i.e., chemometrics).[33] In the present case, we treat each of the 11 carbon−carbon bonds that are relevant to the quinoidal structure as a variable. The PCA method then sequentially selects orthogonal linear combinations of these 11 variables to accommodate the variance in the bond lengths that remain. Typically, the variables are transformed to a new set of orthogonal variables that decrease in importance. Usually a set of highly correlated variables such as these bond lengths is quite redundant and only the first few linear combinations [also called "scores" or "principal components" (PCs)] would be needed to explain most of the data variability. The remaining scores are usually interpreted as noise. Score plots and loadings plots are commonly used to interpret the derived data. The important advantage of this method is that all of the bonds are used in the analysis so that the larger errors inherent in a bond by bond comparison are avoided, and the results can be quantified numerically and expressed graphically as well.

To apply PCA to this problem, the C−C bond lengths of the thiophene rings and the bonds connecting the rings of each oligomer (**1**, **2**, **6**, $\mathbf{6}^+$) formed the data set (5 by 11 total variables). (Two unique sets are used to interpret the derived data. The important advantage of this method is that all of molecules exist in the crystal structure of $\mathbf{6}^+$ at 106 K, so each molecule was treated as a unique set of data points.) The two scores that contain most of the variance are plotted by projecting the data set onto the PC1−PC2 plane (Figure 10). Quite interesting is the fact that 93% of the variance lies within PC1. This means that 93% of the change in all the single and double bonds in this system can be described by a single variable. This variable describes the quinoid

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[33] (a) Jurs, P. C.; Bakken, G. A.; McClelland, H. E. *Chem. Rev.* **2000**, *100*, 2649−2678. (b) Jackson, J. E. *A User's Guide to Principal Components*; Wiley and Sons: New York, 1991.

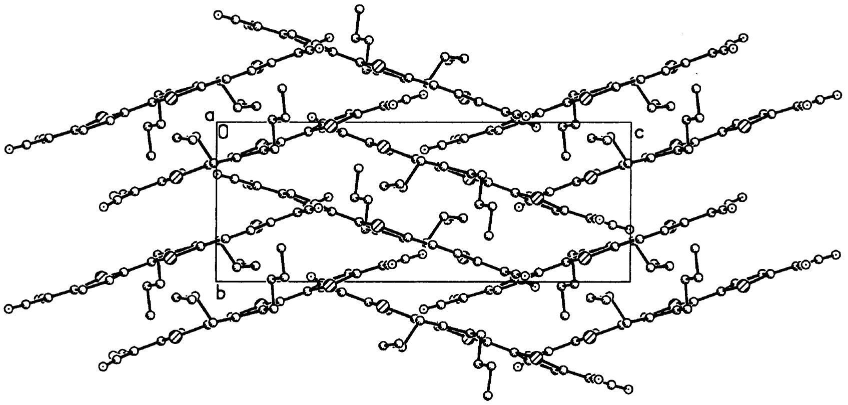

FIGURE 8. Packing view of **2** viewed along the *a*-axis.

TABLE 3. ^{1}**H NMR Data for Terthiophene Oligomers**

	coupling constant (Hz)	
compd	$H_{3,4}$	$H_{3'',4''}$
6	3.9	3.9
5	3.6	3.6
7A	4.5	3.6
1	4.5	4.5
2	5.4	5.4

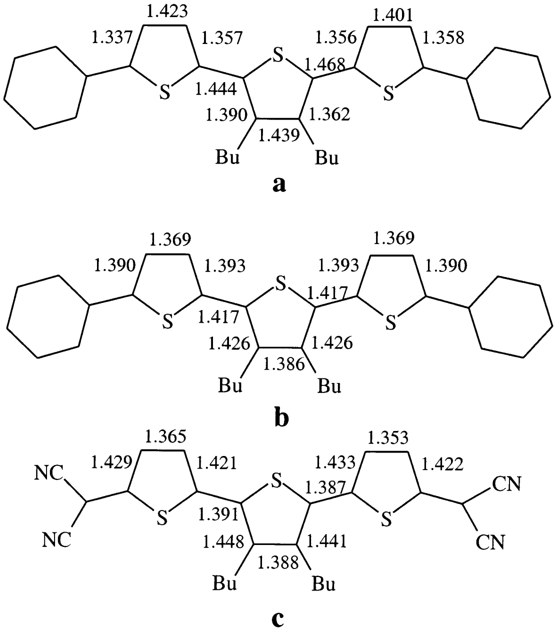

FIGURE 9. Bond lengths of the oligomers in three unique oxidation states: **6** (a), **6**$^+$ (b), and **2** (c).

character of the compound. All of the remaining intra- and intermolecular forces are not a significant factor (7% or less) in determining these bond lengths.

