Bis- and Tetrakis(1,4-dithiafulven-6-yl)-Substituted Tetrathiafulvalenes and Dihydrotetrathiafulvalenes: A Novel Class of Planar Donor Molecules with Multiple Redox Functionalities and the Demonstration of a Novel Type of Two-Dimensional Association in the Solid State

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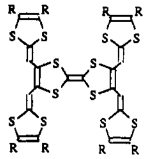
The field of organic conductors and superconductors was launched by the discovery of a wealth of fascinating physics in one dimension[1] subsequent to the conception and preparation of a few prototypical systems such as TTF-TCNQ and the Bechgaard salts, $(TMTSF)_2X$. A substantial amount of research is dedicated to new systems with higher dimensionality where the Peierls instability or charge localization effects inherent to one-dimensional conducting systems are far less effective. In that respect, the ability of sulfur-rich cation radical molecules, such as the bisethylenedithiotetrathiafulvalenium ($BEDT\text{-}TTF^{\bullet+}$), to self-associate in two-dimensional arrays to give the so-called β and κ phases has been well documented.[2]

The present paper focus on new extended, sulfur-rich planar analogues of TTF in which the central olefinic linkage is replaced by larger conjugated fragments.[3] The synthesis of the TTF analogues **1**, **2**, and **3** in which the TTF or dihydro-TTF[4] cores bear two or four 1,4-dithiafulven-6-yl sidearms has been reported recently.[5] In this communication, the potential of those novel π donors is demonstrated by the synthesis of the salt $\mathbf{3c}^{\bullet+}ClO_4^-$ in which the central molecular cores are strongly overlapping in stacks coupled in the transverse direction by the overlap of the outer dithiafulvenyl arms to create an unprecedented type of 2D network. It is further shown that two-dimensional electron delocalization is in fact also occurring in this slab, a consequence of the actual electronic conjugation on the entire molecule. The latter has been made effective by the enhancement of the branching carbon coefficients in the donor HOMO when compared to those in the TTF HOMO.

Table I. Peak Potentials in V/SCE, Pt Electrode, 200 mV s^{-1} if Unspecified, 20 °C, Bu_4NClO_4 (0.1 mol L^{-1})

compound	solvent	$E_{p_a}{}^1$	$E_{p_a}{}^2$	$E_{p_a}{}^3$
TTF	DMF	0.42	0.72	
	TCE	0.40	0.82^d	
1a	DMF^a	0.32	$(0.65)^c$	$0.81^{b,d}$
	TCE	0.34	0.65	0.95
1c	DMF^a	0.19	0.34	0.50^d
1d	DMF^a	0.13	0.29	0.48
	TCE	0.08	0.17	0.51
2c	DMF	0.29		
	DMF^e	0.22	0.30	
3a	DMF	0.51	0.58	
	TCE	0.51	0.74	
3c	DMF	0.29		
	TCE	0.26	0.39^a	

[a] Poorly resolved for this sparingly soluble compound. [b] Exaltation of the oxidation peak. [c] Poorly defined. [d] Irreversible system. [e] Sweeping rate 50 mV s^{-1}.



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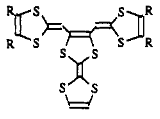

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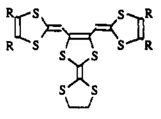

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a R = CO2Me
b R-R = (CH=CH)2
c R = H
d R-R = (CH2)4

The donor abilities of **1**–**3** (Table I) appear to be quite strong since, for most of them, the first oxidation potential ($E_{p_a}{}^1$) is markedly lower than that of TTF. Of particular note is **1a**, a better donor than TTF despite its eight electron-withdrawing methoxycarbonyl substituents. The HOMO of molecules **1**, **2**, and TTF are shown in Figure 1a–c, respectively. The more noticeable difference between them is that the outer carbons of the TTF core have a small contribution to the HOMO of TTF itself but quite a large one in those of **1** and **2**. This essential difference is intimately related to the very strong donor character of **1**, **2**, and **3**. The orbitals in Figure 1 are essentially the antibonding combinations of the π-type HOMO of the $S_2C{=}CS_2$ inner core of TTF with that of the ethylene or hexatriene fragments (at this point, the contribution of the outer vinylenedithio fragment is neglected). As schematically shown in Figure 1d, the HOMO energy of an outer [$4n+2$] conjugated fragment increases with its

