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Bromophenyl substituted dithiafulvenes and tetrathiafulvalene vinylogues: synthesis, structure, and electronic properties

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ABSTRACT

Bis(bromophenyl) substituted tetrathiafulvalene vinylogues (TTFVs) were prepared via oxidative dimerization reactions of corresponding bromophenyl substituted dithiafulvene precursors. The synthesis of *ortho*-bromophenyl TTFVs led to the formation of an unexpected bis-spiro product, the structure of which was clearly elucidated by single crystal X-ray crystallography. Electronic and redox properties of the bromophenyl substituted dithiafulvenes, TTFV derivatives, and the related bis-spiro compound were investigated by UV–vis spectroscopic and cyclic voltammetric analyses. Detailed structure–property relationships have been discussed.

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Tetrathiafulvalene vinylogues (TTFVs) belong to an attractive branch in the field of widely studied tetrathiafulvalene (TTF) chemistry, owing to their excellent electron-donating properties and unique conformational switching behavior associated with the redox processes taking place in TTFV.¹ Taking advantage of their unique redox and structural properties, TTFV derivatives have been recently employed as functional building blocks in the preparation of various intriguing molecular materials and devices, ranging from molecular rods,² conjugated polymers,^{2,3} shape-persistent macrocycles,² redox-active ligands,⁴ and chemical sensors.⁵ Aryl substituted dithiafulvenes (DTF) are the commonly used precursors for the synthesis of TTFV scaffolds, following an oxidative dimerization mechanism⁶ as illustrated in Scheme 1.

In the neutral state, the steric crowding around the butadienylene moiety of a diaryl substituted TTFV tends to drive the molecule into a pseudo cisoid conformation.^{1g,5,7} Upon a two-electron oxidation process, the diaryl-TTFV is converted into a dication, in which significant Coulombic repulsion between the two dithiolium rings rotates the molecular skeleton into a transoid structure.^{1g,7,8} Diaryl-TTFVs that prefer a transoid structure in the neutral state are, however, scarcely known. Previously, Yamashita and co-workers^{7a} hypothesized that diphenyl-TTFVs would favor the transoid conformation when *ortho*-substituents were introduced to increase steric interactions. This argument is legitimate and sound, but has never been convincingly validated by concrete experimental evidence. Very recently, we reported the first example of a fully planar transoid bisnapthyl-TTFV, wherein the allylic strain in the

Scheme 1. General mechanism for the oxidative dimerization of an aryl-DFT to form a diaryl-TTFV product.

1-naphthyl group was enlisted to direct the conformation.⁹ This result hence led us to revisit the *ortho*-substitution effect on the properties of diphenyl-TTFV derivatives, since gaining better controllability over the conformation of TTFV offers an effective approach for rational design and fine tuning of new TTFV-based functional materials.

In this work, a series of bis(bromophenyl) substituted TTFV isomers **1a–c** was targeted (Fig. 1). These compounds were chosen as models in our study because of the relatively large atomic radius and high electronegativity of bromine, which are expected to impose significant steric and electronic (inductive) effects when





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Figure 1. Molecular structures and calculated torsion angles for bis(bromophenyl)substituted TTFVs **1a-c**.

bromine is placed at different positions of the phenyl group. Especially, our theoretical modeling study using the density functional theory (DFT) method has revealed that the torsion angle (θ) about the butadienylene segment in *ortho*-bromo isomer **1c** is considerably smaller than the other two isomers **1a** and **1b**.¹⁰ The conformational differences should in turn have a direct impact on the electronic and redox properties, and therefore would be ideal for systematic examination of the structure–property correlations in diphenyl substituted TTFVs.

The synthesis of bis(bromophenyl)-TTFVs was undertaken via the approaches described in Scheme 2. *p*-Bromobenzaldehyde (**2a**) was first subjected to an olefination reaction¹¹ with thione **3** in the presence of trimethylphosphite under heating, affording dithiafulvene **4a** in a yield of 60%. Compound **4a** was a yellow-colored crystalline solid. By careful recrystallization, good-quality crystals of **4a** suitable for single-crystal X-ray diffraction analysis were obtained (see Fig. 2). Compound **4a** then underwent an oxidative dimerization reaction at room temperature using iodine as the oxidant. After a reductive workup with aqueous Na₂S₂O₃, neutral TTFV **1a** was acquired in 54% yield. In the same way, *meta*-bromo



Scheme 2. Synthesis of bis(bromophenyl) substituted TTFVs 1a, 1b, and spiroderivative 5.



