JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 1, 47–51 (1988)

SHORT COMMUNICATIONS

ETHENEDIYLIDENE-2,2′-BIS(1,3-DITHIOLE) AND BUTATRIENE-1,4-DIYLIDENE-2,2′-BIS(1,3-DITHIOLE)

HIROSHI AWAJI, TOYONARI SUGIMOTO, AND ZEN-ICHI YOSHIDA
Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto 606, Japan

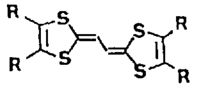
ABSTRACT

This paper describes the synthesis and electrochemical behavior of dicationic salts of ethenediylidene-2,2′-bis(1,3-dithiole) (**3**) and butatriene-1,4-diylidene-2,2′-bis(1,3-dithiole) (**4**). These are expected as donor components for developing organic conducting and superconducting materials, on the grounds of high electron donating ability and of rigid skeletal structure with two and four cumulenic carbons inserted between two 1,3-dithioles. These salts were obtained in good overall yields by several steps starting from (2-morpholino-4,5-dimethyl or -diphenyl)-1,3-dithiolylium salt. From the ^{1}H and ^{13}C NMR, and electronic spectra it is suggested that the π conjugation between two 1,3-dithiolylium ions through an acetylenic bond is less effective than that through an olefinic bond of the corresponding salts of ethanediylidene-2,2′-bis(1,3-dithiole) (**1**) and 2-butene-1,4-diylidene-2,2′-bis(1,3-dithiole) (**2**). The cyclic voltammetric study shows that the corresponding radical cations, and in particular **3** and **4**, are less stable even at −40 °C, thus providing reasons for our current lack of success in isolation of **3** and **4**. From comparison of the first redox potentials of neutral species, it is deduced that the donating ability increases in the order of TTF < **1** ≃ **2** $\lesssim$ **3** << **4**.

Tetrathiafulvalene (TTF) and its chalcogen analogs are crucial as donor components for developing organic conducting and superconducting materials.[1] Nevertheless, creation of new donors having different skeletal structures from TTF is necessary for successful development of these materials. For such new donors we previously synthesized ethanediylidene-2,2′-bis(1,3-dithiole) (**1**)[2] and 2-butene-1,4-diylidene-2,2′-bis(1,3-dithiole) (**2**),[3] in which two and four sp^2 carbons are inserted between two 1,3-dithioles, respectively. Unfortunately, these donors have the following drawbacks: (1) the metal–insulator transition occurs at comparatively high temperature (ca. 200 K) for the **1** – tetracyanoquinodimethane 1:1 charge-transfer (CT) complex in single crystals,[4] and (2) the CT complexes of **2** and the radical cation salts of **1** and **2** are not obtained as single crystals, presumably for lack of tight intermolecular stacking by the presence of a flexible central C—C bond in the molecules. Our attention was directed to the synthesis of other new donors, ethenediylidene-2,2′-bis(1,3-dithiole) (**3**) and butatriene-1,4-diylidene-2,2′-bis(1,3-dithiole) (**4**), which have respectively two and four rigid cumulenic carbons inserted between two 1,3-dithioles. Herein we wish to report the synthesis of dicationic salts of **3** and **4**, and their electrochemical study in order to clarify the properties of **3** and **4** themselves. The diperchlorate salts of **3** and **4** ($\mathbf{3}^{2+}\cdot 2\mathrm{ClO_4}^-$

