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First Fused Perpendicular Hybrid Tetrathiafulvalene (TTF) Dimers: A New Strategy in π-Extended and Rigidified TTF

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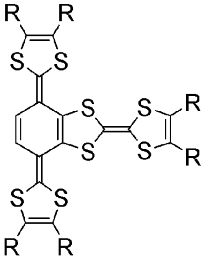
ABSTRACT



The synthesis, theoretical calculations, and crystallographic and electrochemical properties of fused perpendicular tetrathiafulvalene (TTF) dimers incorporating both a TTF unit and a quinonoid π-extended TTF are described as a new strategy for obtaining π-extended, rigidified, and sulfur-rich analogues of TTF.

Since the discovery of tetrathiafulvalene (TTF) and its unique properties as a π-donor, considerable work has been devoted to the search for more sophisticated derivatives[1] that are prone to generation of charge-transfer complexes or radical cation salts exhibiting two-dimensional networks upon oxidation.[2] This increase of dimensionality has been identified as a priority to prevent the metal-to-insulator transitions at low temperature, as well as to achieve highly conducting or superconducting materials.[3] On this basis, space-extended and sulfur-rich analogues of TTF constitute promising candidates.[4] Thus, bis(1,4-dithiafulven-6-yl)TTFs were proven to afford original two-dimensional electroconductive materials held by intermolecular intra- and interchain S···S contacts.[5] Nevertheless, some difficulties were found in the preparation of mixed valence salts from compound **1**, the crystals obtained being of insufficient quality to perform physical measurements.[6] The explanation found was an unwanted intramolecular cyclization reaction occurring under acidic or oxidative conditions.[7]

With the aim of suppressing such a side reaction, we recently reported the “T-shaped” TTF dimer **2**.[8] This kind of dimeric TTF derivative displaying multistage redox behavior should provide the possibility of controlling the stoichiometry and molecular assembly in the desired conduc-

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[1] Segura, J. L.; Martín, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 1372.

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[3] Farges, J. P. In *Organic conductors. Fundamentals and applications*; Marcel Dekker Inc.: New York, 1994.

[4] (a) Martín, N.; Sánchez, L.; Seoane, C.; Ortí, E.; Viruela P. M.; Viruela, R. *J. Org. Chem.* **1998**, *63*, 1268. (b) Pérez, I.; Liu, S.-G.; Martín N.; Echegoyen, L. *J. Org. Chem.* **2000**, *65*, 3796 and references therein.

[5] (a) Sallé, M.; Jubault, M.; Gorgues, A.; Boubekeur, K.; Fourmigué, M.; Batail P.; Canadell, E. *Chem. Mater.* **1993**, *5*, 1196. (b) Sallé, M.; Gorgues, A.; Jubault, M.; Boubekeur, K.; Batail P.; Carlier, R. *Bull. Soc. Chim. Fr.* **1996**, *133*, 417.

[6] Morisson, V.; Sallé, M.; Frère, P.; Belyasmine, A.; Gorgues, A.; Jubault, M.; Uriel, S.; Batail, P.; Boubekeur, K.; Orduna, J.; Garín, J. *Synth. Met.* **1995**, *70*, 1155.

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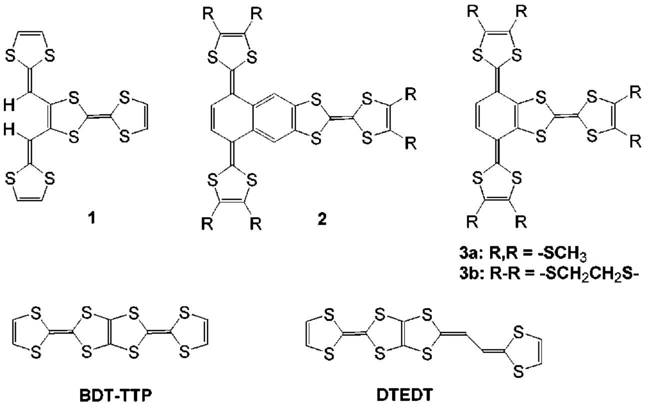
tive complexes.[9] Thus, compound **2** exhibited three reversible oxidation peaks following the sequence: $2 \rightleftharpoons 2^{2+} \rightleftharpoons 2^{3.+} \rightleftharpoons 2^{4+}$, in which the first two-electron process was related to the π-extended TTF moiety and both TTF units appeared to be electrochemically independent.