Figure 2. ORTEP plots (50% ellipsoid probability) of compounds **4a** and **5**: (A) front view of **4a**, (B) side view of **4a**, (C) front view of **5**, and (D) side view of **5**. Atomic color code: Gray = C, Green = S, Blue = Br, H represented by spheres.

isomer **1b** was synthesized using *m*-bromobenzaldehyde (**2b**) as the starting material. In the synthesis of *ortho*-bromo isomer **1c**. however, some unexpected result was attained. As shown in Scheme 2, dithiafulvene intermediate 4c was successfully prepared from o-bromobenzaldehyde (2c) via the trimethylphosphite-promoted olefination. Oxidative dimerization of 4c in the presence of iodine followed by treatment with Na₂S₂O₃ resulted in the formation of several products as manifested by thin-layer chromatographic (TLC) analysis. After flash column chromatographic separation and recrystallization, a yellow crystalline solid was isolated as the major product in yield of 50%. To our great surprise, the structure of this compound as characterized by NMR and MS analyses (see the Supplementary data) turned out to be the bis-spiro compound **5** (see Scheme 2) instead of the expected TTFV **1c**. ¹H NMR analysis of the crude reaction mixture suggested 1c was also formed, but only as a minor product. Pure 1c could not be isolated due to low yield and tremendous difficulty in separation.

Besides NMR and MS characterizations, single-crystal X-ray crystallography also offered conclusive evidence for molecular structural elucidation. Figure 2 shows the single-crystal structures of 4a and 5.12,13 The molecular structure of dithiafulvene precursor 4a assumes a slightly twisted conformation along the π -conjugated framework, with the torsion angle between the phenyl and vinylene units being 19.4°. It is noteworthy that the C-S-C bond angles in the dithiole ring are around 95°, which is consistent with the known fact that sulfur atom prefers to adopt a 90° bond angle.¹⁴ The relatively small C-S-C bond angle hence drives the dithiole five-membered ring to take a non-planar structure as can be clearly seen in Figure 2B. Of great interest is the unusual bis-spiro motif in compound 5. Compound 5 crystallized with two chemically identical molecules in the asymmetric unit, but for simplicity only one is shown in Figure 2. As a result of significant steric crowding in 5, the two dithiole and two phenyl rings surrounding the central tetrahydrothiophene unit are in a nearly perpendicular orientation. The two bromo groups are positioned in a trans configuration so as to reduce the net molecular dipole moment.

Compound **5** was at first speculated to result from the dicationic intermediate interacting with some kind of sulfur nucleophiles

immediately after the radical dimerization step as shown in Scheme 1. To test this hypothesis, control experiments were performed, where a large excess of dimethylsulfide (Me₂S) was added as a nucleophile to the dimerization reactions of **2a-c**. The results of these reactions were, however, no different from the normal dimerization reactions done previously. It was therefore reasonable to believe that the central sulfur bridge of 5 was introduced at the workup stage, where the reducing agent, Na₂S₂O₃, severed as the nucleophile. A tentative mechanism as outlined in Scheme 3 was proposed to account for this transformation. The fact that there were no cyclized products observed in the dimerization reactions of **2a** and **2b** indicates that this unique reactivity must originate from the ortho-bromo substitution effect. In the general oxidative dimerization mechanism (see Scheme 1), rapid deprotonation (elimination) would occur right after the dicationic intermediate is formed. In the case of *ortho*-bromophenyl substituted dithiafulvene, this dication can form double intramolecular Br...H hydrogen bonds, given the close distance between the acidic benzylic hydrogen and ortho-bromine. In the crystal structure of 5, the Br...H distance is observed at a close distance of 2.68 Å (Fig. 2D), which substantiates our hypothesis. The intramolecular hydrogen bonding thus provides stabilization to the dication and hinders the benzylic protons from deprotonation. In the following reductive workup process, nucleophilic addition of $[S_2O_3]^{2-}$ competes against the deprotonation pathway, leading to the formation of 5 as the major product.

The electronic properties of dithiafulvene precursors **4a–c**, TTFVs **1a,b**, and spiro-compound **5** were investigated by UV–vis spectroscopic analysis. Figure 3 compares the normalized UV–vis spectra of these compounds. It can be clearly seen that the absorption spectra of dithiafulvenes **4a–c** are nearly superimposable, and so are the spectra of TTFVs **1a** versus **1b**, suggesting that changing the bromo-substitution position has little effect on the electronic absorption properties.

