7,7,8,8-Tetra(2-thienyl)-*p*-quinodimethanes. New Electron-Donating *p*-Quinodimethanes

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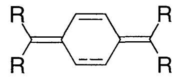
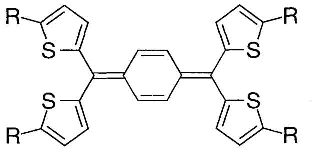
Tetra(2-thienyl)-*p*-quinodimethanes, a new family of electron-rich *p*-quinodimethane, show good amphoteric redox properties: in particular, the tetrakis(methylthio) derivative is an excellent electron-donor to form charge transfer complexes of good electrical conductivity.

While a good number of electron-accepting *p*-quinodimethanes and analogs represented by tetracyano-*p*-quinodimethane (TCNQ) **1** have been synthesized, relatively few electron-donating *p*-quinodimethanes have been known except for 2,2'-*p*-quinobis(1,3-dithiole) **2** and its derivatives.[1,2] We here report on the synthesis and properties of tetra(2-thienyl)-*p*-quinodimethane (TTQ) **3a** and its derivatives **3b**,**c**,**d**, new electron-rich *p*-quinodimethanes. Their redox properties, particularly amphoteric properties, are much superior to that of tetraphenyl-*p*-quinodimethane (Thiele's hydrocarbon) **4**[3] and are approaching that of **2** owing to the stabilizing effect of 2-thienyl group on both carbocations and carbanions.[4]



1: R = CN
4: R = Ph



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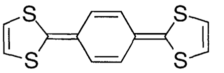
a: R = H **b**: R = Me
c: R = SMe **d**: R = TMS



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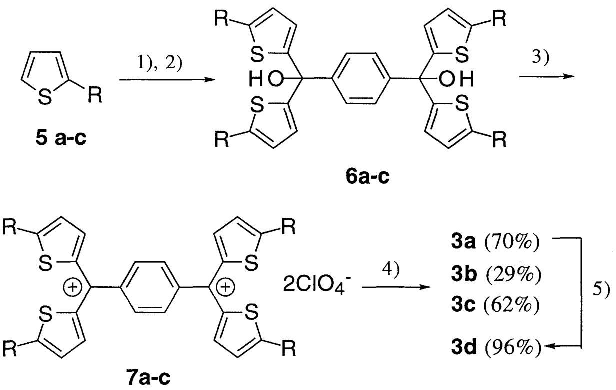


Reagents and Conditions: 1) *n*-BuLi/THF, -70 °C, 2) 0.2 eq. dimethyl terephthalate, -70-0 °C, 3) 60% $HClO_4/Ac_2O$, <5 °C, 4) Zn/THF, 0 °C, 5) LDA/TMSCl/THF, -70-0 °C.

Scheme 1.

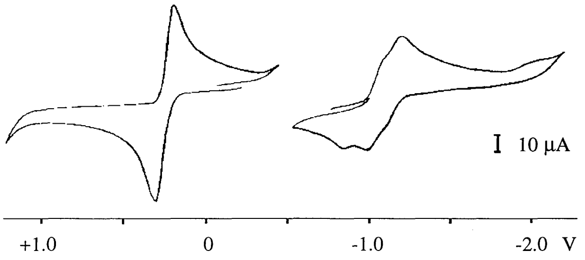


Figure 1. Cyclic voltammograms of **3C**.

Reaction of dimethyl terephthalate with five equivalents of 2-thienyllithiums **5a**-**c** gave the diols **6a**-**c** in 93-98% yield (Scheme 1). Treatment of **6a**-**c** with 60% perchloric acid in acetic anhydride below 5 °C followed by addition of ether precipitated the dication salts **7a**-**c** as stable, green to black fine crystals in high yields. Reduction of **7a**-**c** with zinc powder (20 equivs) in tetrahydrofuran at 0 °C afforded TTQs **3a**-**c** in 29-70% yield. TTQ **3a** itself can be used as a synthon for a certain kind of derivatives: although attempted lithiation of **3a** with alkyl- and aryl-lithiums have failed probably owing to electron transfer reaction from the organolithiums to **3a** forming its anion radical,[5] treatment of **3a** with lithium diisopropylamide (5 equivs), a weaker base than aryllithium, in the presence of excess amount of chlorotrimethylsilane afforded tetrakis(trimethylsilyl) TTQ **3d** in 96% yield.[6]

TTQs **3a**-**d** are highly colored substances showing strong absorptions in visible region (λ_{max} = 493 nm of **3a** to 619 nm of **3c**; Table 1), fairly stable in solid state, but rather labile in solutions. A reason for the lability in solutions is their high sensitivity to acids: addition of a small amount of trifluoroacetic acid to a dichloromethane solution of **3a** cleanly formed monocation **8**,[7] reflecting high tendency of aromatization of the quinodimethane skeleton and good stability of dithienylphenylmethyl cation. Thus, ^{1}H-NMR spectra of **3a**-**d** in chloroform show line-broadening more or less probably due to equilibrium with a small amount of protonated species. Addition of a small amount of tertiary amines as 1,4-diazabicyclo-[2.2.2]octane (DABCO) gave sharp signals.[8]

