ORGANIC
LETTERS

2004
Vol. 6, No. 10
1569−1572

Oligomeric Tetrathiafulvalenes: A New Route toward Conjugated TTF Dimers and Trimers

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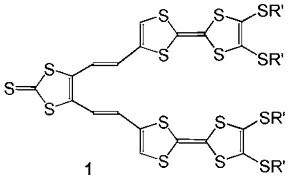
Received March 1, 2004

ABSTRACT



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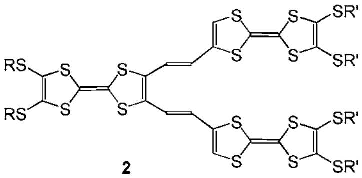

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The synthesis of bis-TTF 1 and tris-TTF 2, linked by an ethenyl spacer, is described using new useful Wittig-type reagents with the introduction of phosphonate functionality on 1,3-dithiole and TTF frameworks. Electrochemical and spectroscopic studies show intramolecular electronic interactions between conjugated TTF units.

Since the discovery of the properties of tetrathiafulvalene (TTF),[1] much effort has been devoted to achieve the synthesis of sophisticated derivatives of this π-donor in order to improve the electroconducting properties of the corresponding charge-transfer complexes or cation radical salts.[2] It has been widely recognized that the conductive properties depend on their crystal structures and electronic states. Dimeric TTF molecules and higher oligomers, in which the TTF units are linked by one or two spacer groups, have been identified as an opportunity to increase the dimensionality[3] and to control both degree of charge transfer and stoichiometry in desired conductive complexes.[4] Such systems display multistage redox behavior which should provide the possibility of controlling the stoichiometry and molecular assembly in the desired conductive complexes. Several oligoTTFs have been reported, and this topic was recently reviewed.[5] Thus, it was clearly shown that the possibility to synthesize varied dimeric or trimeric TTF derivatives in which TTF units are separated by an ethenyl spacer was limited because of the lack of suitable versatile building blocks. Conjugated dimeric TTF **3** was prepared by a McMurry reaction starting from formylTTF.[6] On the other hand, 1,1-bis(TTF)ethene **4** was synthesized to examine spin−spin interaction and conductivity of corresponding molecular materials which could present both magnetic and electrical behavior.[7] The hybrid π-donor system **5**, in which the parent TTF was linked to a quinonoid π-extended TTF through a conjugated ethenyl spacer, was also described.[8] To our knowledge, only the conjugated tris-TTF **6** was reported as an equivalent of tris-TTF **2**, this latter being different by the presence of ethenyl spacers (Scheme 1).[9]

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(1) Wudl, F.; Smith, G. M.; Hufnagel, E. J. *J. Chem. Soc., Chem. Commun*. **1970**, 1453.

(2) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M. H. *Organic Superconductors (including fullerenes)*; Prentice Hall: Englewood Cliffs, NJ, 1992.

(3) (a) Bryce, M. R. *J. Mater. Chem.* **1995**, *5*, 1481. (b) Fabre, J.-M. *J. Solid State Chem*. **2002**, *168*, 367.

(4) (a) Adam, M.; Müllen, K. *Adv. Mater*. **1994**, *6*, 439. (b) Otsubo, T.; Aso, Y.; Takimiya, K. *Adv. Mater.* **1996**, *8*, 203.

(5) Becher, J.; Lau, J.; Mørk, P.; Kristensen, G. J.; Becher, J. In *Electronic Materials: the Oligomeric Approach*; Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998; p 198.

(6) Otsubo, T.; Kochi, Y.; Bitoh, A.; Ogura, F. *Chem. Lett.* **1994**, 2047.

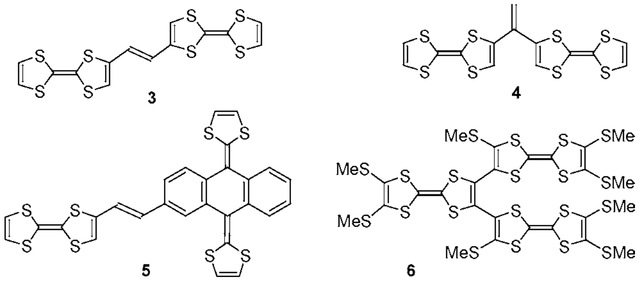
(7) Iyoda, M.; Sasaki, S.; Miura, M.; Fukuda, M.; Yamauchi, J. *Tetrahedron Lett*. **1999**, *40*, 2807.

