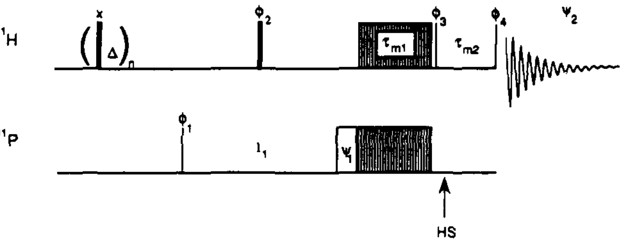

Figure 1. Pulse sequence diagram for 2D hetero-TOCSY-NOESY. The hatched boxes represent a matched multiple pulse mixing sequence for cross polarization. The choice of mixing sequence is discussed elsewhere;[10,12,13,28] the sequence used here was DIPSI-2. The phase cycling is as follows: $\phi_1 = (y, -y)$; $\phi_2 = (x, x, -x, -x)$; $\psi_1 = x$; DIPSI2 = x; $\phi_3 = y$; $\phi_4 = -x$; $\psi_2 = (+, -, +, -)$.

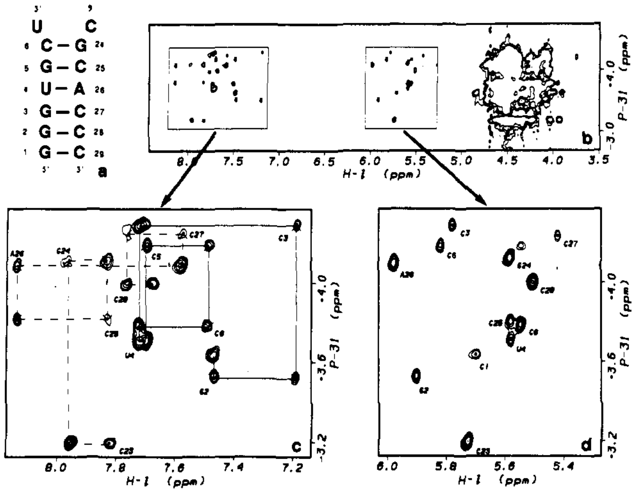

Figure 2. (a) Sequence and secondary structure of the RNA molecule used in this work. The phosphorus atoms are numbered according to the nucleoside on their 5′ side. (b) 2D hetero-TOCSY-NOESY spectrum for the molecule illustrated in part a. The spectrum was recorded using a 3 mM RNA sample in D_2O at 30 °C on a Bruker AM-500 spectrometer (500 MHz, protons; 202 MHz, phosphorus). Other parameters were as follows: $\tau_{m1} = 72$ ms, $\tau_{m2} = 500$ ms, ^1H width = 4000 Hz, ^{31}P width = 600 Hz: 94 increments of 320 scans each were recorded. (c) Expanded plot of the ^1H aromatic region of the spectrum in part b. For both strands the sequential connectivities are traced with either a solid or a dashed line. Each intraresidue ^{31}P–$^1H8$ or ^{31}P–$^1H6$ cross peak is labeled. (d) Expanded plot of the ^1H anomeric region of the spectrum in part b. Each of the 12 intraresidue ^{31}P–$^1H1'$ cross peaks is labeled.

that a powerful ^{31}P assignment method would result.

The 2D hetero-TOCSY-NOESY pulse sequence is shown in Figure 1. ^{31}P magnetization is excited after elimination of ^1H magnetization by saturation and is allowed to evolve with refocusing of heteronuclear coupling.[10] The two mixing periods are then applied sequentially. A 3D version of this experiment could be achieved by inserting a second incrementable delay between the mixing times. The 2D experiment was carried out on the oligoribonucleotide whose sequence is shown in Figure 2a. The entire spectrum is shown in Figure 2b. The cross peaks of most interest are in the ^1H aromatic (7.0–8.2 ppm) and anomeric (5.0–6.0 ppm) regions.

An expansion of the ^1H aromatic region is shown in Figure 2c. Except for G1, each ^{31}P resonance correlates with two aromatic ^1H resonances, and each internal aromatic resonance correlates with two ^{31}P resonances. Therefore it was possible to draw a complete set of connectivities for the length of each strand, and all 12 ^{31}P resonances were unambiguously identified. The accuracy of this procedure was confirmed by conventional sequential resonance assignment procedures.[4,19–23] Thus sequential ^{31}P resonance assignments were obtained for this sample without isotopic labeling, even in the absence of prior information about ribose ^1H assignments.