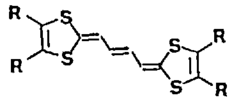
0894–3230/88/010047–05$05.00

Received 28 September 1987
Revised 15 October 1987



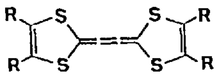
1a: R=Me

1b: R=Ph



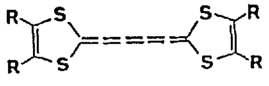
2a: R=Me

2b: R=Ph



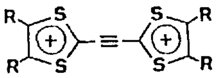
3a: R=Me

3b: R=Ph



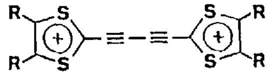
4a: R=Me

4b: R=Ph



3a^{2+}: R=Me

3b^{2+}: R=Ph



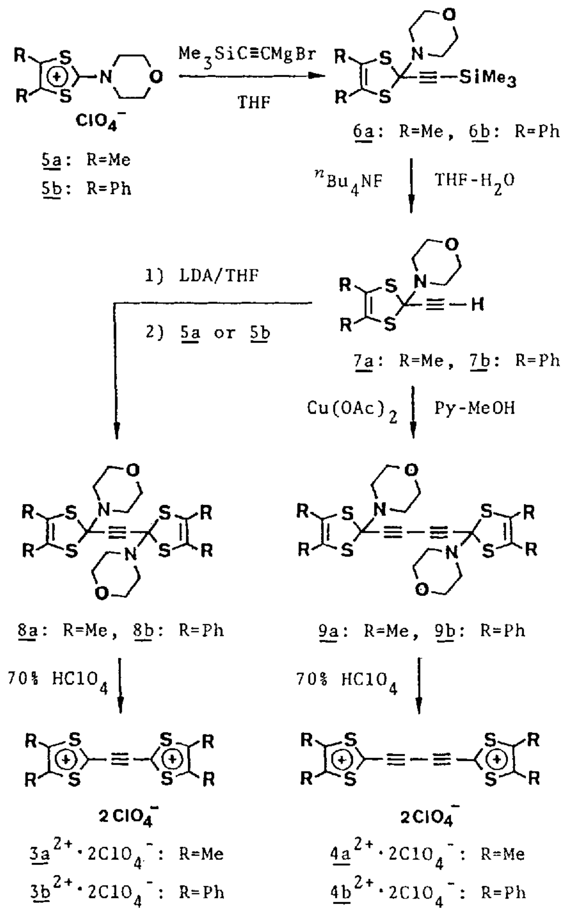
4a^{2+}: R=Me

4b^{2+}: R=Ph

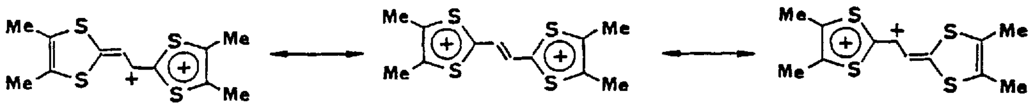
and **4**$^{2+}\cdot 2ClO_4^-$), were synthesized as shown in Scheme I. Thus, the reaction of (2-morpholino-4,5-dimethyl)-1,3-dithiolylium perchlorate (**5a**)[5] with trimethylsilylethynylmagnesium bromide[6] gave 2-morpholino-2-trimethylsilylethynyl-4,5-dimethyl-1,3-dithiole (**6a**), which was further converted to a detrimethylsilylated derivative (**7a**) by the aid of tetra-*n*-butylammonium fluoride in THF—H_2O.[7] By treatment of **7a** with lithiumdiisopropylamide (LDA) and then with **5a** bis(2-morpholino-4,5-dimethyl-1,3-dithiole)acetylene (**8a**) was obtained. On the other hand, Eglinton coupling of **7a** with $Cu(OAc)_2$ in pyridine-methanol[8] yielded the corresponding diacetylenic derivative (**9a**). In a similar procedure the corresponding tetraphenyl derivatives of **8** and **9**, (**8b** and **9b**), were also prepared by using (2-morpholino-4,5-diphenyl)-1,3-dithiolylium perchlorate (**5b**)[5] as a starting material. When **8a** and **9a** were reacted with 70% perchloric acid and successively dehydrated with propionic anhydride, **3a**$^{2+}\cdot 2ClO_4^-$ and **4a**$^{2+}\cdot 2ClO_4^-$ [9] were obtained as yellow crystals in respective overall yields of 89 and 87%, which are very explosive in contact with metallic spatula (*handle with care*). A similar treatment of **8b** and **9b** gave **3b**$^{2+}\cdot 2ClO_4^-$ and **4b**$^{2+}\cdot 2ClO_4^-$ [9] in 73 and 74% overall yields as purple solids, which are proved to contain small amounts of the corresponding radical cations by ESR measurement.

