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LETTERS

1,1-Bis(tetrathiafulvalenyl)ethylene. A Unique Cross-Conjugated Dimeric Tetrathiafulvalene

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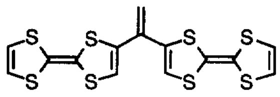
Abstract: 1,1-Bis(tetrathiafulvalenyl)ethylenes, synthesized using the palladium-catalyzed cross-coupling of 4-trimethylstannyl-TTF with 2,2-disubstituted 1,1-dibromoethylenes, were converted into the corresponding CT-complexes and cation-radical salts to determine the electric conductivities and magnetic properties.

Keywords: coupling reactions; electron donors; physical properties; X-ray crystal structures.

Since the discovery of the properties of tetrathiafulvalene (TTF) in 1970,[1] much effort has been devoted to designing new analogues of this π-donor in order to improve the electroconducting properties of the corresponding salts.[2] Fukutome reported theoretical calculations[3] and predicted that the dication-diradical **2** derived from 1,1-bis(tetrathiafulvalenyl)ethylene **1** shows a high-spin ground state (i.e., a triplet ground state) which possesses somewhat lower energy as compared with a low-spin ground state. This presumption suggests that molecular materials containing both magnetic and electrical behavior may be constructed from TTF derivatives. An attempt along this line has been reported for bis(tetrathia-fulvalenyl)ketone **3** and its derivatives and the results show that the dication-diradical **4** derived from **3** possesses a singlet ground state, presumably due to the fairly stabilized singlet ground state in **4**.[4] Since the triplet ground state in **2** has been calculated to be more stable than that in **4**, 1,1-bis(tetrathiafulvalenyl)ethylenes **5**-**9** have been synthesized to examine the spin-spin interaction and conducting properties of CT-complexes and cation-radical salts derived from new donors **5**-**9**.



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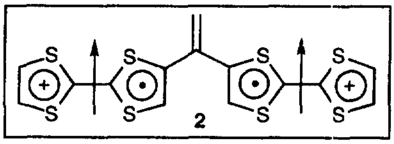

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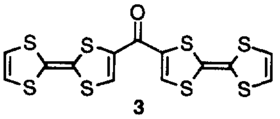

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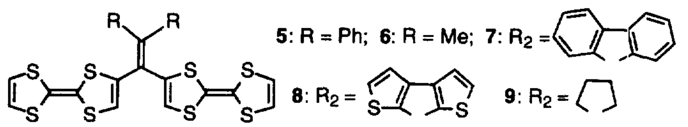

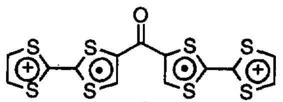

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The synthesis of **5**-**9** was carried out using the palladium-catalyzed cross-coupling reaction of 4-trimethylstannyl-TTF **11** with 2,2-disubstituted 1,1-dibromoethylenes (Scheme 1).[5] Thus, the reaction of **11** (2 equiv.) with 1,1-dibromo-2,2-diphenylethylene **12** (1 equiv.) in the presence of $Pd(PPh_3)_4$ (0.1 equiv.) proceeded smoothly in refluxing benzene for 24 h to produce **5** in 57% yield.[6] Although the reaction of **11** with 1,1-dibromo-2-methylpropene **13** in the presence of $Pd(PPh_3)_4$ (0.1 equiv.) produced **6** in a low yield (19%),

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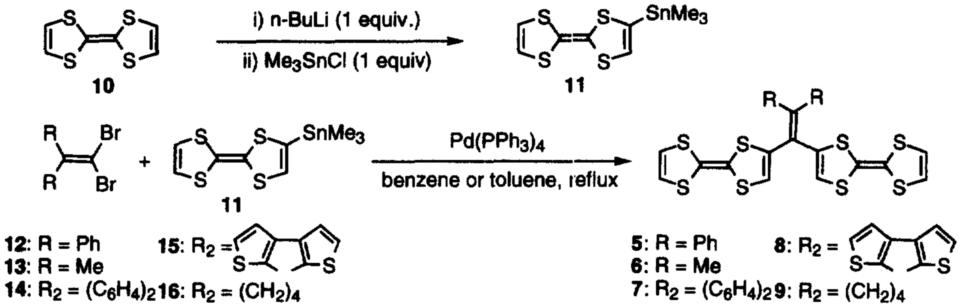
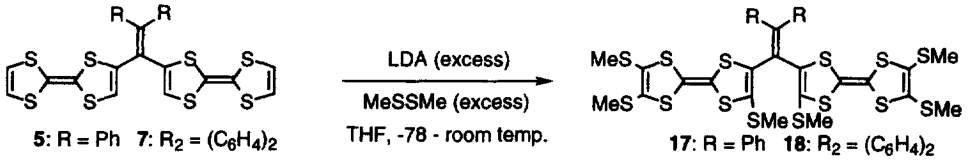
the yield of **6** was improved to 26% when the reaction was carried out in refluxing toluene. In a similar manner, the palladium-catalyzed reactions of **11** with **14**, **15** and **16** in refluxing benzene or toluene afforded the corresponding products **7**, **8** and **9** in 52, 41 and 28% yields, respectively.



