ORGANIC LETTERS

2012
Vol. 14, No. 2
506–509

Spring Open Two-plus-Two Electron Storage in a Disulfide-Strapped Methyl Viologen Derivative

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Received November 19, 2011

ABSTRACT

The synthesis of a disulfide-strapped viologen derivative is described starting from 4,4′-bipyridinyl-3,3′-diol. The first two one-electron reduction potentials, as determined by cyclic voltammetry, occur at $E_{1/2}$ = −0.03 V and $E_{1/2}$ = −0.16 V vs Ag/AgCl. This is accompanied by two more well separated one-electron reductions at $E_{1/2}$ = −1.26 V and $E_{1/2}$ = −1.54 V vs Ag/AgCl and the breaking of the disulfide bridge. To alleviate electrostatic repulsion between the two thiolate ions the molecular system must twist or "spring open" to accommodate the final two electrons.

The efficient and high-density storage of charge in materials, in the form of positive holes or electrons, is of fundamental importance,[1] and it is easy to see how battery technology has revolutionized mobile phones. Instead of the cumbersome large battery operated phones seen in the late 1980s, pocket-size long-lasting devices are now commonplace. This shift in technology can be traced to the development of high-density lithium carbon-based storage cells.[2] Generally speaking, inorganic materials, especially metal oxides (e.g., IrO_2), are abundantly capable of multiple charge storage, their electronic band shape, lattice defect structure, and mixed-valence oxidation state formation often providing the means to support mass charge accumulation.[3] One problem often encountered is the slowness by which charging the material takes place.[4] By comparison, multiple charge storage, at a reasonable thermodynamic potential, within a single organic molecule is less easy to achieve.[5]

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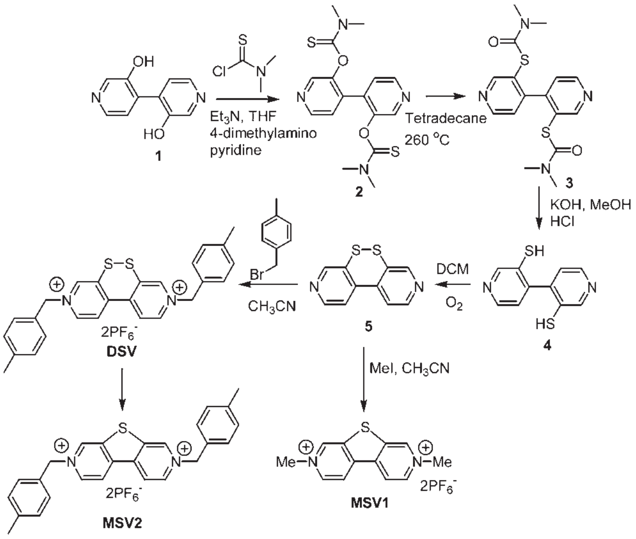
The advantage, however, is the fast charging/discharging generally observed in organic molecules.[6] The example of C60 is probably the most well-known molecular system capable of storing in solution up to six electrons within a potential window of -3.5 V (vs Fc^+/Fc).[7] Certainly the witnessed rise in popularity of C60, and other higher order fullerenes, for artificial photosynthesis applications can be traced, in part, to their propitious electrochemical properties.[8] Other organic compounds for multiple electron storage include the dithiines,[9] and clearly polymeric structures and surfaces grafted with electroactive subunits.[10]

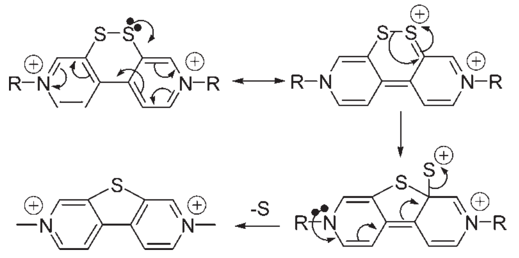
In the search for new molecular systems for charge storage we turned first to Nature for inspiration, and the use of the two electron reducible S–S bond used in cysteine-rich peptides.[11] The well-known reversible electrochemical behavior of the N,N-alkylated bipyridinium cation (viologen) seemed another appropriate starting point.[12] The viologens accumulate two electrons and their reduction potentials are readily manipulated by controlling the dihedral angle.[13] The amalgamation of the S–S unit and viologen led us to develop the new electron-affinic cation, **DSV** (Scheme 1).