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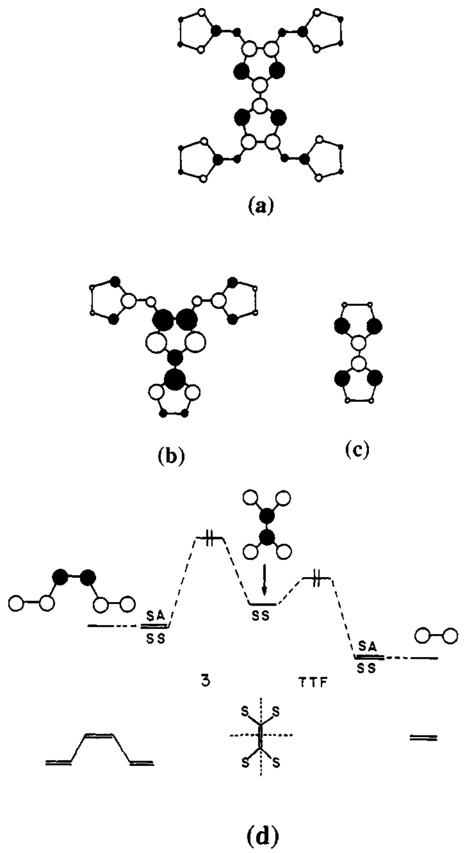

Figure 1. HOMO of (a) **1**, (b) **2**, and (c) TTF. Schematic interaction diagram (d) illustrating the main difference between the HOMO of TTF and **1** (see text).

length, and so does the mixing between the two orbitals and the donor character of the molecule. The role of the outer ethylenedithio fragments is to provide an additional energy rising of the HOMO, which is possible because the carbon orbitals at the end of the extended conjugated fragments are large.

The cyclic voltammograms of **1**–**3** are solvent dependent,[6] revealing (i) in the case of **2** and **3**, two reversible one-electron processes, almost coalesced in most solvents but fairly well discriminated at slow sweeping rates, and (ii) in the case of **1**, three successive reversible one- and two-electron redox processes in 1,1,2-trichloroethane, which implies a good stability of the cationic species up to $\mathbf{1}^{4+}$.[7]

Another remarkable, albeit expected feature of these extended redox molecules is the close proximity of the successive oxidation steps which clearly indicates the lowering of the intramolecular coulombic repulsions in the multicationic states. For instance, $\Delta(E_p{}^2 - E_p{}^1)$ barely amounts to 0.10 V for **1d**, **2c**, and **3c**, and $\Delta(E_p{}^4(=E_p{}^3) - E_p{}^2) = 0.30$ V only for **1d**, whereas $\Delta(E_p{}^2 - E_p{}^1) = 0.25$ V for TTF itself. These observations are also consistent with the very low potential value ($E_p{}^3 = E_p{}^4 = 0.50$ V/SCE) at which are formed the tri- and tetracationic species issued from **1c** and **1d**.[8]

All new donors react readily with tetracyanoquinodimethane (TCNQ), in solution or by grinding of the solids.[9] Thus, with **3c**, a dark blue microcrystalline complex is obtained and analyzed[10] as $(\mathbf{3c})_2(\mathrm{TCNQ})_3$, with a room-temperature compressed pellet conductivity of 1 S cm^{-1}. Shiny, black needlelike single crystals of a semiconducting cation-radical salt, formulated as $\mathbf{3c}^{\bullet+}\mathrm{ClO}_4{}^-$, were grown on a platinum wire anode upon constant low-current density (1 μA cm^{-2}) oxidation of the donor in the presence of a 10/1 1,1,2-trichloroethane/ethanol solution of tetrabutylammonium perchlorate (0.1 mol L^{-1}). The room-temperature conductivity measured in four points along the needle axis is remarkably higher (0.38 S cm^{-1}; $E_a = 170$ meV) than expected for a 1:1, fully charge-transferred salt. In addition to the cyclic voltammetry data, this is another strong indication that the on-site Colomb repulsion U is quite small in this large, extensively conjugated molecule.

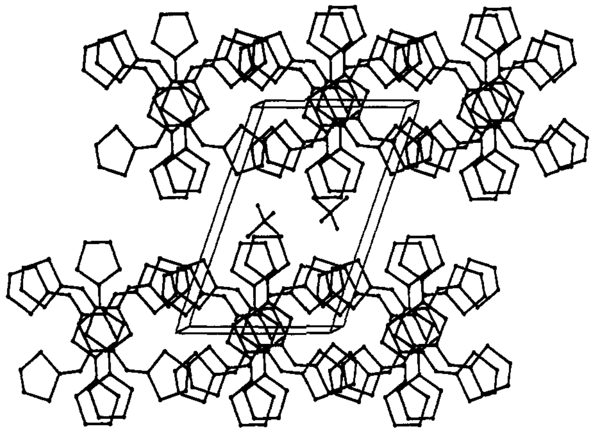

Figure 2. Structure of $\mathbf{3c}^{\bullet+}\mathrm{ClO}_4{}^-$. The *b* axis runs horizontally and the *c* axis vertically. The *a* axis is approximately normal to the figure.

As exemplified in Figure 2, the main feature of the crystal structure[11] of $\mathbf{3c}^{\bullet+}\mathrm{ClO}_4{}^-$ is the presence of slabs of cation radical molecules separated by the anions along the transverse *c* axis direction. Within a slab, an head-to-tail overlap of the dissymetrical central cores of the planar $\mathbf{3c}^{\bullet+}$ molecules occurs along *a*. This mode of overlap provides the possibility for the pairs of outer dithiafulvenyl fragments to reach out and become intertwinned along *b*. This unique pattern of overlap, a manifestation of the shape and planar character of the molecule, creates a novel type of two-dimensional association for cation radical salts.