To increase the intramolecular interactions between the TTF entities, we have designed new space-extended donors **3** in which the 1,3-dithiol-2-ylidene moieties of **1** are connected using the vinylene group (Scheme 1).

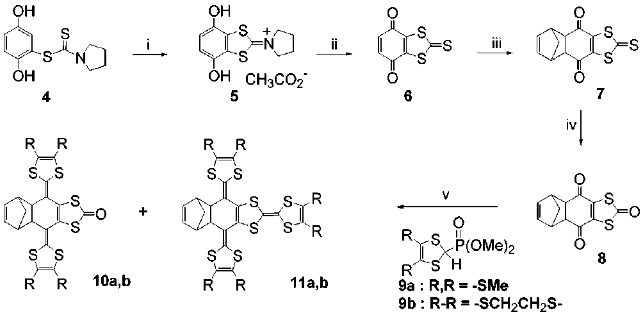
Scheme 1



This constitutes the first example of a fused perpendicular hybrid TTF dimer incorporating both the TTF unit and the quinonoid π-extended TTF and introduces a new strategy in bis-fused TTF. To our knowledge, this approach was restricted to the synthesis of BDT-TTP[10] and derivatives, for which interest has significantly increased since the discovery of the superconducting properties found from vinylogous DTEDT.[11]

As described in Scheme 2, the synthesis first used *p*-benzoquinone which reacted with the dithiocarbamate salt (resulting from the addition of pyrrolidine to carbon disulfide) in the presence of glacial acetic acid. The corresponding Michaël addition was followed by aromatization, producing compound **4** in 75% yield. The latter was oxidized using *p*-benzoquinone, and the following cyclization upon treatment with glacial acetic acid afforded iminium salt **5** in 68% yield for both steps. After quantitative conversion into the corresponding 2-thioxo-1,3-dithiole using sodium sulfide, the oxidation was improved using DDQ to furnish **6** in 74% yield.

Scheme 2[a]



[a] Reagents and conditions: i, *p*-benzoquinone, CH_3OH then glacial AcOH, 80 °C, 68% (lit.[12] 63%); ii, $Na_2S{\cdot}9H_2O$, MeOH, 98% (lit.[12] 71%); then DDQ, 74% (lit.[12] 54% using *p*-benzoquinone); iii, cyclopentadiene, THF, 25 °C, 94%; iv, $Hg(OAc)_2$, CH_2Cl_2/glacial AcOH, 93%; v, phosphonate **9**, *n*-BuLi, THF, −78 to 20 °C.

Cyclic voltammetry of **6** exhibited two reversible one-electron reduction peaks, the first one appearing at $E_1^{red} = -0.15$ V.[13] To avoid the electron transfer of the phosphonate anion of **9** to the quinonic functionality that occurred during the following olefination step,[8] the accepting character of **6** was suppressed by a prior Diels−Alder cycloaddition of cyclopentadiene in THF, affording 2-thioxo-1,3-dithiole **7** in 94% yield ($E_1^{red} = -0.87$ V).[13] The latter was converted into the key intermediate **8** in 93% yield using the classical transchalcogenation reaction ($E_1^{red} = -0.95$ V).[13] The single-crystal X-ray structure of **8** revealed that the unique kinetic isomer with respect to the endo rule was compatible with the reported cycloaddition of cyclopentadiene to *p*-benzoquinone.[14]