Preparation of the electron acceptor **DSV** is depicted in Scheme 1, starting from the readily prepared 4,4′- bipyridinyl-3,3′-diol.[14] The basic design idea was to introduce the two sulfur atoms via the thermal Newman–Kwart rearrangement reaction.[15] Thus, reaction of **1** with *N,N*-dimethylthiocarbamoyl chloride in THF in the presence of Et_3N afforded derivative **2** in 81% yield. The controlled heating of **2** in tetradecane at 260 °C afforded the S-bonded derivative **3** in good yield, 88%, after column chromatography. Hydrolysis of **3** in degassed MeOH and acidified with HCl (2 M) afforded compound **4** which can be isolated, but this is not necessary since simply leaving a DCM solution open to the air gave **5** as a yellow solid. The alkylation of **5** turned out to be surprisingly troublesome since different alkylating reagents and conditions afforded what appeared to be different products. In addition, reproducibility of results with the same agent and conditions was sometimes difficult to achieve. The first tested alkylating agent of MeI produced after reflux with **5** in CH_3CN and metathesis with hexafluorophosphate, the monosulfur derivative **MSV1**. The six-membered disulfide ring appears to eject one sulfur to form the central five membered ring. Under milder conditions and controlled reaction times, it was possible to alkylate **5** with 1-bromomethyl-4-methylbenzene to afford **DSV**. However, this sample when left in acetonitrile solution for prolonged times, especially in the presence of water, again decomposed to give the monosulfur adduct **MSV2**. It is possible to rationalize the decomposition by invoking an intramolecular ring contraction (Scheme 2), owing to presence of the quaternerized nitrogens. The reaction may even proceed once one nitrogen is alkylated.

Scheme 1. Preparation of the Sulfur-Based Viologen Derivatives



Scheme 2. Possible Mechanism for Decomposition of the Disulfur Bridged Viologen Derivatives via Intramolecular Sulfur Attack at the Proximal Site



Several X-ray structures were determined during the studies, especially when it was realized that the disulfide unit suffered from decomposition. The first important point to clear up was the unequivocal identity of **5**, since the simplest explanation for the monosulfur viologen compounds was use of the wrong starting material. The X-ray structure determined molecular structure for **5** is depicted in Figure 1. The disulfide ring is as expected

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puckered; the C−S−S bond angle being 96.86°. The twist in the molecule as measured by the dihedral angle between planes created using the two pyridine groups is 32°.

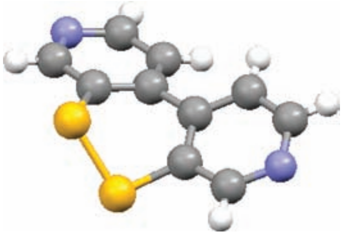

Figure 1. Single-crystal X-ray crystallographically determined molecular structure for compound **5**.

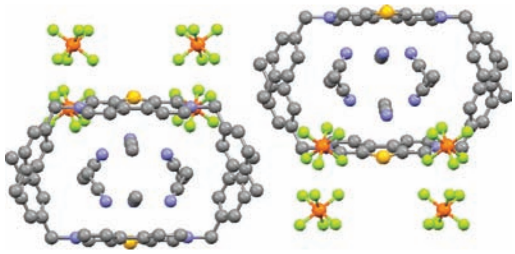

Figure 2. Partial crystal packing diagram for **MSV2** showing the tunnel-like structure and the CH_3CN solvate molecules. Hydrogen atoms are omitted for clarity.

Suitable crystals for **DSV** could not be obtained, and one problem was the possible facile sulfur loss during the slow crystallization process. However, the unequivocal identify of **MSV1** and **MSV2** was again established by X-ray analysis of single crystals. The molecular structures for these two compounds are shown in Supporting Information. The crystal packing diagram for **MSV2** was especially notable as illustrated in Figure 2. The asymmetric units align, as viewed along the *a*-axis, to create a tunnel-like motif. The tolyl groups of one molecular unit appear to point inward toward another subunit creating a hollow for CH_3CN solvent molecules. Each asymmetric unit is in fact slightly displaced from each other. The PF_6^- counterions appear to reside in channels as observed along the *b*-axis direction.