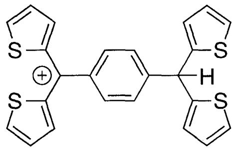
Favorable substituent effects of the 2-thienyl groups are most obvious in their redox properties. Cyclic voltammetry of **3a**-**d** show one reversible (for **3c**) or pseudo-reversible (for **3a**,**b**,**d**) oxidation wave and two reversible reduction waves at appreciably low potentials (Figure 1 for **3c** and Table 1). The oxidation waves involve two-electron transfer in consonance with good stability of dications **7a**-**c**. Differences between the oxidation and the first reduction potentials of **3a**-**d** (E^1sum = 1.22-1.66 V) are significantly smaller than that of **4** (E^1sum = 2.16 V)[9] and even smaller than thienoquinoid analog **9**[10] (E^1sum = 2.06 V)[9]. Besides the improved amphotericity, most noteworthy is highly electron-donating property of tetrakis(methylthio) compound **3c** whose oxidation potential (+0.25 V vs. Ag/AgCl) is lower than that of tetrathiafulvalene (+0.36 V)[9], though seems a little higher than that of **2**. In fact, **3c** formed black crystalline charge transfer (CT) complexes with I_2 (D:A = 1:2), TCNQ (1:1), and

Table 1. Selected physical data of **2a**, **2b**, **9a**, and **9b**

	^{1}H-NMR (δ/ppm)^a	UV-Vis. (λ_{max}/nm (log ε))^b	Redox Potentials (V)^c			
			E_{ox}	E_{red}^1	E_{red}^2	$E^1{}_{sum}{}^d$
3a	7.38 (dd, J = 5.0, 1.3 Hz, 4H), 7.16 (dd, 3.6, 1.3 Hz, 4H), 7.14 (s, 4H), 7.06 (dd, J = 5.0, 3.6 Hz, 4H)	493 (4.68), 322 (4.17), 234 (4.31)	+0.49^e	-0.89	-1.20	1.38
3b	7.12 (s, 4H), 6.95 (d, J = 3.6 Hz, 4H), 6.70 (dd, J = 3.6, 1.0 Hz), 2.49 (s, 12H).	515 (4.65), 336 (4.21), 236 (4.36)	+0.42^e	-0.94	-1.25	1.36
3c	7.15 (s, 4H), 7.01 (brd, 4H), 6.97 (brd, 4H), 2.53 (s, 12H).	619 (4.12), 548 (4.59), 362 (4.21), 278 (4.31)	+0.25	-0.97	-1.14	1.22
3d	7.16 (br, 12H), 0.31 (s, 36H)	517 (4.79), 335 (4.41), 239 (4.49)	+0.57^e	-1.09	-1.38	1.66
4	7.22 - 7.32 (m, 20H), 6.77 (s, 4H)	424 (4.57), 275 (4.08)	+0.74^e	-1.42	-1.64	2.16
9	ref. 10	ref. 10	+0.75	-1.34	-1.60	2.09

^{a} In $CDCl_3$ containing a small amount of DABCO at 30 °C (270 MHz),. ^{b} In CH_2Cl_2. ^{c} V vs Ag/AgCl in 0.1 M nBu_4NClO_4/DMF (Fc/Fc+ = +0.49 V), sweep rate 100 mV/sec, 20 °C. ^{d} $E^1{}_{sum} = E_{ox} + (-E_{red}{}^1)$. ^{e} Peak potential.

TCNQ-F_4 (2:1), which showed fairly good electrical conductivity (3.5 x 10^{-3}, 4.8 x 10^{-4}, and 3.1 x 10^{-2} S cm^{-1}, respectively).[11,12]



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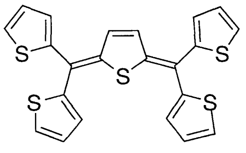

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5 Upon addition of alkyllithiums to THF solutions of **3a** at low temperature, the solutions turned to deep purple from red and addition of electrophiles mostly resulted in the recovery of **3a**.

6 Lithium diisopropylamide is strong enough for lithiation of thiophenes in equilibrium,[13] and therefore the present tetrafold trimethylsilylation probably proceeds through stepwise lithiation and trimethylsilylation.

7 **8**: ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 9.06 (dd, J = 4.8, 1.0 Hz, 2H), 8.16 (br. s, 2H), 7.82 (t, J = 4.6 Hz, 2H), 7.73 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.34 (dd, J = 5.2, 1.2 Hz, 2H), 7.04 (dd, J = 5.2, 3.4 Hz, 2H), 6.96 (m, 2H), 6.15 (s, 1H); ^{13}C-NMR (67.8 MHz, CD_2Cl_2) δ 175.31, 158.27, 155.83, 150.13, 145.25, 144.62, 138.08, 137.30, 135.31, 130.26, 127.53, 127.38, 126.16, 47.89.

8 Sharp NMR signals are also obtained in C_6D_6.

9 Measured under the same conditions for **3a-d** (see Table 1).

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11 The D:A ratios were determined by elemental analyses and the electrical conductivity was measured on compressed pellets by two-probe technique at room temperature.

12 The nitrile stretching frequency of the TCNQ-F_4 complex (2194 cm^{-1}) in the IR spectrum is comparable to those of the CT complexes of TCNQ-F_4 with dibenzotetrathiafulvalene and tetraselenafulvalene.[14]

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