In instances where aromatic–^{31}P correlations are less complete, ambiguities can be resolved by comparing the ^1H anomeric region (Figure 2d) with assignment data obtained by homonuclear ^1H methods. Each ^{31}P resonance should give rise to a single, strong anomeric ^1H peak, via the pathway ^{31}P–H3′–H2′–H1′, which is precisely what is seen in Figure 2d.

In summary, a single hetero-TOCSY-NOESY spectrum can lead to sequential assignments for ^{31}P resonances, and for H1′, H8, and H6 resonances in RNA oligonucleotides. The assignment strategy depends, of course, on reasonably efficient transfer from ^{31}P to the 3′ and 2′ protons and NOE connectivities onward to anomeric and aromatic protons. The experiment is necessarily less sensitive than ^1H–^1H spectroscopy, and the sensitivity of the first step will decrease for larger macromolecules. Nonetheless, it has provided crucial assignment information for a 29-nucleotide RNA under study in this laboratory.[21] This experiment is likely to be most useful for the study of unusual nucleic acid structures,[24–27] drug–nucleic acid interactions, and protein–nucleic acid interactions.

Acknowledgment. G.W.K. thanks Prof. James Prestegard for a number of very illuminating conversations. This work was supported by grants from the NIH (GM41651 and AI09167) to P.B.M.

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Oligothiophene Cation Radical Dimers. An Alternative to Bipolarons in Oxidized Polythiophene

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Current understanding of the structure, spectra, and conductivity of oxidized polythiophene and other conducting polymers is dominated by the theory that polarons and bipolarons are formed along single conjugated chains.[1] Because polarons and bipolarons have small-molecule analogues in cation radicals and dications, it is natural to explore that theory by generating these cations and studying their properties.[2] We report that the cation radicals of terthiophenes reversibly dimerize even at low concentration. We suggest that these are π-dimers and that such dimers are reasonable alternatives to bipolarons. As a consequence, π-dimers and π-stacks deserve attention as entities responsible for the properties of oxidized polythiophene and other conducting polymers.

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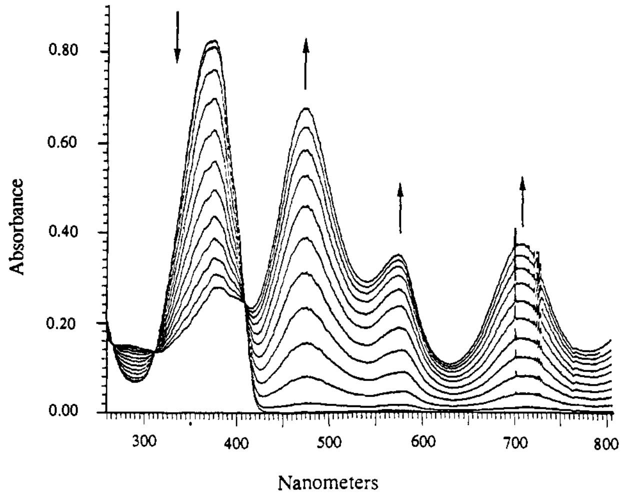
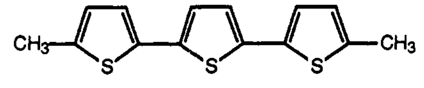


Figure 1. Spectroelectrochemical oxidation of **1** under conditions cited in the text. Scans were taken every 5 s.

In this report, we focus on $2,5''$-dimethylterthiophene (**1**),[3] chosen because oligothiophenes blocked at their terminal α-positions do not readily undergo oxidative polymerization[4] and because the electronic spectrum of the cation radical (1^+) has previously been reported.[2d] **1** was studied by cyclic voltammetry (CV) and UV-vis spectroelectrochemistry[5] in acetonitrile with tetrabutylammonium fluoroborate as the supporting electrolyte. CV at sweep rates from 10 to 1000 mV s^{-1}, **1** (4.1×10^{-4} M), gave a reversible one-electron oxidation ($E_{pa} = 1.02$ V, $E_{pc} = 0.96$ V vs SCE) at a glassy carbon electrode.