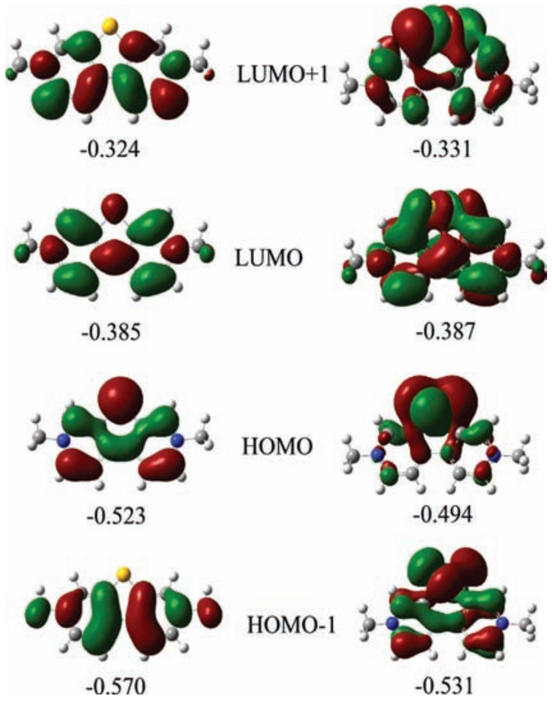

Figure 3. Illustrations of selected molecular orbitals associated with **MSV1** (left) and **DSV** (right) calculated using DFT (B3LYP) and the 6-311G^{++} (3df) basis set. Energies are given in hartrees.

The need to elucidate more information on the two disparate sulfur-based viologen derivatives led us to undertake a high-level computational study. To simplify the calculations, the *N*-methyl group was chosen instead of the more flexible tolyl group. In the first case, the basic energy-minimized ground-state molecular geometries for **MSV1** and **DSV** were calculated in the gas phase at the Hartree−Fock level (6-31G) using Gaussian 03.[16] Further refinement was then carried out using DFT (B3LYP) and the 6-311G^{++}(3df) basis set to account for the two sulfur atoms. The computer-generated energy-minimized structures for the two derivatives are shown in Supporting Information. For comparison purposes, a selection of the generated HOMOs and LUMOs associated with the two cations are shown in Figure 3. The HOMO for **DSV** is located almost exclusively on the two sulfur atoms; a somewhat similar picture is seen for the HOMO-1. In comparison, the HOMO, and to a greater extent the HOMO-1, for **MSV1** is situated on the viologen moiety. The energies for the LUMOs of both cations are remarkably similar, but their localization is very different. The LUMO for **DSV** is delocalized over the entire cation, whereas the LUMO+1 is localized on the disulfide bridge. Both the LUMO and LUMO+1 for **MSV1** are situated on the viologen moiety.

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We infer from these calculations that addition of the first electron to **MSV1** is very much viologen-based, but the case for **DSV** is somewhat less clear-cut. However, assuming that addition of two electrons to **DSV** is exclusively viologen-based, the neutral product formed contains double bond character in the C−C connector bond. Addition of a single electron to this species produces a radical anion. A DFT energy minimization calculation (B3LYP, 6-311G^{++}(3df) starting from this compound is interesting. To alleviate steric strain, the sulfur−sulfur bond increases significantly to ca. 3.5 Å; this certainly supports the idea of S−S bond breakage (see the Supporting Information). In addition, the connector C−C bond length (1.43 Å) is elongated and hence has reduced double bond character.