Scheme 1

Because of the low solubility of the aryl-substituted **5** and **7** in common organic solvents such as ether, CH_2Cl_2, benzene, etc., we converted **5** and **7** into the hexamethylthio derivatives **17** and **18** (Scheme 2). The reactions of **5** and **7** with excess amounts of lithium diisopropylamide (LDA) in THF at -78 °C, followed by treatment with dimethyldisulfide (excess) at -78 °C to room temperature produced the corresponding fully thiomethylated **17** and **18** in 48 and 13% yields, respectively.



Scheme 2

Table 1. Cyclic voltammetric data for **5-9** and **17-18**.[a]

Compound	$E^1_{1/2}$	$E^2_{1/2}$	ΔE	Compound	$E^1_{1/2}$	$E^2_{1/2}$	ΔE
TTF	0.36	0.73	0.37	**8**	0.48	0.82	0.34
5	0.40	0.79	0.39	**9**	0.39	0.73	0.34
6	0.39	0.72	0.33	**17**	0.53	0.79	0.26
7	0.45	0.80	0.35	**18**	0.56	0.77	0.21

[a] Experimental conditions: *n*-Bu_4NClO_4 (0.1 mol dm^{-3}) in dry benzonitrile at room temperature; Pt working and counter electrodes. Potentials were measured against an Ag/Ag^+ electrode and converted to the value *vs* SCE (Fc/Fc^+ = 0.31 V).

In order to estimate the donor ability and the interactions between two TTF moieties in **5-9** and **17-18**, redox potentials of these new donors were measured by cyclic voltammetry. All 1,1-bis(tetrathiafulvalenyl)-ethylenes show the reversible two two-electron redox waves. As shown in Table 1, the potentials of **5**, **6**, and **9** show similar values for the first and second oxidations as unsubstituted TTF does, whereas the electron-withdrawing cyclopentadienylidene unit in **7** and **8** decreases the donor ability of the TTF moieties.[7] In the case of **17** and **18**, the first and second oxidation potentials are similar to those of tris(methylthio)-TTF.[8] These results indicate that the redox processes of **5-9** and **17-18** display no separation of each two-electron transfer in their cyclic voltammograms, presumably due to the weak interaction between the two TTF moieties in these molecules. The weak interaction in the neutral state of **5-9** and **17-18** may reflect the twisted structure which has been elucidated by the X-ray analysis of **5** and **17** (Figs. 1 and 2).[9]

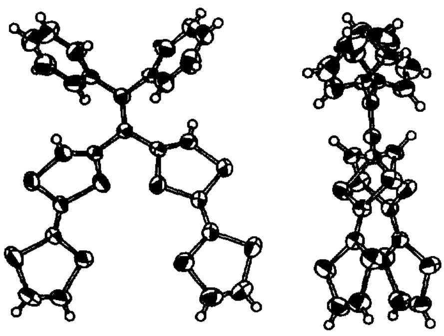

(a) (b)

Figure 1. ORTEP Drawings of **5**. (a) Top View. (b) Side View.