The ^1H and ^{13}C NMR spectra of **3a**$^{2+}\cdot 2ClO_4^-$ and **4a**$^{2+}\cdot 2ClO_4^-$ were measured and compared with those of the diperchlorate salts of tetramethyl-substituted derivatives of **1** and **2**, (**1a**$^{2+}\cdot 2ClO_4^-$ and **2a**$^{2+}\cdot 2ClO_4^-$), prepared by the reaction of **1a** and **2a** with an equimolar amount of Br_2 in dry CCl_4, followed by the treatment with $KClO_4$ aq. In the ^1H NMR spectra (CF_3CO_2D) methyl protons of **3a**$^{2+}$ and **4a**$^{2+}$ appeared at δ 2·99 and 2·95 as singlet, respectively. On the other hand, for **1a**$^{2+}$ and **2a**$^{2+}$ the corresponding signals were observed at δ 2·91 and 2·81, respectively. The ^{13}C NMR spectrum (60% $HClO_4$) of **3a**$^{2+}$ consisted of four signals at δ 14·5 ($\underline{C}H_3$), 98·8 ($\underline{C}\equiv C$), 158·3 (S—$\underline{C}$=C—S), and 185·1 (S—$\underline{C}$—S), and for **1a**$^{2+}$ the corresponding signals appeared at δ 14·2 ($\underline{C}H_3$), 127·1 (C—$\underline{C}$=C—C), 155·3 (S—$\underline{C}$=C—S), and 180·0 (S—$\underline{C}$—S). However, for **4a**$^{2+}\cdot 2ClO_4^-$, and also **3b**$^{2+}\cdot 2ClO_4^-$ and

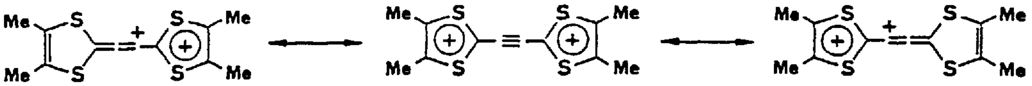
Scheme I



4b^{2+}·2ClO$_4^-$ the ^{13}C NMR spectral measurement was impossible because of their extremely poor solubility in any solvent. From the NMR spectral data it is shown that the two positive charges are much more localized in the two 1,3-dithiolylium rings for **3a**$^{2+}$ than for **1a**$^{2+}$ and **2a**$^{2+}$. This can be understood by taking account of the fact that the π conjugation between two



1a^{2+}



3a^{2+}

1,3-dithiolylium ions through an acetylenic bond is less effective than that through an olefinic bond, because of the participation by an energetically unfavorable vinylium ion in the former case. In the visible spectra measured in 70% $HClO_4$ aq. **3a**$^{2+}$ revealed strong absorption bands at 424 (sh, log ε = 4·17) and 454 nm (4·29), while **4a**$^{2+}$ at 388 (sh, 4·29), 431 (4·45) and 465 nm (4·52). In a comparison of the longest wavelength bands between **3a**$^{2+}$ and **1a**$^{2+}$ and between **4a**$^{2+}$ and **2a**$^{2+}$, the bands of **3a**$^{2+}$ and **4a**$^{2+}$ shift to the comparatively shorter wavelength region than those of **1a**$^{2+}$ (446 (4·32) and 464 nm (sh, 4·29)) and **2a**$^{2+}$ (468 (4·52) and 493 nm (sh, 4·47)) also suggesting the less effective π through-conjugation for the former systems.

In order to clarify the properties of **3** and **4** and to attempt their isolation if possible, CV studies were made on **3**$^{2+}$ and **4**$^{2+}$ and also on **1**$^{2+}$ and **2**$^{2+}$ for comparison. Figures 1 and 2 show cyclic voltammograms of **1a**$^{2+}$ and **3a**$^{2+}$, and of **2a**$^{2+}$ and **4a**$^{2+}$, respectively, which were measured in CH_3CN containing 0·1 M Et_4NClO_4 as supporting electrolyte at −40 °C (scan rate, 43 mV/s). Both **3a**$^{2+}$ and **4a**$^{2+}$ revealed two pairs of irreversible redox waves at +0·31 (E_2) and +0·07 (E_1), and +0·25 (E_2) and −0·12 V (E_1), respectively, vs. Ag/AgCl each of which involves one-electron migration (E_2 and E_1 are used for denoting the second and first redox potentials of the neutral species, **3a** and **4a**, respectively). For **1a**$^{2+}$ and **2a**$^{2+}$ the corresponding waves were reversible and appeared at +0·31 (E_2) and +0·10 (E_1), and +0·14 V ($[E_2 + E_1]/2$: the average of potentials of first and second pairs of waves). The CV results suggest that the radical cations (**3a**$^{+\cdot}$ and **4a**$^{+\cdot}$)[9] and also **3a** and **4a** are not so stable as to

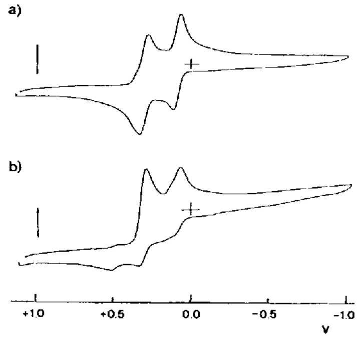


Figure 1. Cyclic voltammograms of (a) **1a**$^{2+}\cdot 2ClO_4^-$ and (b) **3a**$^{2+}\cdot 2ClO_4^-$ in CH_3CN containing 0·1 M Et_4NClO_4 (−40 °C, scan rate, 43 mV/s)

