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Synthesis of New Donors, "TTF-dimer"s

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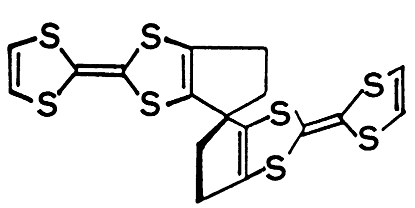
New donors, "TTF-dimer"s in which two TTF units are perpendicularly fixed have been synthesized. Redox potentials indicate that their donor abilities are somewhat reduced compared with those of corresponding "TTF-monomer"s. Present donors form CT complexes with DDQ.

Since the discovery of superconducting nature of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) salts, much efforts have been directed toward the synthesis of two- or three-dimensional conducting solid by the chemical modification of tetrathiafulvalene (TTF) using sulfur atoms.1) Owing to their large van der Waals radius and high polarizability, sulfur atoms form multidimensional network in crystals. Another possibility for the establishment of two- or three-dimensionality in organic crystals is, we think, to prepare donor molecules having two TTF units with a certain dihedral angle. These donors are expected to form segregated stacks in their radical salts or CT complexes as "TTF-monomer"s do. If the two TTF units in the molecule participate in the stacking simultaneously, two directions of TTF columns fixed with such an angle will be



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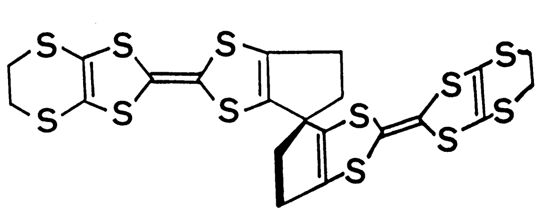

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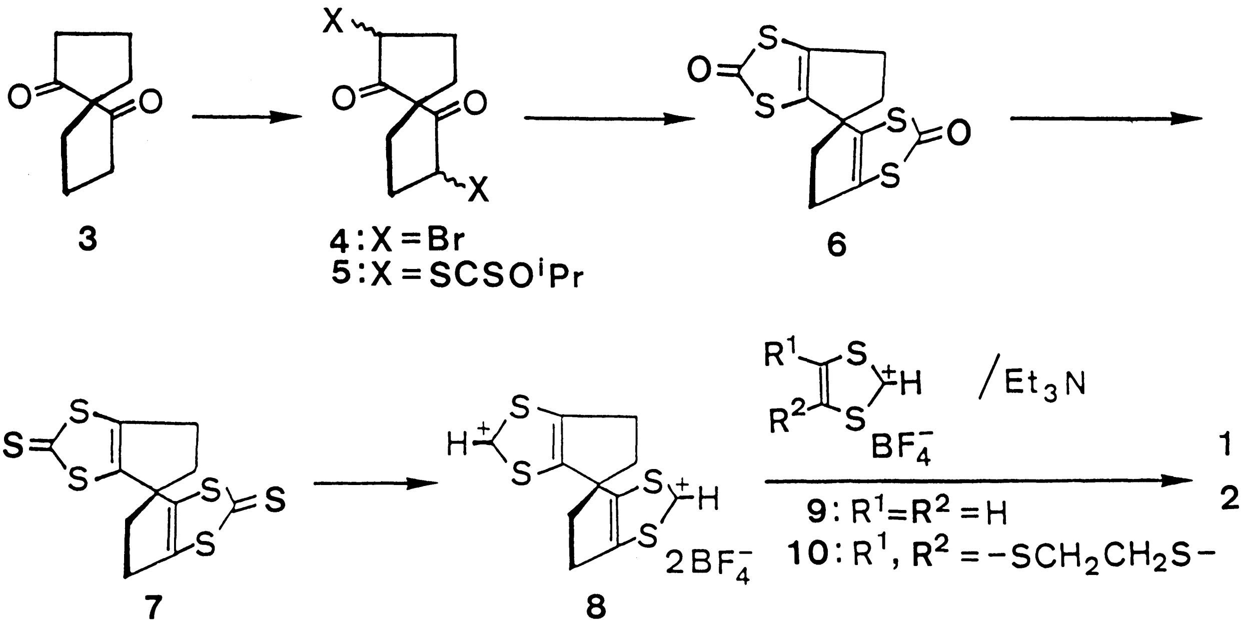
possible and the crystal will show two dimensional transport property. Here we report the first synthesis of TTF dimers **1**-**2**, where two TTF units are fixed perpendicularly.

