Bipolarons

DOI: 10.1002/anie.201306969

Multiple Reduction of 2,5-Bis(borolyl)thiophene: Isolation of a Negative Bipolaron by Comproportionation**

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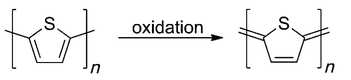
Organic semiconducting oligomers and polymers consisting of π-conjugated aromatic heterocycles, such as thiophenes, have emerged as highly attractive materials owing to their tuneable electronic and optical properties.[1] In such systems, chemical or electrochemical doping is known to increase the electronic conductivity by inducing characteristic structural distortions within the polymer backbone, such as a change from an aromatic ($\mathbf{1}_{\text{aromatic}}$) to a quinoidal ($\mathbf{1}_{\text{quinoidal}}$) structural motif (Scheme 1).[2]



$\mathbf{1}_{\text{aromatic}}$ $\mathbf{1}_{\text{quinoidal}}$

Scheme 1. Structural change in oligothiophenes caused by oxidation.

The specific nature of how the extended π-bond system is altered in this redox process is of great interest, as these changes directly affect the conductive and optical properties of the polymer. Intensive theoretical and experimental investigations, often on well-defined model systems, have led to a good understanding of the charge transport mechanism, in which so-called polarons and bipolarons, charged species generated by one- and two-electron oxidation/reduction, respectively, are thought to play a pivotal role.[3] Although numerous accounts of positive bipolarons derived from two-electron oxidation of conjugated molecules, such as oligothiophenes or oligoanilines, provided detailed information on the structural consequences of accommodating the excess charge, corresponding reports on dianions remain scarce.[3c,g,n,p,q,s]

Inspired by the work on bis(triarylamine) dications, which have been described as positive bipolarons, we sought to prepare an isoelectronic analogue by two-electron reduction of a thiophene substituted with two highly Lewis acidic, antiaromatic borolyl moieties.[3j,m,o,p,4] Based on the character of the molecular orbitals of related diboryl-substituted thiophenes, a substantial quinoidal bonding pattern in the bridging thiophene unit can be anticipated by populating the LUMO with two electrons.[5] Herein, we present the synthesis and reduction of 2,5-bis(borolyl)thiophene (**2**) and describe the electronic and structural characteristics of a negative bipolaron ($[\mathbf{2}]^{2-}$).

Bis(borole) **2** was synthesized by tin–boron exchange between 2,5-bis(dibromoboryl)thiophene and two equivalents of 1,1-dimethyl-2,3,4,5-tetraphenylstannole. ^{11}B NMR spectroscopic analysis of the reaction showed clean formation of **2** with a boron resonance at 60.0 ppm, which is slightly shifted to lower frequencies compared to 1,2,3,4,5-pentaphenylborole (**3**) ($\delta = 65.4$ ppm) owing to the more electron-rich thiophene group at the boron atom.[6] After recrystallization from toluene, compound **2** was obtained as a green solid in 61 % yield. The green color of **1** is rather surprising given that pentaarylboroles are usually deep blue in color (**3**: $\lambda_{\max} = 560$ nm; $\varepsilon = 361\ \mathrm{L\,mol^{-1}\,cm^{-1}}$).[6] It can be attributed to two distinct absorption bands in the UV/Vis spectrum, one at $\lambda_{\max} = 566$ nm ($\varepsilon = 752\ \mathrm{L\,mol^{-1}\,cm^{-1}}$) and the other at $\lambda_{\max} = 395$ nm ($\varepsilon = 23\,900\ \mathrm{L\,mol^{-1}\,cm^{-1}}$; see the Supporting Information). Interestingly, X-ray crystallographic analysis of **2** revealed a nearly coplanar arrangement between the two borole rings and the thiophene spacer with interplanar angles of 10.4(1)° and 11.2(1)°, respectively (Figure 1). A similar conformation of the five-membered rings, which can be rationalized by π–π interactions between the antiaromatic and aromatic rings, has been observed for monoborolyl-substituted thiophene, furan, and pyrrole compounds.[7]