(8) Pérez, I.; Liu, S.-G.; Martín, N.; Echegoyen, L. *J. Org. Chem*. **2000**, *65*, 3796.

(9) Iyoda, M.; Hara, K.; Kuwatani, Y.; Nagase, S. *Org. Lett*. **2000**, *2*, 2217.

10.1021/ol049620l CCC: $27.50

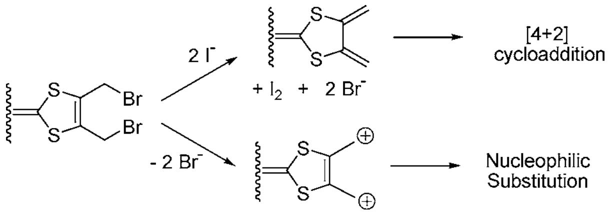
Scheme 1. TTF Oligomers



Since the methodology for preparing oligomeric TTF is still very limited, we now present a new approach to construct the extended TTF framework using useful Wittig-type reagents. Effectively, the synthesis of π-electron donors based on the TTF core has been particularly varied,[10] but the introduction of (dimethylphosphono)methyl groups on 1,3-dithiole or TTF units has never been considered.

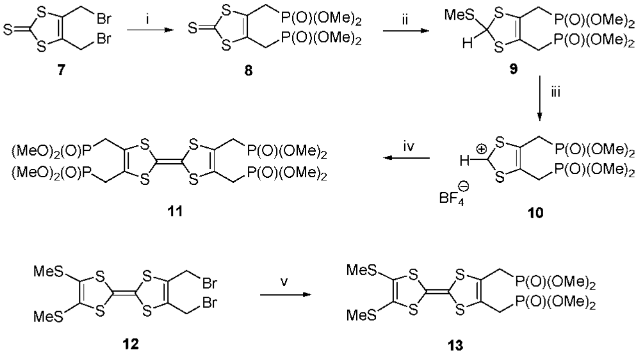
We had previously shown that the vicinal bis(bromomethyl) group grafted on the 2-thioxo-1,3-dithiole[11] or TTF[12] moieties could generate the corresponding diene (prone to undergo Diels–Alder cycloaddition) by reductive elimination using naked iodide anion.[13] We report here the possibility of direct nucleophilic substitution on this group which thus acts as a dication synthetic equivalent (Scheme 2).

Scheme 2. Versatile Synthetic Applications of the Vicinal Bis(bromomethyl) Group



This dication synthetic equivalent nature of bis(bromomethyl) derivatives was exploited for the preparation of corresponding phosphonates by a classical Arbuzov reaction using trimethyl phosphite. Thus, compound **8** in the 1,3-dithiole series and TTF **13** were isolated in 46% and 40% yield, respectively, from 2-thioxo-1,3-dithiole **7** or TTF **12**. After different failures in the direct transformation of tetrakis(bromomethyl)TTF, we considered an alternative route to reach the corresponding tetraphosphonate **11**. Methylation of **8** with methyl triflate then reduction with sodium borohydride afforded compound **9** in an overall 93% yield. The 1,3-dithiolium salt **10** was produced in quantitative yield by dethiomethylation with tetrafluoroboric acid in acetic anhydride. Treatment with an excess of triethylamine afforded TTF **11** by carbenoid coupling in 81% yield (Scheme 3).

Scheme 3[a]



[a] Reagents and conditions: (i) $P(OMe)_3$, 100 °C, 46%; (ii) CF_3SO_3Me then $NaBH_4$, *i*-PrOH/CH_3CN, 93%; (iii) HBF_4, Ac_2O, 97%; (iv) Et_3N, CH_3CN, 81%; (v) $P(OMe)_3$, 40%.