1

Although the cation radical 1^+ is not very stable at room temperature, rapid (ca. 2 min) coulometric oxidation gave a 1 F/mol process which could be reversed to regenerate the starting material in greater than 95% yield. Figure 1 shows the UV-vis spectroelectrochemical oxidation of **1** (4×10^{-4} M) at −25 °C. During oxidation the band at 360 nm due to the reactant disappeared and three new bands grew in at longer wavelengths. When the electrolysis was stopped, the spectrum was unchanged after several minutes. Several experimental observations indicated that the new absorbance at 572 nm was due to one species (assigned as monomeric cation radical), while the bands at 466 and 708 nm were due to a second species (assigned as a cation radical dimer). The band intensities from Figure 1 were analyzed to obtain the concentrations of monomer and dimer as they increased during oxidation. These values were then fit to the equilibrium equation, $K = [\text{dimer}][\text{monomer}]^{-2}$, yielding $K = 3800$ M^{-1} ($r^2 = 0.98$).

Several temperatures and concentrations (see Figure 2) were used for spectroelectrochemistry, and in each case good fits to the equilibrium expression were obtained. As expected, lower temperature and/or higher concentration favored dimerization. Van't Hoff plots of the K values were made, giving $\Delta H = -10$ kcal mol^{-1} and $\Delta S = -25$ eu, values quite compatible with the proposed equilibrium. A change in temperature resulted in an immediate change in the spectrum, demonstrating rapid equilibration. Significantly, temperature-dependent spectra were recorded under conditions wherein no neutral **1** was present, abrogating the possibility of a disproportionation of cation radicals to dications and neutrals.

Electron spin resonance (ESR) measurements on 1^+ gave the spectrum in Figure 3.[6] Cooling the sample decreased the signal intensity dramatically, so that at about −20 °C the doubly integrated signal was only 15% as intense as at 23 °C. This was reversible. Thus, we conclude that the monomer cation radical is ESR active, but the dimer has no ESR signal and is presumably diamagnetic.

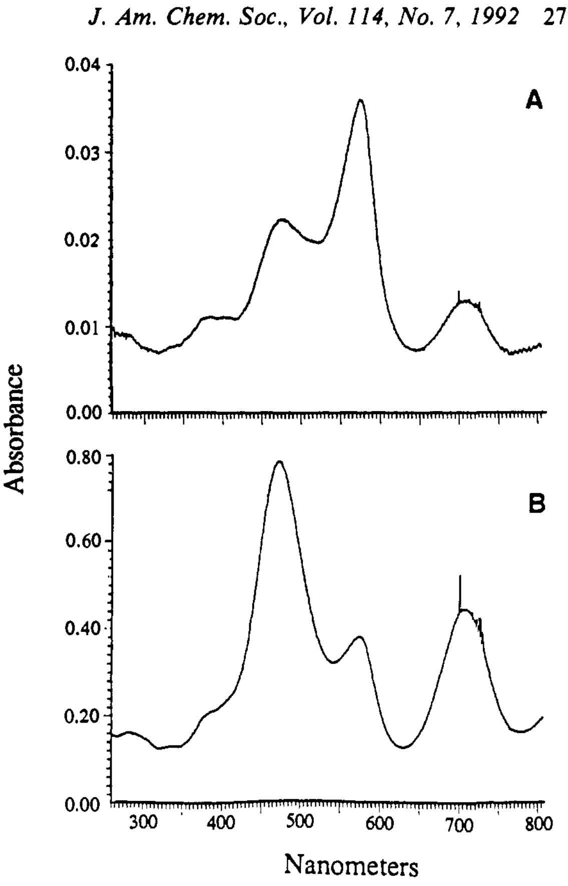


Figure 2. Spectra from the oxidation of **1** at −12 °C. Initial concentration of **1**: A, 5×10^{-5} M; B, 1.2×10^{-3} M.

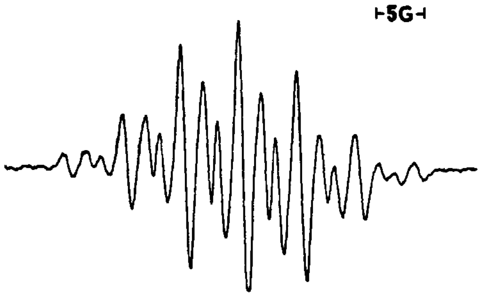


Figure 3. ESR spectrum of 1^+ at 23 °C electrogenerated in CH_3CN, 0.1 M Bu_4NBF_4.