The UV–vis spectrum of **5** shows a maximum absorption peak at 311 nm, which is considerably blueshifted in comparison with those of other compounds at ca. 357 nm. It is also notable that there is a significantly long absorption tail extending to ca. 470 nm in the spectrum of **5**.



Scheme 3. Proposed mechanism for a $Na_2S_2O_3$ involved cyclization pathway leading to product **5** after oxidative dimerization.



Figure 3. Normalized UV-vis absorption spectra of compounds 4a-c, 1a,b, and 5 measured in CH₂Cl₂ at room temperature.

Electrochemical redox properties of these compounds were studied by cyclic voltammetry (CV) and their cyclic voltammograms are shown in Figure 4. In Figure 4A, compound **4a** exhibits a pair of redox peaks at +0.78 V and +0.46 V, which are attributed to a single-electron oxidation process on the dithiafulvene unit and reduction of the resulting TTFV dication respectively.² The voltammogram of **4b** shows very similar patterns with the redox peaks slightly shifted to the positive potential direction. The voltammogram of *ortho*-bromo isomer **4c** shows a similar anodic peak at



Figure 4. Cyclic voltammograms for (A) bromophenyl dithiafulvene **4a–c**, and (B) TTFVs **1a,b** and bis-spiro compound **5**.

+0.81 V, but the profile of the reverse scan appears to be very complex, with a number of weak anodic peaks observable. Such a feature is indicative of chemical irreversibility and is likely due to some electrochemical reaction (EC) mechanisms (e.g., electrochemical hydrodehalogenation¹⁵); however, the exact mechanisms still await further investigations to clarify.

The voltammograms of TTFV isomers **1a** and **1b** feature a similar pair of reversible redox peaks that can be assigned to the known simultaneous two-electron transfer on the TTFV unit.² Unlike the case of dithiafulvene precursors, the different bromo-substitution positions in **1a** and **1b** result in noticeable differences in the redox potentials. As shown in Figure 4B, the redox peaks of *meta*-bromo isomer **1b** are shifted to the negative potential direction by ca. 40 mV relative to **1a**. The redox properties of **5** appear to be complex. Two anodic peaks are clearly seen at +0.63 and +1.05 V in the positive scan. On the reverse scan, several cathodic peaks emerge. Clearly, the *ortho*-bromo substitution induces some kinds of electrochemical reactions, the exact origins of which await further investigations to clarify.

In summary, we have prepared a series of bromophenyl substituted dithiafulvenes and subjected them to oxidative dimerization to form TTFV isomers for the study of structure–property relationships. In our work, *ortho*-bromo substitution has been found to give rise to abnormal redox properties and reactivity. Of particular note is that an unprecedented bis-spiro compound **5** was obtained and its formation could be rationalized on the basis of an intramolecular Br...H hydrogen bonding model. Our findings underscore the uniqueness of *ortho*-substitution effect on diphenyl-TTFV synthesis and related property tuning.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013. 06.077.

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 Crystal data for **4a**: C₁₂H₁₁BrS₄, M = 363.36, orthorhombic, a = 8.275(4) Å, b = 11.616(5) Å, c = 14.704(7) Å, α = 90.00°, β = 90.00°, γ = 90.00°, V = 1413.4(11) Å³, T = 123(2) K, space group P2₁2₁2₁, Z = 4, μ(Mo Kα) = 3.482 mm⁻¹, 14,131
- reflections measured, 3206 independent reflections, 3151 with $I > 2\sigma(I)$ ($R_{int} = 0.0444$). $R_1 = 0.0265$ ($I > 2\sigma(I)$), $wR(F^2) = 0.0584$ (all data). The goodness of fit on F^2 was 1.069. Flack parameter = 0.006(7). CDC 936355.
- 13. Crystal data for **5**: $C_{24}H_{22}Br_{2}S_{9}$, M = 758.79, triclinic, a = 10.990(10) Å, b = 13.760(11) Å, c = 20.50(2) Å, $\alpha = 75.00(4)^{\circ}$, $\beta = 88.43(5)^{\circ}$, $\gamma = 73.35(4)^{\circ}$, V = 2865(4) Å³, T = 123(2) K, space group $P\bar{1}$, Z = 4, μ (Mo K α) = 3.509 mm⁻¹, 23751 reflections measured, 1,714 independent reflections, 9071 with $I > 2\sigma(I)$ ($R_{int} = 0.0773$). $R_{I} = 0.0695 (I > 2\sigma(I))$, $wR(F^{2}) = 0.2086$ (all data). The goodness of fit on F^{2} was 1.073. CCDC 936356.
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