Tetra(2-thienyl)butatrienes: New Butatriene Derivatives with Highly Amphoteric Multistage Redox Properties and a Short Central Double Bond

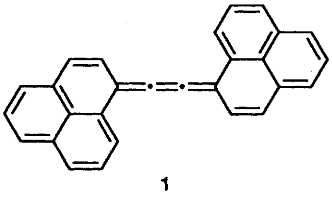
Takeshi Kawase, Seiji Muro, Hiroyuki Kurata and Masaji Oda*

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Tetra(2-thienyl)butatrienes **2a–c** show highly amphoteric redox properties; an X-ray structure of the tetrakistrimethylsilyl derivative **2b** reveals a short bond length for the central double bond.

A number of butatrienes are known, but so far only one derivative **1** has shown highly amphoteric redox properties.[1] This excellent electrochemical characteristic of **1** was attributed to the unusual electronic properties of the two terminal phenalenyl groups which can exist in three electronically stable oxidation states. However, the instability of **1** seems to have limited further studies on it and related compounds.

We report here the synthesis and some properties of tetra(2-thienyl)butatriene and its derivative **2a–c** which show good stability as well as highly amphoteric redox properties. In addition, a short bond length for the central double bond was found for tetrakistrimethylsilyl derivatives **2b**.



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Dichloromethylenation of di(2-thienyl) ketone[2] with Ph_3P–CCl_4[3] gave 1,1-dichloro-2,2-di(2-thienyl)ethene **3a**[4] in good yield (Scheme 1). Compound **3a** turned out to be a versatile synthon for tetrathienylbutatrienes, because it is regioselectively lithiated at either the thienyl group or the dichloroethene unit by choice of lithiating agent. Thus, lithium diisopropylamide (LDA) selectively dilithiated the thienyl group of **3a** to lead to a variety of derivatives such as **3b** and **3c** by quenching with electrophiles.† Lithiation of **3a–c** with n-butyllithium below −90 °C and subsequent treatment with copper(I) cyanide afforded the corresponding tetrathienyl

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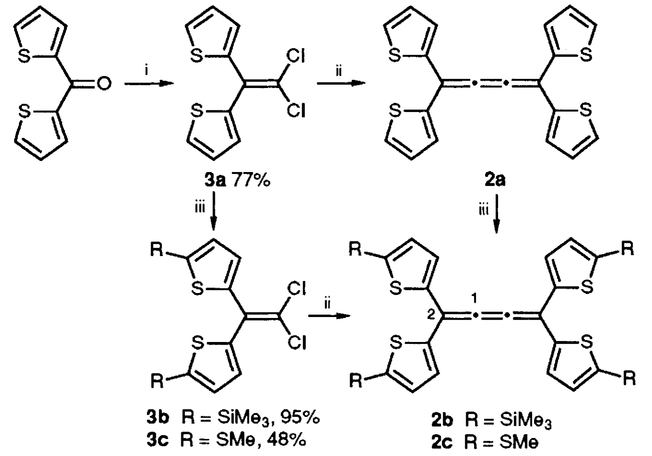
† Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds.



Scheme 1 *Reagents and conditions*: i, Ph_3P, CCl_4, reflux, 12 h; ii, Bu^nLi (1 equiv.), tetrahydrofuran (THF), $<-90\,°C$, 30 min., then CuCN (0.5 equiv.), then allowed to warm at room temp., 12 h; iii, excess of LDA, THF, $-50\,°C$, then Me_3SiCl or MeSSMe

Table 1 Selected spectroscopic data of **2a–c** and $Ph_2C{=}C{=}CPh_2$ **4**

	^{13}C NMR chemical shift,[a] δ C-1[d]	^{13}C NMR chemical shift,[a] δ C-2[d]	Raman,[b] $\nu_{C=C}/cm^{-1}$	UV-VIS,[c] λ_{max}/ nm(log ε)
2a	140.53	108.95	2035	501 (4.54)
2b	139.90	108.91	2023	530 (4.79)
2c	138.89	108.50	2032	562 (4.59)
4	151.9[e]	122.6[e]	2037	419 (4.51)

[a] $CDCl_3$ at 67.5 MHz. [b] KBr disk. [c] In CH_2Cl_2; longest absorption max. [d] For numbering, see Fig. 1. [e] Ref. 6.