We hypothesize that the cation radical forms a π-dimer. Ion radicals commonly form π-dimers,[7,8] and both the shift in the 1^+ π-π^* band from 572 (monomer) to 466 nm (dimer) and the observation of a new longer wavelength band at 708 nm for the dimer are fully analogous to the changes observed for monomer/π-dimer cation radicals like Wurster's blue[7a] or viologens.[7b]

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[6] The ESR spectrum was simulated using $a_H(6H) = 5.0$ G, $a_H(2H) = 3.1$ G. We presume the couplings for the other four ring hydrogens are less than the line width (0.4 G).

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We also note that the monomeric **1**$^+$ (and the dication **1**$^{2+}$), but not our dimerized **1**$^+$, is seen (λ_{max} 560 nm) in the channels of the oxidizing zeolite Na-ZSM-5, where π-dimerization should be prohibited by the channel size.[2d] Because the monomer/dimer equilibration is fast in solution, it is abundantly clear that the bond between monomers is weak and does not perturb the electronic structure very much. This rules out a carbon-carbon bound dimer of the type involved in polymerization of thiophenes.

Terthiophenes blocked with 2,5″-dibromo- or 2,5″-bis(methylthio) groups behave in a qualitatively identical fashion, with the additional features that more stable dications are formed and identified optically and that evidence for further aggregation of the cation radicals beyond the dimer stage occurs at high concentration.[8,9] The cation radicals have spectra shifted to slightly longer wavelengths than those from **1**.

The formation of dimer structures at such low concentrations has important implications for oxidized conducting polymers. In the solid polymer the cation radicals are more concentrated, and there must be extensive intermolecular interactions of the type demonstrated here. Clearly, *diamagnetic π-dimers can be an alternative to diamagnetic bipolarons* as an explanation for the small ESR signal from highly oxidized polythiophenes. π-Dimers and π-stacks[1a,9] can also help explain optical spectra. Indeed we believe that this hypothesis will explain certain data already reported for oxidized oligothiophenes in solution.[2a] Considering the high formation constant of these dimers, we suggest that π-stacks (analogous to those present in conducting charge-transfer salts[1a,7a]) should be considered as conducting entities in polythiophene and other conducting polymers.

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(9) To be reported in a full paper.

A New Monocarbon Insertion Reaction. Synthesis and Structural Characterization of the First Polyhedral Arachno Tricarbon Carborane: *arachno*-6-$(NCCH_2)$-5,6,7-$C_3B_7H_{12}$

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We have previously shown that nitrile carbons are susceptible to nucleophilic attacks by polyhedral borane anions and that these reactions can result in either CN or monocarbon cage-insertion products in high yields.[1] These results suggested that other species such as polarized acetylenes might also be susceptible to similar nucleophilic reactions and that these reactions could result in new routes for either mono- or dicarbon insertions into polyhedral boranes. In agreement with these expectations, we report here that the *arachno*-6,8-$C_2B_7H_{12}^-$ anion reacts readily with cyanoacetylene to give the first example of a polyhedral arachno tricarbon carborane, *arachno*-6-$(NCCH_2)$-5,6,7-$C_3B_7H_{12}$.

In a typical reaction, a cyanoacetylene/THF solution was added dropwise to a stirred solution containing an equivalent amount of the *arachno*-6,8-$C_2B_7H_{12}^-$ anion at room temperature. The reaction mixture was then neutralized with HCl, the THF vacuum evaporated, the residue extracted with CH_2Cl_2, and the extract filtered through silica gel. Evaporation of the filtrate gave an 82% yield of crude product. Further sublimation (50 °C) gave white *arachno*-6-$(NCCH_2)$-5,6,7-$C_3B_7H_{12}$ as a slightly air-sensitive crystalline solid.[2]

$$\textit{arachno}\text{-6,8-}C_2B_7H_{12}^- + HC{\equiv}CCN \xrightarrow[\text{2. H}^+]{\text{1. room temperature}} \textit{arachno}\text{-6-}(NCCH_2)\text{-5,6,7-}C_3B_7H_{12}$$