The phenyl groups of both borolyl moieties display the characteristic propeller-like arrangement and the $\mathrm{BC_4Ph_4}$ scaffold reveals bond lengths consistent with those of other neutral boroles.[8] Interestingly, the bond lengths B1−C5 [1.532(4)], C6−C7 [1.395(4)], and C8−B2 [1.535(4)] are significantly shortened compared to those in symmetrically 2,5-diboryl-substituted thiophenes and lie in the range between B−C/C−C single and double bonds (Table 1).[9] Accordingly, the C5−C6 [1.391(4)] and distances C7−C8 [1.390(4)] are elongated with respect to the typical values for carbon–carbon double bonds (1.32 Å).[10] This bond-length equalization in the thiophene ring and the nearly coplanar alignment of the five-membered ring systems suggest that the

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[**] This study was performed within the framework of the Graduate College GRK 1221. C.W. thanks the Fonds der Chemischen Industrie for a fellowship. We thank Dr. Charles Gould for magnetic measurements.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201306969.

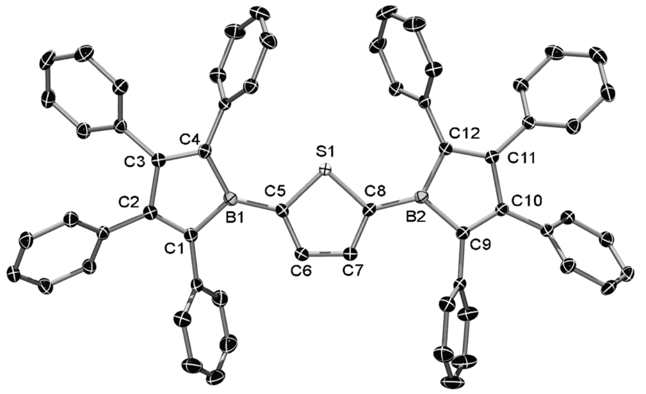


Figure 1. Solid-state structure of **2** determined by single-crystal X-ray diffraction studies. Hydrogen atoms are omitted for clarity; ellipsoids are set at 50% probability. See Table 1 for selected bond lengths and angles.[18]

Table 1: Selected bond lengths [Å] and torsion angles [°] for **2** and $[CoCp^*_2]_2$[**2**].

Bond	**2**	$[CoCp^*_2]_2$[**2**]
B1–C5	1.532(4)	1.523(4)
B2–C8	1.535(4)	1.509(4)
C5–C6	1.391(4)	1.417(3)
C6–C7	1.395(4)	1.374(3)
C7–C8	1.390(4)	1.411(3)
	Interplanar torsion angles:[a]	
B1/S1	10.4(1)	11.9(2)
B2/S1	11.2(1)	6.3(2)
B1/B2	15.0(1)	6.1(2)

[a] Plane B1: B1-C1-C2-C3-C4; Plane S1: S1-C5-C6-C7-C8; Plane B2: B2-C9-C10-C11-C12.

strongly Lewis acidic borolyl groups are withdrawing electron density from the electron-rich thiophene ring. These conclusions are supported by the computed barriers for the rotation of one borole ring out of the thiophene plane in a simplified model system **2′**, in which the phenyl rings have been substituted by hydrogen atoms. The maximum of the barrier for the rotation of one borole ring out of coplanarity to an orthogonal conformation is around 9 $kcal\,mol^{-1}$. This result points to a significant amount of conjugation between the contrasting ring systems in the neutral state (see the Supporting Information for further details).

To study the redox properties of bis(borole) **2**, a cyclic voltammogram was recorded in THF, in which it forms a stable adduct (see the Supporting Information for details). Two distinct sets of irreversible, broad reduction waves at $E_{pc} = -2.53$ V and $E_{pc} = -3.08$ V indicate the formation of a dianion $[\mathbf{2}]^{2-}$ and tetraanion $[\mathbf{2}]^{4-}$, respectively. Slightly better resolved reduction events were obtained by a square-wave voltammetry experiment, which displayed a stepwise reduction to the dianion $[\mathbf{2}]^{2-}$ via a radical monoanion intermediate $[\mathbf{2}]^{\bullet-}$, thus suggesting some degree of charge delocalization between the two borolyl fragments across the thiophene bridge.[11] It is important to note that, owing to the formation of a Lewis adduct with THF in solution, the first redox potential is shifted to significantly more negative potentials compared to 1-ferrocenyl-2,3,4,5-tetraphenylborole (**7**; $E_{1/2} = -1.96$ V).[12]