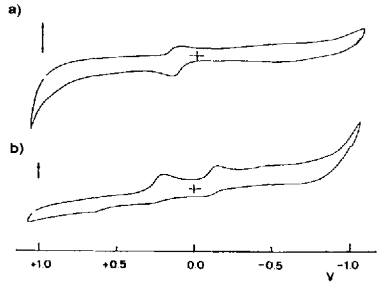


Figure 2. Cyclic voltammograms of (a) **2a**$^{2+}\cdot 2ClO_4^-$ and (b) **4a**$^{2+}\cdot 2ClO_4^-$ in CH_3CN containing 0·1 M Et_4NClO_4 (−40 °C, scan rate, 43 mV/s)

undergo rapid irreversible chemical reactions such as polymerization, in contrast with the high stability of **1** and **2**, and their radical cations. A similar observation was also reported in the reduction of acetylene-bridged non-quartenarized N-heterocycles.[10] In accord with the CV result **3a** and **4a** have still not been isolated successfully, although electrochemical and chemical reductions of **3a**$^{2+}$ and **4a**$^{2+}$ were carried out in several conditions. Both E_1 and E_2 values of **3a**$^{2+}$ are almost the same as those of **1a**$^{2+}$. On the other hand, the E_1 of **4a**$^{2+}$ is more negative by ca. 0·26 V than that of **2a**$^{2+}$, but conversely the E_2 value is more positive by ca. 0·11 V. By comparison of the E_1 values in this series, it is deduced that the donating ability increases in the order of TTF ($E_1 = +0{\cdot}34$ and $E_2 = +0{\cdot}71$ V vs. Ag/AgCl) $< \mathbf{1} \simeq \mathbf{2} \lesssim \mathbf{3} << \mathbf{4}$.

In summary, **3** and **4** should be expected to be more desirable donors than **1** and **2** in view of the more rigid skeletal structure and the greater electron-donating ability. We are now investigating the preparation of electric conducting CT complexes and radical cation salts by using **3**$^{2+}$ and **4**$^{2+}$.

REFERENCES

1. For recent reviews, see: a) B. M. Hoffman, J. A. Ibers, *Acc. Chem. Res.* **16**, 15–21 (1983). b) M. R. Bryce, L. C. Murphy, *Nature (London)* **309**, 119–126 (1984). c) R. L. Green, G. B. Street, *Science (Washington D. C.)* **226**, 651–656 (1984). d) J. M. Williams, *et al.*, *Acc. Chem. Res.* **18**, 261–267 (1985). e) D. O. Cowan, F. M. Wiygul, *Chem. Eng. News* **64**, 28–45 (1986). f) D. O. Cowan, A. Kini in S. Patai (Ed): *The Chemistry of Organic Selenium and Tellurium Compounds, Vol. II*, Wiley, London 1987.
2. Z. Yoshida, *et al.*, *Tetrahedron Lett.* **24**, 3469–3472 (1983).
3. Z. Yoshida, T. Kawase, H. Awaji, S. Yoneda, *Tetrahedron Lett.* **24**, 3473–3476 (1983).
4. T. Sugimoto, *et al.*, *Synth. Metals* **19**, 569–572 (1987).
5. J. Nakayama, K. Fujiwara, M. Hoshino, *Bull. Chem. Soc. Jpn.* **49**, 3567–3573 (1976).
6. L. Brendsma, H. D. Verkrijisse: *Synthesis of Acetylene, Allene and Cumulene*, Elsevier, Amsterdam 1981, p. 55.
7. E. Nakamura, I. Kuwajima, *Angew. Chem.* **88**, 539 (1976); *Angew. Chem. Int. Ed. Engl.* **15**, 498–499 (1976).
8. G. Eglinton, W. McCrae: *Advances in Organic Chemistry, Vol. 4*, Interscience, New York 1963, p. 225.
9. A. Terahara, *et al.*, *Bull. Chem. Soc. Jpn.* **57**, 2591–2595 (1984).
10. K. Deuchert, S. Hünig, *Angew. Chem.* **90**, 927–938 (1978); *Angew. Chem. Int. Ed. Engl.* **17**, 875–886 (1978).