In contrast to the numerous dicarbon carboranes, only a few tricarbon carboranes have been reported: *nido*-2,3,4-$R_2C_3B_3H_5$,[3] *nido*-2,3,5-$R_5C_3B_3H$[4] (R = alkyl or H), *closo*-$C_3B_5H_7$,[5] *nido*-5,6,10-$(CH_3)_3C_3B_7H_9$,[6] *nido*-6-CH_3-5,6,9-$C_3B_7H_{10}$,[1,7] and *hypho*-$C_3B_4H_{12}$.[8] The *arachno*-6-$(NCCH_2)$-5,6,7-$C_3B_7H_{12}$ is both the first example of a polyhedral tricarbon carborane in the arachno electronic class[9] and the first tricarbon carborane to be structurally characterized.[18]

The structure of *arachno*-6-$(NCCH_2)$-5,6,7-$C_3B_7H_{12}$ as determined by a single-crystal X-ray study is shown in the ORTEP drawing in Figure 1.[10] Consistent with its 26-skeletal-electron count, the tricarbon carborane adopts a cage geometry based on an icosahedron missing two vertices, similar to those which have been either confirmed or proposed for other 10-vertex arachno cage systems such as the borane $B_{10}H_{14}^{2-}$,[11] monocarbon carborane 6-$CB_9H_{14}^-$,[12] and dicarbon carborane 6,9-$C_2B_8H_{14}$[13] analogues. The three carbons are adjacent in the 5,6,7-vertex positions on

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(2) Spectroscopic data: ^{11}B NMR (64.2 MHz, CD_2Cl_2) (ppm, Hz) 10.7 (d, B2, J_{BH} = 187), -3.7 (d of d, B8, B10, J_{BH} = 151, $J_{BH(br)}$ = 26), -25.1 (d, B1, B3, J_{BH} = 168), -26.1 (d, B9, J_{BH} obscured), -41.1 (d, B4, J_{BH} = 151); two-dimensional ^{11}B-^{11}B NMR established the connectivities B2-B1,3, B8,10-B1,3, B8,10-B9, B8,10-B4, B1,3-B4, B9-B4; ^{13}C NMR (50.3 MHz, CD_2Cl_2) (ppm, Hz) 116.7 (s, C12), 39.2 (d, C6, J_{CH} = 170), 27.1 (t, C11, J_{CH} = 137), 11.5 (d, C5, C7, J_{CH} = 170); ^{1}H NMR (200 MHz, CD_2Cl_2 ^{11}B spin decoupled) (ppm, Hz) 4.1 (BH), 2.9 (BH), 2.8 (CH, d, J_{HH} = 7.0), 2.1 (BH, t, $J_{HH(br)}$ = 8.6), 2.0 (BH), 1.3 (CH), 0.2 (BH), -0.1 (CH, t, J_{HH} = 7.0), -3.0 (BHB); exact mass calcd for $^{12}C_5{}^{11}B_7{}^{14}N^1H_{14}$ 165.1778, found 165.1780; mp 71-72 °C.

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(9) The formal $R_4C_3B_2H^{3-}$ anions derived from the diborole heterocycles $R_4C_3B_2H$ developed by Siebert also fall into the arachno electronic class, but the neutral *arachno*-$R_4C_3B_2H_4$ is not known. See, for example: (a) Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 943-958. (b) Siebert, W. *Pure Appl. Chem.* **1987**, *59*, 947-954. (c) Siebert, W. *Pure Appl. Chem.* **1988**, 1345-1348. (d) Attwood, A. T.; Fonda, K. K.; Grimes, R. N.; Brodt, G.; Hu, D.; Zenneck, U.; Siebert, W. *Organometallics* **1989**, *8*, 1300-1303. (e) Brodt, G.; Kuhlmann, T.; Siebert, W. *Chem. Ber.* **1989**, *122*, 829-831.

(10) Structural data: space group $P2_12_12_1$, a = 6.895 (1) Å, b = 9.881 (1) Å, c = 14.798 (5) Å, V = 1008.1 (6) Å^3, Z = 4, and d_{calcd} = 1.079 g/cm^3. The structure was solved by direct methods. Refinement was by full-matrix least-squares techniques based on F to minimize the quantity $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Non-hydrogen atoms were refined anisotropically, and hydrogen atom positions were refined with constant isotropic B's of 6.0 Å^2. Refinement converged to R_1 = 0.053 and R_2 = 0.062.

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