Based on these results, we were especially interested in the isolation and electronic structure of species $[\mathbf{2}]^{2-}$ in which, formally, two borolyl radical centers are linked by the thiophene unit. Depending on the coupling of the unpaired electrons through the thiophene bridge, either a closed-shell or open-shell biradical structure can be expected. In a previous study, we have shown that decamethylcobaltocene ($[CoCp^*_2]$; $E^0(Fc/Fc^+) = -1.9$ V) is capable of reducing neutral boroles to the corresponding radical anions.[4h] Therefore, we opted to access the dianion $[\mathbf{2}]^{2-}$ by the same approach. Indeed, two-electron reduction of **2** is successful in benzene at ambient temperature by using two equivalents of $[CoCp^*_2]$. After standing at this temperature for 12 h, we obtained analytically pure black crystals of $[CoCp^*_2]_2$[**2**] in 31% yield. The molecular structure determined by X-ray analysis reveals two bis(borolyl)-substituted thiophene dianions and four $[CoCp^*_2]$ cations in the unit cell (Figure 2). The five-membered rings of $[\mathbf{2}]^{2-}$ lie approximately in the same plane, with slightly smaller torsion angles than **2**.

The interplanar torsion angles formed by the two borolyl planes and the thiophene plane are 11.9(2)° and 6.3(2)°, whereas the two borolyl moieties include an angle of 6.1(2)°. Remarkably, the bond length pattern in the thiophene unit of $[CoCp^*_2]_2$[**2**] exhibits a quinoidal structure with lengthened C5–C6 and C7–C8 bonds and shortened C6–C7 bonds as well as shortened exocyclic B1–C5 and B2–C8 bonds. The bond-length alternation (BLA) between double and single bonds in the thiophene ring of $[CoCp^*_2]_2$[**2**] (ca. 0.04 Å) resides below the value of 0.06 Å for fully quinoidal thiophene derivatives.[13] However, the BLA of $[CoCp^*_2]_2$[**2**] is more distinct compared to the singlet dicationic bis(triarylamine) bipolaron reported by Barlow and co-workers with a BLA of about 0.02 Å in the thiophene unit.[3p]

Although we were able to isolate crystalline material of the dianion from the reaction of **2** with decamethylcobaltocene, further spectroscopic characterization of $[CoCp^*_2]_2$[**2**]

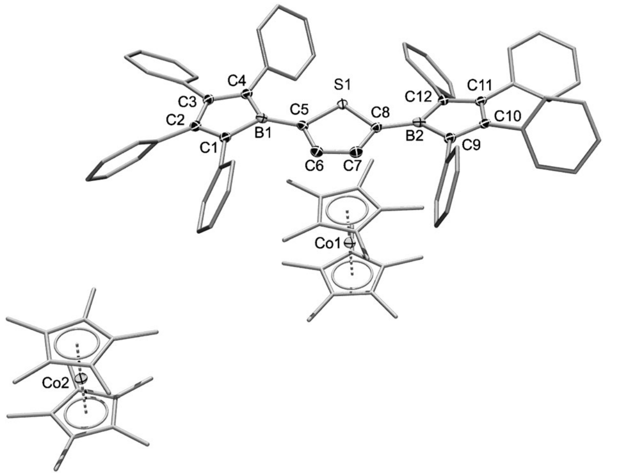
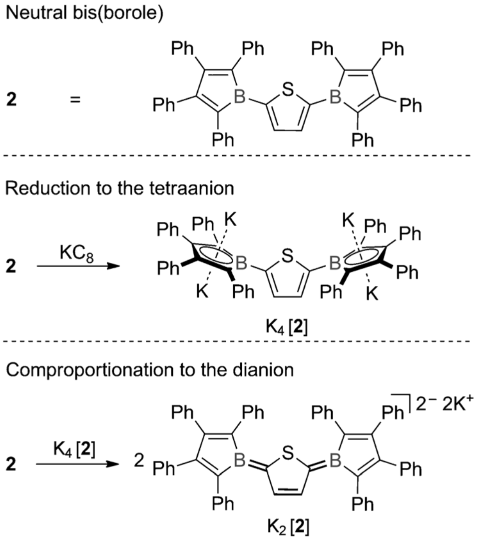