Single crystals of diphosphonate **13** were grown by slow evaporation of a CH_2Cl_2/MeOH solution. X-ray structure showed that dimethylphosphono groups were at the opposite side of the plane defined by the TTF core (Figure 1).[14]

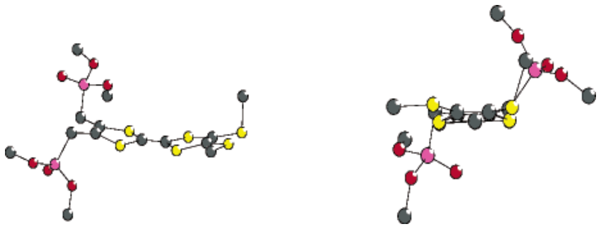


Figure 1. ORTEP views of TTF-diphosphonate **13**. Hydrogen atoms have not been drawn for clarity.

The reactivity of phosphonate reagents was tested by subsequent Horner–Wadsworth–Emmons (HWE) reaction. After deprotonation using *t*-BuOK or BuLi followed by the addition of benzaldehyde, compounds **14**, **15**, and **16**[15] were isolated in satisfactory yields. ^{1}H NMR spectroscopy was

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[10] (a) Narita, M.; Pittman, C. U. *Synthesis* **1976**, 489. (b) Krief, A. *Tetrahedron* **1986**, *42*, 1209. (c) Garín, J. *Adv. Heterocycl. Chem.* **1995**, *62*, 249. (d) Schukat, G. Fanghänel, E. *Sulfur Rep.* **2003**, *24*, 1.

[11] (a) Durand, C.; Hudhomme, P.; Duguay, G.; Jubault, M.; Gorgues, A. *Chem. Commun.* **1998**, 361. (b) Skabara, P. J.; Müllen, K. *Synth. Met.* **1997**, *84*, 345.

[12] Hudhomme, P.; Liu, S.-G.; Kreher, D.; Cariou M.; Gorgues, A. *Tetrahedron Lett.* **1999**, *40*, 2927.

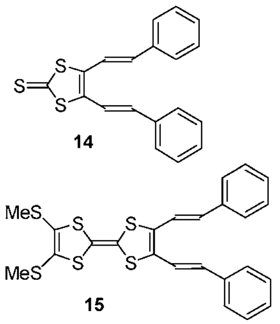
[13] (a) Boulle, C.; Desmars, O.; Gautier, N.; Hudhomme, P.; Cariou, M.; Gorgues, A. *Chem. Commun.* **1998**, 2197. (b) Gautier, N.; Cariou, M.; Gorgues, A.; Hudhomme, P. *Tetrahedron Lett.* **2000**, *41*, 2091. (c) Kreher, D.; Cariou, M.; Liu, S.-G.; Levillain, E.; Veciana, J.; Rovira, C.; Gorgues, A.; Hudhomme, P. *J. Mater. Chem.* **2002**, *12*, 2137.

[14] Crystal data for **13**: $C_{14}H_{22}O_6P_2S_6$, $M = 540.7$ g·mol^{-1}; monoclinic, $P2_1/c$ $a = 14.5507(6)$ Å, $b = 7.4880(5)$ Å, $c = 21.421(2)$ Å, $\beta = 99.22(1)°$, $V = 2303.8(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.56$ g·cm^{-3}, λ(Mo Kα) = 0.710 73 Å, 6445 reflections ($2.5 < \theta < 25°$) were collected at 293 K, 4567 unique reflections and 3491reflections with $I > 3\sigma(I)$ used in refinements, 253 parameters, $R = 0.033$, Rw = 0.042, GOF = 0.97.

[15] Spectroscopic analyses were in agreement with reported data for compound **16**, previously synthesized from tetraformylTTF and the corresponding phosphonium salt in a Wittig reaction: Sallé, M.; Gorgues, A.; Jubault, M.; Boubekeur, K.; Batail, P. *Tetrahedron* **1992**, *48*, 3081.