Table 2 Cyclic voltammetric data (*E*/V) for **2a–c** and related compounds

	E_2^{ox}	E_1^{ox}	E_1^{red}	E_2^{red}	E_1^{sum}	E_2^{sum}
2a[a]		0.98[c,d]	−1.15	−1.64	2.13	2.62
2b[a]		1.01[c,d]	−1.00	−1.40	2.01	2.47
2c[a]		0.54[c]	−0.99	−1.29	1.53	1.83
1[b]	0.78	0.51	−0.83	−1.21	1.34	1.99
4[a]		1.25[c,d]	−1.42	−1.76	2.67	3.01

[a] Measured *vs.* Ag/AgCl in dimethylformamide using Bu_4NClO_4 (0.1 mol dm^{-3}) as supporting electrolyte at $-50\,°C$; sweep rate = 100 mV s^{-1}. [b] Ref. 1. [c] Two electron wave. [d] Peak potentials.

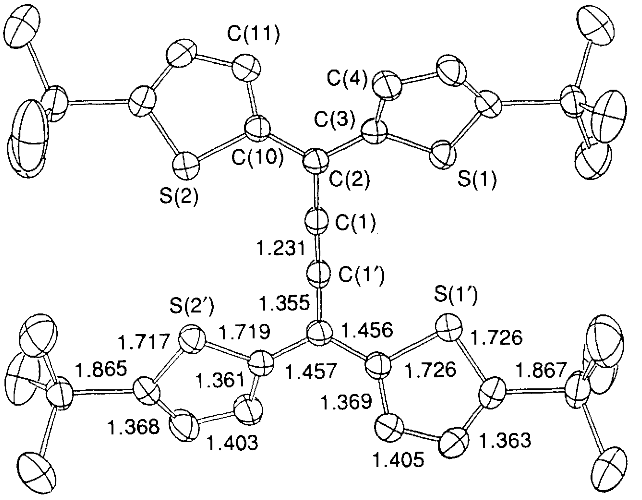


Fig. 1 ORTEP drawing of **2b**. Thermal ellipsoids are 50% probability contours. Important bond lengths (Å) are shown.

butatrienes **2a–c** by reductive coupling[5] as fairly stable crystalline compounds [**2a**, m.p. 199–199.5 °C, 48%; **2b**, m.p. 155–156 °C, 50%; **2c**, 160 °C (decomp.), 40% yield]. Tetralithiation of **2a** is also partially successful with LDA giving **2b** after trimethylsilylation (26%).

Table 1 lists selected spectroscopic data of **2a–c** and tetraphenylbutatriene **4**.[6] In the visible region, the thienylbutatrienes, **2c** in particular, absorb at appreciably longer wavelengths than **4**, and they are red to reddish purple. The ^{13}C chemical shifts of the cumulenic carbons of **2a–c** are much higher than those of **4** probably reflecting the stronger electron-releasing ability of the 2-thienyl than the phenyl group.

The most notable feature of **2a–c** is their highly amphoteric redox properties showing reversible cyclic voltammograms (Table 2). The 2-thienyl groups decrease both the oxidation and reduction potentials; thus, the numerical sums of E^{ox} and E^{red}, *i.e.*, $E^{sum} = E^{ox} + (-E^{red})$, which is an experimental measure for estimating the extent of amphoteric redox properties,[7] are much smaller than those of **4**. In particular, the E^{sum} values of **2c** are comparable to those of **1**.

The tetrathienylbutatriene **2b** formed good single crystals (red prisms from hexane) for X-ray crystallography, and its molecular structure is shown in Fig. 1.‡ The molecule has D_2 symmetry in the solid state with the thiophene rings being twisted by 30.5 and −13.3° out of the butatriene plane. The sulfur atoms of the thiophene rings at each end of the molecule face each other with distance of 3.89 Å, which is longer than the corresponding van der Waals distance (3.70 Å). The length of central double bond (1.231 Å) is shorter, while the side double bonds (1.355 Å) are slightly longer, than those of **4** (1.259 and 1.348 Å[8]) and other butatrienes.[9]

In conclusion, tetra(2-thienyl)butatrienes **2a–c** show good amphoteric multistage redox properties owing to the amphoteric nature of the thiophene unit, and we are further elaborating butatrienes with novel structures and good redox properties.

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‡ *Crystal data* for **2b**: $C_{32}H_{44}S_4Si_4$, M_r = 669.28, monoclinic, space group $P2_1/n$ (No. 14), a = 8.982(1), b = 18.514(2), c = 11.669(1) Å, β = 99.98(1)°, U = 1911.3(4) Å^3. Z = 2, D_c = 1.163 g cm^{-3}; Mo-Kα (λ = 0.71069 Å); 29.4° < 2θ < 30.0°; $R(R_w)$ = 0.040 (0.044) for 3181 unique reflections with $F > 3\sigma(F)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.