Figure 2. Solid-state structure of $[CoCp^*_2]_2$[**2**] as determined by single-crystal X-ray diffraction studies. Hydrogen atoms are omitted for clarity; ellipsoids are set at 50% probability. For clarity, the ellipsoids of the phenyl and Cp* groups are omitted. See Table 1 for selected bond lengths and angles.[18]

was hampered owing to its instability in solution. In an effort to stabilize the negative charges in the system more effectively, we prepared a magnesium salt from the reaction of **2** with magnesium anthracene ($MgC_{14}H_{10}$). Although the synthesis of Mg[**2**] is successful, the reaction is not clean and gives as by-product the monoradical $Mg_{0.5}$[**2**], which was unambiguously identified as a delocalized system by EPR and UV/Vis spectroscopy and an independent synthesis (see the Supporting Information for details).[4c,d,f]

Because of difficulties in the clean preparation of the desired dianion $[\mathbf{2}]^{2-}$, we carried out a comproportionation experiment with the neutral bis(borole) **2** and its fully reduced aromatic tetraanion $[\mathbf{2}]^{4-}$ (Scheme 2). To this end, we synthesized K_4[**2**] by reduction with KC_8, as it is well-established that the antiaromatic borole moiety can be reduced with an excess of strong reductants (Li, Na, K, KC_8) to their corresponding aromatic dianions.[4h,12,14] K_4[**2**] is stable in solution and could be characterized by means of multinuclear NMR and UV/Vis spectroscopy (see the Supporting Information for details), indicating localized negative charge densities on the borolyl rings. Treatment of a THF solution of K_4[**2**] with an equimolar solution of **2** in THF leads to an immediate color change to dark green.

The formation of K_2[**2**] was confirmed by a strong absorption maximum centered at $\lambda_{max} = 800$ nm ($\varepsilon = 40400\ \mathrm{L\,mol^{-1}\,cm^{-1}}$) in the UV/Vis/NIR absorption spectrum (Figure 3), which is diagnostic for a conjugated closed-shell molecule. This can be compared to spectroelectrochemical investigations by Kaim et al. for a 4,4′-bis(dimesitylboryl)biphenyl dianion, which exhibits an absorption centered at 736 nm ($\varepsilon = 67700\ \mathrm{L\,mol^{-1}\,cm^{-1}}$).[3g] K_2[**2**] shows an ^{11}B NMR signal ($\delta(^{11}B) = 29.5$ ppm) that is slightly shifted to higher frequencies compared to the resonance found for K_4[**2**] ($\delta(^{11}B) = 26.1$ ppm) and strongly shifted to lower frequencies compared to the neutral bis(borole) **2** ($\delta(^{11}B) = 60.0$). A comparison of the ^{1}H NMR spectra of **2**, K_2[**2**], and K_4[**2**] clearly supports the notion that the comproportionation reaction is a clean and efficient pathway to synthesize K_2[**2**] (90% yield). The dianion salt could also be isolated in pure form as a dark green solid containing one molecule of THF, as judged by elemental analysis and ^{1}H NMR spectroscopy.



Scheme 2. Synthetic approaches to the potassium compounds of the tetraanion, K_4[**2**], and the bipolaron, K_2[**2**].