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[10] Calcd (C, H, N, S) 51.87, 2.18, 11.34, 34.62; found 50.91, 2.34, 11.09, 34.19.

[11] (a) Crystal structure for $\mathbf{3c}^{\bullet+}\mathrm{ClO}_4{}^-$, $\mathrm{C}_{14}\mathrm{H}_8\mathrm{O}_4\mathrm{ClS}_8$, $M = 532.18$, triclinic, space group $P\bar{1}$, $a = 8.213(2)$, $b = 9.062(1)$, $c = 13.992(2)$ Å, $\alpha = 71.84(1)$, $\beta = 85.68(1)$, $\gamma = 84.50(1)°$, $V = 987.1$ Å^3, $Z = 2$, $d_{\mathrm{calc}} = 1.79$ g cm^{-3}, μ (Mo Kα) = 10.26 cm^{-1}; a black needle-shaped crystal (ca. 0.36 × 0.06 × 0.04 mm^3) was mounted on a glass fiber and the data were collected on an Enraf-Nonius CAD4-F diffractometer at room temperature with monochromaitzed Mo Kα radiation (3868 reflections up to $\theta_{\max} = 26°$ collected with $\omega/2\theta$ scan technique). The structure was solved by direct methods (Multan 11/82). All but one H atoms were identified on Fourier difference maps but simply introduced at calculated positions (C–H = 0.95 Å). Full-matrix least-squares refinement converged at a final R (R_w) value: 0.056 (0.067) for 1354 reflections with $I \geqslant 3\sigma(I)$ (G.O.F = 1.628); highest peak on ΔF: +0.53, –0.36 e Å^{-3}. (b) Premiminary structural data for this compound were included in the Proceedings of the ICSM 1992 Göteborg meeting: Sallé, M.; Jubault, M.; Gorgues, A.; Boubekeur, K.; Fourmigué, M.; Batail, P.; Canadell, E.; Cousseau, J. *Synth. Met.* **1993**, *55–57*, 2132.

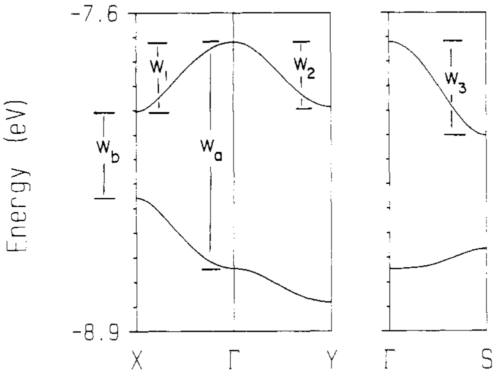

Figure 3. Dispersion relations for the highest two occupied bands of $3c^{\bullet+}ClO_4^-$ where $\Gamma = (0,0)$, X $(a^*/2,0)$, $Y = (0, b^*/2)$, and $S = (-a^*/2, b^*/2)$.

There are four different types of molecule-molecule interactions involving S···S distances shorter than 3.8 Å. Two of them (I and II) are associated with interactions along *a* and two (III and IV) with interactions along *b*. The calculated transfer integrals (t) for interactions I, II, III, and IV are 0.321, 0.115, 0.024 and 0.042, respectively. The band dispersions along a and b are essentially determined by the transfer integrals t_{II} and $2(t_{III} + t_{IV})$, respectively. Hence, the HOMO bands should be two-dimensional. The calculated[12] band structure of Figure 3 substantiates our discussion. It is interesting to compare the calculated band widths for (**3c**)ClO_4 and $(TMTTF)_2Br$. The values of W_1, W_2, W_3, W_a, and W_b for (**3c**)ClO_4/$(TMTTF)_2Br$ are 0.28/0.30, 0.27/0.06, 0.38/0.48, 0.97/0.75, and 0.35/0.09, respectively. W_1 and W_3 for (**3c**)ClO_4 are only slightly smaller that those for $(TMTTF)_2Br$ for which metallic conductivity is observed. Thus, if band fillings different from one-half could be achieved, for example by changing the stoichiometry by using different anions, metallic conductivity would then be expected for two-dimensional slabs with this configuration. Two strategies to increase the band dispersion could be (i) decreasing the gap W_b by applying pressure, and (ii) substituting sulfur for selenium in **3c**. Note finally that the large value of W_2, a consequence of the shape of and extended conjugation within **3c**, confers a significant 2D character to (**3c**)ClO_4. This could suppress the Peierls instability and sustain metallic properties until very low temperatures in these new classes of materials.

Acknowledgment. The authors wish to thank Dr. P. Auban-Senzier for the conductivity measurement.

Supplementary Material Available: Tables of atomic coordinates of all atoms, and anisotropic and isotropic thermal parameters of all non-hydrogen atoms (12 pages); listing of calculated and observed structure factors for (**3c**)ClO_4 (7 pages). Ordering information is given on any current masthead page.

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