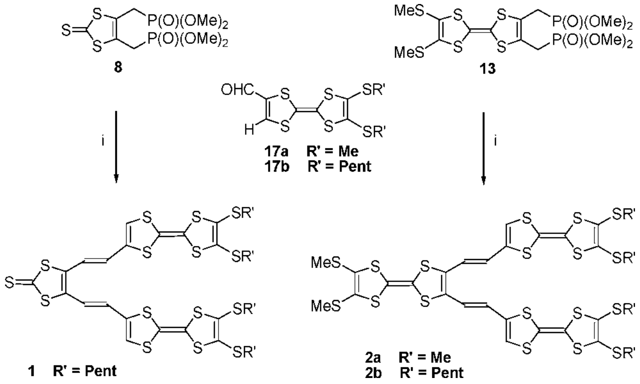
consistent with the *E* configuration for all double bonds thus created (Scheme 4).

Scheme 4. Products of Horner−Wadsworth−Emmons Reaction Using the Corresponding Diphosphonate and Benzaldehyde



Novel dimeric and trimeric TTFs were synthesized by similar HWE reaction using the adequately selected *mono*-formylTTF **17**[16] (Scheme 5). Yields of the reaction were improved by addition of *t*-BuOK to a solution of both electrophilic aldehyde **17** and diphosphonate **8** or **13** at 0 °C (**1**: 79%; **2b**: 55% yields) compared with the experimental procedure in which the anion of diphosphonate **13** was first generated with BuLi at −78 °C followed by the addition of aldehyde **17** (**2a**: 25%; **2b**: 21% yields).[17]

Scheme 5[a]



[a] Reagents and conditions: (i) *t*-BuOK, THF, 0 °C or BuLi, THF, −78 °C then rt.

The cyclic voltammogram of **1** showed a first large reversible oxidation wave which was deconvoluted into two peaks corresponding to a one-electron process for each.[18] The splitting of this first oxidation step is characteristic of a molecular system in which two donor moieties interact (through-conjugation or through-space), the Coulombic repulsion between positively charged species leading to a separation of the oxidation potentials of neutral and oxidized species.[19] The second oxidation wave was attributed to a two-electron process, all these features being in agreement with the sequence: **1** $\rightleftharpoons$ $\mathbf{1}^{+\bullet}$ $\rightleftharpoons$ $\mathbf{1}^{2+}$ $\rightleftharpoons$ $\mathbf{1}^{4+}$ appearing at E^0_{ox} = +0.49, +0.53, and +0.88 V (vs SCE), respectively (Figure 2 A,C).

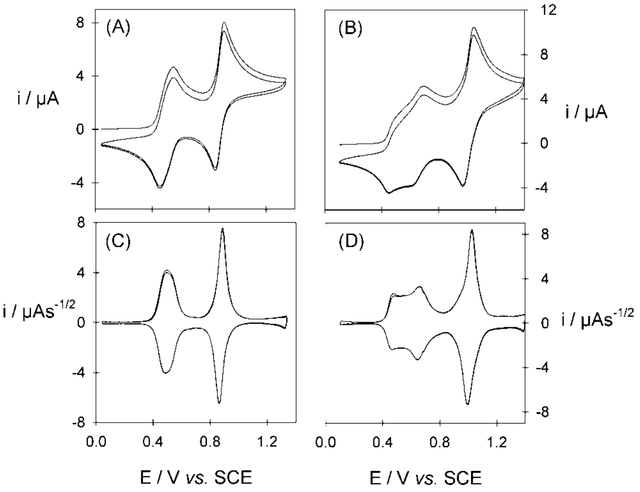


Figure 2. Cyclic voltammogram and deconvoluted voltammogram of 1 mM **1** (A and C, respectively) and 1 mM **2b** (B and D, respectively) in 0.2 M TBAHP/CH_3CN/CH_2Cl_2 (1/9), Pt electrode.