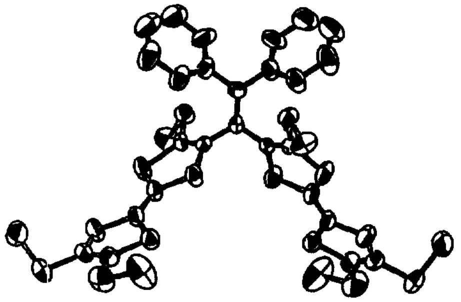
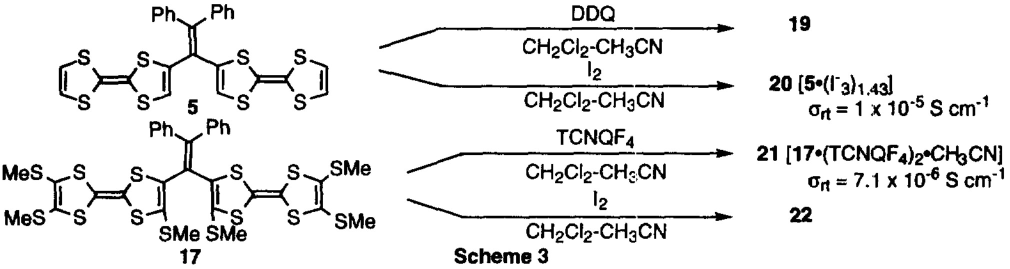


Figure 2. ORTEP Drawing of **17**.

All 1,1-bis(tetrathiafulvalenyl)ethylenes can be expected to form CT-complexes and cation-radical salts. Therefore, solutions of **5** and **17** in CH_2Cl_2 were mixed with solutions of DDQ and $TCNQF_4$ in CH_3CN to produce the corresponding CT-complexes **19** and **21**, respectively (Scheme 3). Similarly, treatment of **5** and **17** with I_2 yielded the cation radical salts **20** and **22**, respectively. Although **19**, **20** and **22** were fine crystals or an amorphous solid, the CT-complex **21** gave black single crystals, whose crystal structure was determined by X-ray analysis (Fig. 3). The cation-radical salt **20** and the CT-complex **21** show the electric conductivities of 1×10^{-5} and 7.1×10^{-6} S cm^{-1}, respectively, whereas **19** and **22** are insulators.



Scheme 3

As shown in Fig. 3, the CT-complex **21** consists of **17** and two $TCNQF_4$ molecules (1:2 complex) together with an equimolar amount of CH_3CN to **17**. The two $TCNQF_4$ molecules adopt an anion-radical form and are stacked face to face. The average exocyclic C-C bond length (1.412 Å) of $TCNQF_4$ in **21** is closely related to that of the $TCNQF_4$ anion-radical [1.407(9) Å][10] but clearly different from that of the neutral $TCNQF_4$ [1.372(2) Å].[11] Similarly, the lengths of the central and peripheral C-C double bonds of the two TTF moieties in **21** are elongated as compared with **17** (Fig. 2), reflecting the cation-radical structure of the TTF cores. Interestingly, the environment around the two $TTF^{+\bullet}$ moieties of $17^{2+\bullet}$ is clearly different. One forms a dimeric structure with the $TTF^{+\bullet}$ moiety of the neighboring $17^{2+\bullet}$, and the other does not have significant intermolecular contacts. The unique crystal structure of **21** is related to the magnetic properties. The field dependence of magnetization below 10 K shown in Fig. 4 is in good agreement with the Brillouin function for the one S = 1/2 spin per $17{\bullet}(TCNQF_4)_2{\bullet}CH_3CN$ unit, which can be rationalized by antiferromagnetic cancellation of the three of the four S=1/2 spins in $17{\bullet}(TCNQF_4)_2{\bullet}CH_3CN$ unit, due to the two types of dimeric structures revealed by X-ray crystallography, and the remaining one S = 1/2 spin of $TTF^{+\bullet}$. It is worth noting that the paramagnetic radical salt **21** is a semi-conductor.

Although the crystal structure of the cation-radical salt **20** is still unknown, **20** showed interesting magnetic and electrical behavior. Thus, the EPR spectra of the powdered sample of **20** at low temperatures consist of a broad signal at the center and a fine structure (g = 2.0074, D = 108 G at 163 K) along with $\Delta m_s = 2$ signals due to a triplet species. The distance between the two spins estimated from the D value by the point dipole approximation (6.36 Å) seems to be comparable to the distance between the two TTF units in **20**. The structure of **20** is now under investigation.

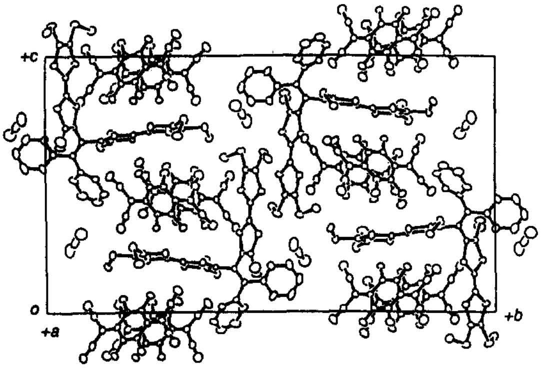


Figure 3. Crystal packing of **21**.