Synthesis of **1**-**2** was carried out as follows. Spiro[4.4]nonane-1,6-dione **3**²⁾ was α-brominated with ether-bromine complex³⁾ to give **4**, which was, without purification, treated with sodium isopropylxanthate in acetone, affording keto-ester **5** in 36% yield from **3**. Cyclization of **5** with concentrated sulfuric acid gave spiro-bis-dithiocarbonate **6** in a yield of 36% [**6**: colorless fine scales from benzene-ethanol; mp 141.5-142 °C; ^{1}H-NMR($CDCl_3$, 360 MHz) 2.37-2.51 (m, 4H), 2.90-2.94 (m, 4H)]. Treatment of **6** with phosphorus pentasulfide in xylene afforded spiro-bis-trithiocarbonate **7** in 77% yield [**7**: red columns from chloroform-ethanol; mp 215-216 °C; ^{1}H-NMR ($CDCl_3$, 360 MHz) 2.58-2.69 (m, 4H), 2.89-2.93 (m, 4H)]. Compound **7** was easily converted to spiro-1,3-dithiolium tetrafluoroborate **8** in 68% yield in the similar manner described before.⁴⁾ Cross coupling of **8** with ten molar excess of 1,3-dithiolium tetrafluoroborate **9**⁵⁾ and with 4,5-ethylenedithio-1,3-dithiolium tetrafluoroborate **10**⁴⁾ in the presence of triethylamine in acetonitrile gave spiro-"TTF-dimer"s **1** and **2** in 18 and 22% yields, respectively. The two donors obtained were purified by column chromatography on silica gel or gel-permeation chromatography [**1**: yellow scales from $CHCl_3$; dec >200 °C; ^{1}H-NMR(CS_2, 360 MHz) 2.36-2.60(m, 8H), 6.20(s, 4H). **2**: orange fine needles from



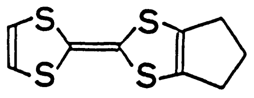
chlorobenzene; dec >225 °C; ^{1}H-NMR(CS_2, 360 MHz) 2.35-2.65(m, 8H), 3.25(s, 8H)].

Cyclic voltammetry of **1**-**2** showed reversible redox potential waves and the values are summarized together with those of references in Table 1. Although all the observed redox waves of **1**-**2** are assigned to one-electron transfer process on the basis of peak to peak separation, it is difficult to find the fourth redox potential (E^4) of **2**, presumably due to overlapping of E^4 with E^3. Judging from E^1 values of "TTF-dimer"s **1**-**2**, donor ability is slightly reduced in both cases compared with those of the corresponding "TTF-monomer"s, i.e. trimethylenetetrathiafulvalene **11**,$^{6)}$ and ethylenedithio(trimethylene)tetrathiafulvalene **12**.$^{4)}$

Table 1. Redox potentials of donors$^{a)}$ and electrical conductivities of their DDQ complexes (σ_{RT}/Scm^{-1})$^{b)}$

	E^1	E^2	E^3	E^4	σ_{RT}
1	0.41	0.50	0.66	0.78	1.5×10^{-6}
2	0.46	0.55	0.78	c	2.7×10^{-6}
11	0.35	0.75			
12	0.43	0.83			

a) Volts vs. SCE at a glassy carbon electrode. Supporting electrolyte: Et_4NClO_4; solvent: CH_2Cl_2; scan rate: 100mV/s. b) Compressed pellets. c) Very close to E^3.



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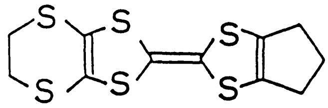

12

Preliminary attempts of complexation of **1**-**2** with TCNQ were unsuccessful. On the other hand, CT complexes with DDQ, which is stronger acceptor than TCNQ, were easily formed as black solids$^{7)}$ and their d.c. conductivities were measured on compressed pellets with two-probe technique as shown in Table 1. As one can see from the table, the conductivities are not excellent, but both values are similar to each other. Detailed explanation for these conductive properties as well as for the multi-dimensionality must await crystal structure analysis and we are now working along this line.

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7) Elemental analyses showed that the ratios of donor to acceptor in **1**-DDQ and **2**-DDQ were 1:1.7-2 and 1:0.5-0.8, respectively. The reason for such an ambiguous stoichiometry in these complexes is not clear.

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