The position of each molecule along PC1 is a measurement of increasing quinoid character in the terthiophene unit; the oligomers lie in the following order: **6** < **1** < **6**$^+$ < **2**.

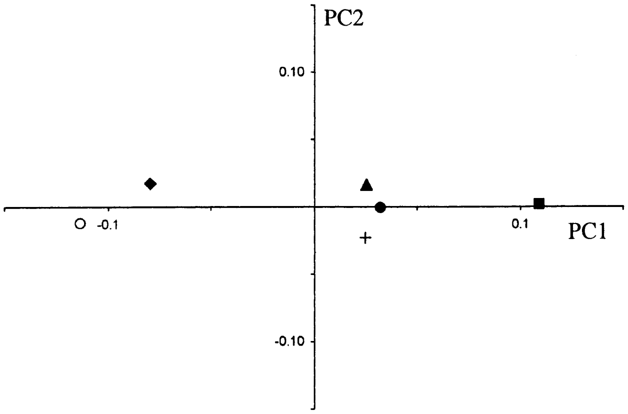

FIGURE 10. PCA scores plot: **6** (O), **1** (◆), **6**$^+$ at 106 K, molecule A (▲), **6**$^+$ at 295 K (●), **6**$^+$at 106 K, molecule B (+), **2** (■).

This analysis confirms the less rigorous conclusions reached above and in particular confirms the slight quinoid character of **1.** The analysis suggests that the quinoid character of other oligothiophene compounds could be compared and quantified. Indeed, where crystallographic data exist it should be possible to evaluate quinoid character in various conjugated compounds and their redox partners.

Understanding the Electronic Spectra of Compound 2. The electronic spectra of **2** and its redox partners are rather complex and initially were difficult to understand. We noticed, however, a similarity between these spectra and those of oxidized species from oligothiophenes such as **6**. Indeed, consideration of the above PCA analysis suggests that **2** might be formally considered as a quinoidal terthiophene dication attached to a pair of dicyanomethylene anions. If this is true, there should be correlations between the spectra of the following pairs **2**/**6**$^{2+}$, **2**$^-$/**6**$^+$, and **2**$^{2-}$/**6**. These pairs are matched in this formalism because they have the same number of electrons in the thiophene moieties.

The experimental correlation is good, both in terms of the number of bands and their approximate positions. **2** shows a strong band in the vis-NIR at 670 nm, while **6**$^{2+}$ shows a strong band at 805 nm. Radical anion **2**$^-$ has two intense electronic transitions at 779 and 1580 nm, which are comparable to the bands of **6**$^+$ at 654 and 1106 nm. Dianion **2**$^{2-}$ has a single band at 451 nm comparable to a single band at 384 nm from **6**.

The successful correlation for the low oxidation states of these terthiophenes suggests that the spectrum of the oxidized form **2**$^+$ would correlate with that of a terthiophene trication radical. Although no spectral data for a terthiophene trication are available for comparison, the spectral features of **2**$^{+}$ (two bands in the NIR region) are remarkably similar to those observed for a trication of a diphenylsexithiophene we have recently investigated when allowance is made for the increase in the conjugation length.

Conclusions

Two new and unusual crystal structures are reported. The molecules of **1** have an unusual cisoid arrangement of the thiophene rings and they stack cofacially, even though they are not quite planar. The structure of **1** analyzed by the PCA method gives clear evidence for the quinoid character in the outer rings, and it seems that PCA should be useful for analyzing the quinoid character of other conjugated molecules. The quinoid molecule **2** is planar in the crystal and forms π-stacks of cofacial π-dimers. These compounds provide unusual examples of oligothiophenes that can be easily oxidized and reduced. The spectra of the resulting cation radicals, anion radicals, and dianions are reported and analyzed. Of special interest is the correlation of the spectra of **2** with **6**$^{2+}$, **2**$^{-}$ with **6**$^{+}$, and **2**$^{2-}$ with **6**. As crystalline examples of thiophenes that can be both easily oxidized and reduced, compounds **1** and **2** are clearly interesting for materials chemistry.

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Supporting Information Available: X-ray crystallographic files in CIF format for **1.** Crystallographic and refinement data for **1** and **2.** Selected bond lengths for **1** and **2.** This material is available free of charge via the Internet at http://pubs.acs.org.

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