We then carried out a Horner−Wadsworth−Emmons olefination to create the TTF core.[8a] After the reaction of **8** with phosphonate anion **9**,[15] a silica gel column chromatography (CS_2/CH_2Cl_2 (8/1) as the eluent) was used to separate the bis-olefinated and tris-olefinated compounds **10** and **11**, respectively. The yields of the reaction appeared to be dependent on the excess of phosphonate (for 6 equiv of **9a**: **10a** = 32% and **11a** = 44%; for 10 equiv of **9b**:**10b** = 47% and **11b** = 36%). Considering that the decomposition of **11a** and **11b** occurred at 156 and 125 °C, respectively, cyclopentadiene was removed quantitatively by thermal treatment to reach the bis-fused TTF **3** (Scheme 3).[8] All new compounds gave satisfactory spectroscopic data.[16]

The X-ray structure of a single crystal of **11a** showed that the π-extended unit presents a butterfly-shaped nonplanar

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(7) (a) Benahmed-Gasmi, A.; Frère, P.; Belyasmine, A.; Malik, K. M. A.; Hursthouse, M. B.; Moore, A. J.; Bryce, M. R.; Jubault M.; Gorgues, A. *Tetrahedron Lett.* **1993**, *34*, 2131. (b) Frère, P.; Gorgues, A.; Jubault, M.; Riou, A.; Gouriou Y.; Roncali, J. *Tetrahedron Lett.* **1994**, *35*, 1991. (c) Mézière, C.; Sallé, M.; Fourmigué, M. *Acta Crystallogr.* **1998**, *C54*, 2005.

(8) (a) Boulle, C.; Desmars, O.; Gautier, N.; Hudhomme, P.; Cariou, M.; Gorgues, A. *Chem. Commun.* **1998**, 2197. (b) Gautier, N.; Mercier, N.; Riou, A.; Gorgues, A.; Hudhomme, P. *Tetrahedron Lett.* **1999**, *40*, 5997.

(9) For reviews on TTF dimers, see: (a) Otsubo, T.; Aso, Y.; Takimiya, K. *Adv. Mater.* **1994**, *6*, 439. (b) Becher, J.; Lau, J.; Mørk, P. In *Electronic Materials: The Oligomer Approach*; Müllen, K., Wegner, G., Eds.; Wiley-VCH: Weinheim, 1998; p 198.

(10) Misaki, Y.; Matsui, T.; Kawakami, K.; Nishikawa, H.; Yamabe T.; Shiro, M. *Chem. Lett.* **1993**, 1337.

(11) (DTEDT)$[Au(CN)_2]_{0.4}$ showed superconductivity below 4 K at ambient pressure: Misaki, Y.; Higuchi, N.; Fujiwara, H.; Yamabe, T.; Mori, T.; Mori H.; Tanaka, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1222.

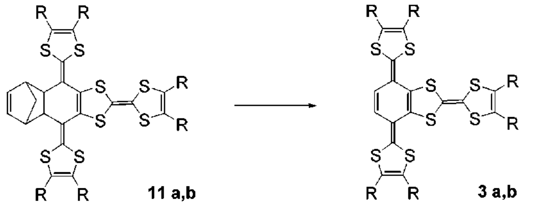
(12) Compound **6** was synthesized according to a previously described methodology, with several yields being improved by modifications of experimental procedures or reagents: Sun, D.; Krawiec, M.; Watson, W. H. *J. Chem. Crystallogr.* **1997**, *27*, 515.

(13) Conditions of cyclic voltammetry: Pt electrode, 1.5 mM in $CH_2Cl_2-n\text{-}Bu_4NPF_6$ 0.1 M, $v = 100$ mV s^{-1}, E^{red} in V/SCE.

(14) O'Brien D. F.; Gates, J. W., Jr *J. Org. Chem.* **1965**, *30*, 2593.

(15) Moore, A. J.; Bryce, M. R. *Synthesis* **1991**, 26.