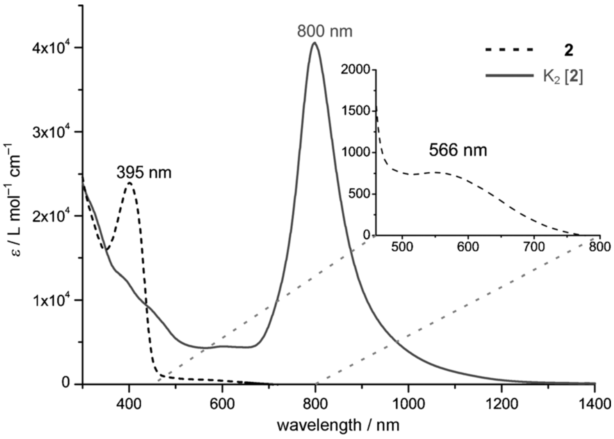


Figure 3. UV/Vis/NIR spectrum of **2** (dashed line) in CH_2Cl_2 at a concentration of 116 μmol L^{-1} and bipolaron K_2[**2**] (solid line) in THF at a concentration of 49.0 μmol L^{-1}.

Single-crystal X-ray diffraction confirmed the expected quinoid structure of K_2[**2**], which is consistent with the structural data for $[CoCp^*_2]_2$[**2**] (see the Supporting Information for details). The red-shift in the absorption spectra by 234 nm from the neutral **2** to the dianion salt K_2[**2**] demonstrates the lowering of the HOMO–LUMO energy gap by redox doping (Figure 3). Furthermore, magnetic susceptibility measurements at room temperature using the Evans method corroborate the diamagnetic nature of the dianion.[15]

The experimental evidence for the singlet ground state discussed above was augmented by CASPT2/aug-cc-pVDZ calculations for the model system $[\mathbf{2'}]^{2-}$ and B3LYP/aug-cc-pVDZ calculations for $[\mathbf{2}]^{2-}$, which predicted a vertical singlet–triplet gap of 0.59 eV for $[\mathbf{2'}]^{2-}$ and 0.27 eV for $[\mathbf{2}]^{2-}$ (see the Supporting Information for details). Because of the sulfur atom, significant singlet–triplet mixing could occur, which is due to spin–orbit interaction. The elements of the spin–orbit coupling matrix for thiophene have been evaluated by Marian et al., which we used as an approximation for the coupling elements of $[\mathbf{2}]^{2-}$.[16] As only one of the two open-shell MOs involved in the triplet state has a significant coefficient on the sulfur atom, the coupling is expected to be well below 50 cm^{-1} (see the MO scheme in the Supporting Information).[17] Consequently, the amount of triplet admixture is negligible (< 0.05%) and a diamagnetic character for the dianion is expected. In a [2,2]-CASSCF[15] calculation, the population numbers of the HOMO (1.65) and LUMO (0.35), as well as the weight of the doubly excited configuration (18%), indicate that the system is mainly closed-shell in nature, with a rather weak biradical character. Although an orthogonal configuration of the borole rings would significantly lower the charge repulsion, the rotational barrier for the model system $[\mathbf{2'}]^{2-}$ in the singlet state is higher than for **2′** (see the Supporting Information). In line with the experimental data are also calculations of the excited states of both $[\mathbf{2'}]^{2-}$ and $[\mathbf{2}]^{2-}$ that predict one strongly absorbing band, which is significantly red-shifted (see the Supporting Information for more details).

In summary, we have studied in detail the reduction behavior of 2,5-bis(borolyl)thiophene (**2**), a conjugated acceptor–π–acceptor system. Whereas single-electron reduction gives the monoradical anion $[\mathbf{2}]^{\bullet-}$, two-electron reduction yields the diamagnetic dianion $[\mathbf{2}]^{2-}$ featuring a quinoidal structural motif across the thiophene spacer in the solid state. The dianion was also successfully prepared as the potassium salt by a comproportionation reaction between **2** and the tetraanion salt $K_4[\mathbf{2}]$. Along with the structural characterization by X-ray diffraction and NMR spectroscopy, the closed-shell singlet configuration is further identified by a diagnostic strong absorption maximum in the near-IR region ($\lambda_{max} = 800$ nm). Calculations support the singlet ground state and description of the dianion as a negative bipolaron, in which the two excess electrons are spin-paired across the thiophene bridge.

Received: August 8, 2013

Keywords: bipolarons · boroles · conjugation · quinoidal structures · thiophene

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[18] CCDC 937544 (**2**) and CCDC 937545 ($[CoCp^*_2]_2[\mathbf{2}]$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.