Cyclic voltammogram of **2b** showed three one-electron reversible oxidation waves at E^0_{ox} = +0.43, +0.49, and +0.60 V (vs SCE) corresponding to the successive generation of the cation radical for each TTF unit. Two other reversible waves at higher positive potentials [E^0_{ox} = +0.84 (one-electron process) and +1.00 V (two-electron process)] were related to the formation of dication on each TTF, the second wave being attributed to both equivalent TTF moieties.[18] All these observations characterized the following electrochemical behavior of trimeric TTF **2b**: **2b** $\rightleftharpoons$ $\mathbf{2b}^{+\bullet}$ $\rightleftharpoons$ $\mathbf{2b}^{2+}$ $\rightleftharpoons$ $\mathbf{2b}^{3+\bullet}$ $\rightleftharpoons$ $\mathbf{2b}^{4+}$ $\rightleftharpoons$ $\mathbf{2b}^{6+}$, suggesting that there are significant intramolecular interactions between TTF units (Figure 2B,D).

To elucidate the sequence leading to the cation radical on each TTF core in **2b**, DFT calculations were performed on tris-TTF (bearing no substituent on different TTFs) using Gaussian 98 at the B3LYP/6-31G* level of theory for a full geometry optimization. The molecular orbital analysis showed that the largest coefficients in the HOMO orbital are mainly located on TTF noted **A** (Figure 3), in the HOMO-1 on TTF noted **A′** and in the HOMO-2 on TTF **B**. The coefficients in the LUMO orbital were centered on both ethenyl moieties. Moreover, since the coefficients of the HOMO for each individual TTF are concentrated on the central $S_2C{=}CS_2$ fragment and are small at the bridging carbon atoms, through-bond interactions between TTFs are expected to remain weak. An important distortion from planarity was also shown, probably due to steric interactions between hydrogens H_1 and H_6.

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(16) Garín, J.; Orduna, J.; Uriel, S.; Moore, A. J.; Bryce, M. R.; Wegener, S.; Yufit, D. S.; Howard, J. A. K. *Synthesis* **1994**, 489.

(17) Studies of the pentameric TTF resulting from the HWE reaction between tetraphosphonate **11** and aldehyde **17** will be reported later.

(18) The number of electrons was determined by thin-layer cyclic voltammetry (TLCV) using 2,3-dichloro-1,4-naphthoquinone as the one-electron standard reference.

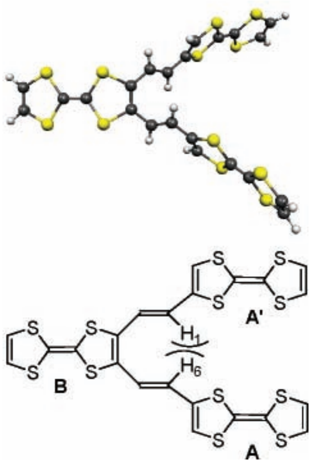

Figure 3. Geometry optimization of *tris*-TTF.

Electronic interactions between TTFs could result from through-space, as reported for flexible linked cyclic dimeric TTF[20] or noncyclic trimeric TTF,[21] or through-bond manner because of the conjugation between different TTF units. For comparison, it should be pointed out that cyclic voltammogram of dimeric TTF **3** showed only two reversible one-electron oxidation waves[6] confirming that through-bond electronic interaction between TTF units in conjugated dimers is generally weak in the ground state.[22] Nevertheless, through-bond interactions were suggested for the hybrid dimer **5** in which the planarity of the ethenyl spacer with TTF and π-extended TTF was shown.[8]

Chemical oxidation of **1** and **2b** in acetonitrile solution was carried out by successive aliquot addition of (diacetoxyiodo)benzene in the presence of triflic acid ($PhI(OAc)_2$/CF_3SO_3H) used as oxidizing reagent.[23] UV−vis−NIR spectra of oxidized species were recorded. In both cases, chemical oxidation led to the disappearance of neutral TTF derivative (band at 507 nm) and to the development of new bands characteristic of the cation radical or π-dimer[24] (832 nm) and then of the dication (429 nm) (Figure 4). The concomitant appearance of the broad band centered around 1800 nm was attributed to the formation of a mixed-valence state which occurs when the cation radical of one TTF shares its positive charge with another not yet oxidized TTF (inset of Figure 4).[25]