Scheme 3[a]



[a] Reagents and conditions: for **11a**, refluxing *o*-dichlorobenzene; for **11b**, refluxing chlorobenzene, quantitative yields.

geometry (Figure 1).[4a] This distortion from planarity could be described in terms of the angle γ which defines the tilting of the dithiole units and is obtained as the supplement of the C16−C4−C22−C3 dihedral angle. This crystallographic angle ($\gamma = 20°$) was found to be remarkably lower than the one observed for the equivalent precursor of **2** ($\gamma = 34.5°$), in which the conformation is strongly controlled by the short distance between the *peri*-hydrogens of the benzene ring and the sulfur atoms of the 1,3-dithiole units.[17] In the case of compound **11a**, this gain in planarity is justified by strong intramolecular S···S interactions, with the distances S1···S7 = 3.029(3) Å and S2···S9 = 3.055(3) Å, lower than the sum of van der Waals radii (3.70 Å) and in good agreement with the distances observed for derivatives of **1**.[5]

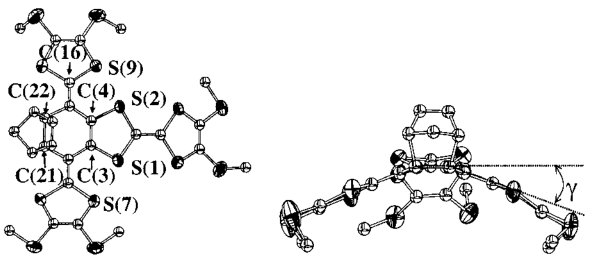


Figure 1. ORTEP views of **11a**. Ellipsoids are drawn at 50% probability.

Density functional theory (DFT) calculations were performed with the GAUSSIAN 98[18] package at the B3LYP/6-31G* level of theory for a full geometry optimization of compound **11** (R = H). The calculated angle ($\gamma = 24.7°$ and the intramolecular S···S distances (3.22 Å) confirm the trend observed for the experimental X-ray data. These theoretical calculations were extended to compound **3** (R = H) for which the recovery of the quinonoid structure induces an important gain of planarity ($\gamma = 6.8°$). The calculated angle was compared with the one computed for compound **2** ($\gamma = 19.2°$), the difference being attributed to the S···S interactions (3.08 Å) between both TTF moieties in **3**.

Comparison of deconvoluted cyclic voltammograms (CV) of the dimeric TTF **2** and the fused TTF-extended TTF **3b** gave fundamental structural information (Figure 2). Although the CV for **2** was characterized by both CVs of extended TTF and TTF moieties, the interesting feature of dimer **3** concerns its ability to undergo four sequential reversible oxidation processes. With this phenomenon being independent of the concentration, the existence of intramolecular electronic interactions is clearly shown. These separated oxidation processes could arise from Coulombic repulsions between the two different TTF moieties in the oxidized states.

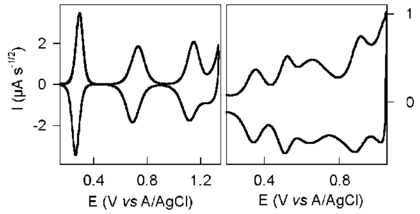


Figure 2. Deconvoluted cyclic voltammograms of **2** (left) and **3b** (right): Pt electrode; *n*-Bu_4NPF_6 0.1 M in CH_2Cl_2; $v = 100$ mV s^{-1}.

In these preliminary results, we have introduced a new strategy for perpendicular bis-fused TTF. Further electrochemical studies and electrocrystallizations to reach promising radical cation salts from **3** are in progress.

Acknowledgment. Financial support was provided by the MENRT for a research studentship to N. Gautier. All theoretical calculations were performed at the national CINES computing center.

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(16) Crystal data for **11a**: $C_{27}H_{26}S_{14}$, $M = 799.4$, monoclinic, $a = 14.189(2)$, $b = 9.568(1)$, and $c = 26.106(1)$ Å, $\beta = 96.09(1)°$, $V = 3524(1)$ Å^3, space group $P2_1/n$, $Z = 4$, calculated density 1.5 ($\lambda_{\mathrm{Mo\ K\alpha}} = 0.71069$). A total of 6595 reflections werer collected in the 2.5−25°θ range; 235 parameters from 2989 reflections with $I/\sigma(I) > 3$ converged to $R = 0.052$, $R_W = 0.074$.

(17) This X-ray structure analysis will be published later. Gautier, N. *Thesis of Nantes and Angers Universities, France*, October 24th 2000.

(18) Gaussian 98 (Revision A.9). Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.