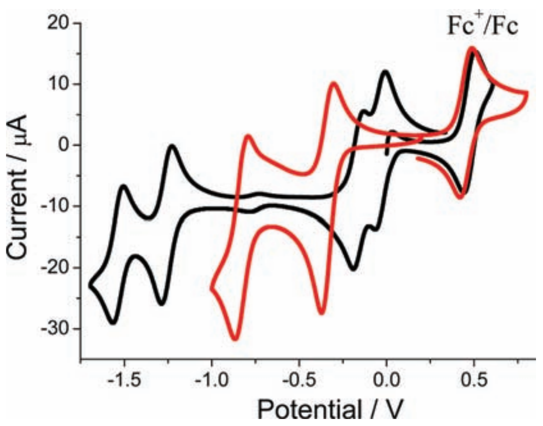

Figure 4. Cyclic voltammograms recorded for **DSV** (black) and **MSV1** (red) in dry CH_3CN containing 0.2 M TBATFB. Scan rate = 50 mV s^{-1} and working electrode = glassy carbon.

The reductive electrochemistry for **DSV** and **MSV1** was obtained using cyclic voltammetry in dry CH_3CN containing 0.2 M tetra-*N*-butylammonium tetrafluoroborate (TBATFB) background electrolyte (Figure 4). The redox behavior for **MSV1** is readily understood since two reversible one-electron waves are observed at $E_{1/2}$ = −0.34 V (70 mV) and −0.83 V (80 mV) vs Ag/AgCl. The first wave is associated with the production of the monocation, and the potential is slightly more anodic when compared to simple methyl viologen ($E_{1/2}$ = −0.40 V vs Ag/AgCl) measured under identical conditions. The five-membered sulfur ring essentially forces the two pyridinium units to be nearly coplanar. This geometry is highly favorable to facilitate one-electron reduction, since this process introduces more double-bond character into the connector C−C bond. The second wave, to produce the neutral species, is as expected well separated from the first and more cathodic because of increased π-conjugation. In comparison, the reductive electrochemistry for **DSV** is far more richer displaying four distinctive reversible one-electron waves. The first two one-electron reduction waves are closely spaced occurring at $E_{1/2}$ = −0.03 V (54 mV) and $E_{1/2}$ = −0.16 V (60 mV) vs Ag/AgCl. After the addition of two electrons the species produced is neutral irrespective of the sites for reduction. Preliminary EPR data is consistent with production, in the first instance, of a non sulfur-based radical. The final two one-electron reducion waves are well separated from the first two and occur at $E_{1/2}$ = −1.26 V (70 mV) and $E_{1/2}$ = −1.54 V(60 mV) vs Ag/AgCl. It is noted that the difference (ΔE) between these two waves is only 280 mV, supporting the notion that the two negative charges are separated spatially. By comparison to the electrochemical behavior for dibenzo[1,2]dithiine[17] the final two waves are attributed to sulfur-based reduction. However, there is one major difference: for dibenzo[1,2]-dithiine the process consists of a single two-electron reduction which is irreversible. The electrochemical irreversibility is removed by the incorporation of the disulfur bridge into the viologen unit.

As discussed previously for the molecular structure calculations, the addition of one electron to the doubly reduced neutral species facilitates sulfur−sulfur bond cleavage. On electrostatic repulsion grounds, energy minimized structures and in fitting with the ΔE value, the final one-electron addition must occur in the conformation where the two sulfurs are anti to each other. In essence, the molecule "springs open" to assist this process (see the Supporting Information for more details). Again, such behavior is dissimilar to dibenzo[1,2]dithiine where only after concurrent two-electron reduction does the molecule twist to alleviate electrostatic repulsion.[18]

By incorporation of the disulfur bridge into viologen a dication is produced that is capable of storing up to four electrons at a potential less than ca. −1.6.V vs Ag/AgCl. Furthermore, the addition of the first two electrons is extemely facile, making **DSV** one of the easiest to reduce viologen derivatives to date.[19] We expect to exploit the rather unique redox properties of **DSV** in multiple charge accumulation for applications in artificial photosynthesis and molecular memory devices.

Acknowledgment. We thank the Engineering and Physical Sciences Research Council (EP/G04094X/1) and Newcastle University for funding. The EPSRC-sponsored Mass Spectrometry Service at Swansea is also thanked for the collecting of mass spectra.

Supporting Information Available. Experimental details, ^{1}H NMR spectra of compounds, additional analytical data, X-ray structures for **MSV1** and **MSV2** (CIF), and computer generated structures.This material is available free of charge via the Internet at http://pubs.acs.org.

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