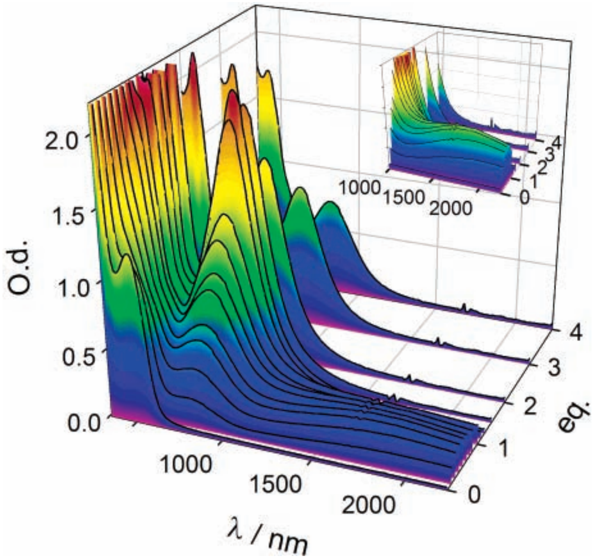

Figure 4. UV−vis−NIR spectra of **2b** and its corresponding oxidized species. In the inset, extension of the part corresponding to the formation of the mixed-valence band.

To interpret the nature of this mixed-valence interaction, experiments depending on concentration were carried out. It was found for bis-TTF **1** that the intensity of the mixed-valence band was not obeying the Beer−Lambert's law suggesting that both inter- and intramolecular interactions could coexist. On the other hand, it was found for tris-TTF **2b** that the intensity of the mixed-valence band was perfectly obeying to the Beer−Lambert's law, demonstrating the intramolecular and probably through-space nature of electronic interactions between TTF units.

In these preliminary results, we have extended the reactivity of the 1,3-dithiole and TTF frameworks by introducing the phosphonate functionality, and the possibility to reach conjugated oligomeric TTF through the Horner−Wadsworth−Emmons reaction. This methodology may be applied to synthezise conjugated TTF-acceptor assemblies using the appropriate electrophilic aldehyde on the accepting moiety. Electrochemical and optical properties of described dimeric and trimeric TTF evidenced the presence of intramolecular electronic interactions and a multistage redox behavior which can provide the opportunity to control the stoichiometry and the band-filling in corresponding promising cation radical salts.

Acknowledgment. Financial support was provided by the MENRT for the Ph.D. thesis of N.G. and for the postdoctoral stay of R.S. Dr N. Mercier is acknowledged for crystallographic determination.

Supporting Information Available: Experimental synthetic procedures, analytical data, X-ray crystallographic file (CIF); figures of molecular orbital calculations of **2b**; UV−vis−NIR spectra of oxidized species of **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Khodorkovsky, V.; Becker, J. Y. In *Organic Conductors: Fundamentals and Applications*; Farges, J.-P., Ed.; Marcel Dekker: New York, 1994; Chapter 3, p 75.

(20) Takimiya, K.; Oharuda, A.; Aso, Y.; Ogura, F.; Otsubo, T. *Chem. Mater.* **2000**, *12*, 2196.

(21) Carcel, C.; Fabre, J.-M. *Synth. Met.* **2002**, *130*, 99.

(22) Fourmigué, M.; Huang, Y.-S. *Organometallics* **1993**, *12*, 797.

(23) Giffard, M.; Mabon, G.; Leclair, E.; Mercier, N.; Allain, M.; Gorgues, A.; Molinié, P.; Neilands, O.; Krief, P.; Khodorkovsky V. *J. Am. Chem. Soc.* **2001**, *123*, 3852.

(24) (a) Huchet, L.; Akoudad, S.; Levillain, E.; Roncali, J.; Emge, A.; Bäuerle, P. *J. Phys. Chem. B* **1998**, *102*, 7776. (b) Spanggaard, H.; Prehn, J.; Nielsen, M. B.; Levillain, E.; Allain, M.; Becher, J. *J. Am. Chem. Soc.* **2000**, *122*, 9486.

(25) All the results obtained by chemical oxidation were also confirmed by time-resolved spectroelectrochemistry coupled to cyclic voltammetry.