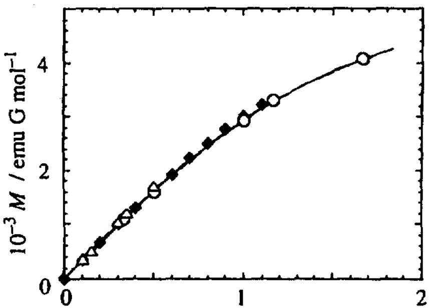


Figure 4. Field dependence of magnetization of **21** at 3 (O), 5 (♦), and 10 (Δ) K. Brillouin function for S = 1/2 is shown as a solid line.

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6. All new compounds described in this communication were fully characterized by spectroscopic analyses. Selected data were as follows. **5**: dark red needles, mp 213-214 °C (decomp.), FAB-MS (positive, *m*-nitrobenzyl alcohol) *m/z* 585 (M+1); ^{1}H NMR ($CDCl_3$) δ 7.29-7.28 (m, 6H), 7.21-7.20 (m, 4H), 6.27 (s, 4H), 6.06 (s, 2H); ^{13}C NMR (CD_2Cl_2) δ 147.4, 141.2, 135.3, 131.1, 128.2, 121.8, 119.2, 118.8. **6**: yellow fine cryst., mp 59-60 °C, FAB-MS (positive, *m*-nitrobenzyl alcohol) *m/z* 461 (M+1); ^{1}H NMR ($CDCl_3$) δ 6.33 (s, 4H), 6.21 (s, 2H), 1.47 (s, 6H); ^{13}C NMR (CD_2Cl_2) δ 143.4, 134.0, 119.6, 119.2, 118.9, 117.3, 110.2, 110.1, 22.7. **17**: red cryst., mp 81-82 °C, FAB-MS (positive, *m*-nitrobenzyl alcohol) *m/z* 861 (M+1); ^{1}H NMR (CD_2Cl_2) δ 7.32-7.27 (m, 10H), 2.43 (s, 6H), 2.41 (s, 6H), 2.05 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 153.4, 140.5, 133.2, 129.6, 128.1, 127.6, 127.3, 127.0, 126.0, 111.4, 107.1, 18.9, 18.8, 18.3.
7. Cf., Iyoda, M.; Okabe, T.; Kondo, T.; Sasaki, S.; Matsuyama, H.; Kuwatani, Y.; Katada, M. *Chem. Lett.*, **1997**, 103.
8. Cf., Iyoda, M.; Kuwatani, Y.; Hara, K.; Ogura, E.; Suzuki, H.; Ito, H.; Mori, T. *Chem. Lett.*, **1997**, 599.
9. X- Ray diffraction data were collected on a Rigaku AFC7R diffractometer. The structures were solved by direct methods and refined using full-matrix least-squares analyses using reflections with $I > 3.00\sigma(I)$. Anisotropic thermal parameters were used for non-hydrogen atoms. Crystal data for **5**: $C_{26}H_{16}S_8$, Mw = 584.89, triclinic, space group P1 (#2), a = 10.171(1), b = 21.257(2), c = 6.3169(8) Å, α = 93.196(8)°, β = 100.66(1)°, γ = 102.074(8)°, V = 1306.2(3) Å^3, Z = 2, Dc = 1.487 g cm^{-3}, R = 0.038, Rw = 0.027 for 4392 observed reflections out of 6040 unique reflections. Crystal data for **17**: $C_{32}H_{28}S_{14}$, Mw = 861.41, monoclinic, space group C2/c (#15), a = 21.089(2), b = 15.768(2), c = 13.144(2) Å, β = 117.483(6)°, V = 3877.7(7) Å^3, Z = 4, Dc = 1.475 g cm^{-3}, R = 0.083, Rw = 0.082 for 2207 observed reflections out of 3017 unique reflections. Crystal data for **21**: $C_{58}H_{28}N_9F_8S_{14}$, Mw = 1451.75, monoclinic, space group $P2_1/n$ (#14), a = 9.165(1), b = 34.473(2), c = 19.575(2) Å, β = 94.62(1)°, V = 6164.7(10) Å^3, Z = 4, Dc = 1.564 g cm^{-3}, R = 0.052, Rw = 0.058 for 6548 observed reflections out of 9370 unique reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
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