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Synthesis and Properties of Bis[oxybis(methylenethio)]tetrathiafulvalene and Its Sulfur Analog: π-Donors for Organic Metals

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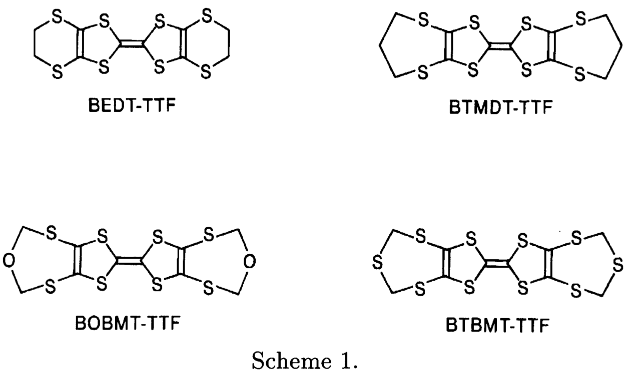
Bis[oxybis(methylenethio)]tetrathiafulvalene (BOBMT- TTF) and bis[thiobis(methylenethio)]-tetrathiafulvalene (BTBMT-TTF) were synthesized in two steps starting from 1,3,4,6-tetrathiapentalene-2, 5-dione. The electrochemical and donor properties of both compounds are discussed. BOBMT-TTF forms a highly conducting charge transfer complex with TCNQ ($\sigma_{\mathrm{RT}} \cong 10$ S cm^{-1}).

The discovery of interesting solid state properties, such as high electrical conductivity or even superconductivity in the radical cation salts of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) has attracted considerable attention.[1—3] Attempts to match the success of BEDT-TTF in the preparation of new conducting solids have spurred the search for structurally related molecules.[4,5] Modifications of the ET-skeleton such as bis(methylenedithio)tetrathiafulvalene (BMDT-TTF) or bis(trimethylenedithio)tetrathiafulvalene (BTMDT-TTF) are well-known,[6,7] whereas little information is available about ET-based donors bearing additional heteroatoms in the outer rings.[8,9]

In this communication we wish to report on the synthesis and donor properties of bis[oxybis(methylenethio)]tetrathiafulvalene (**4a**; BOBMT-TTF) and bis[thiobis(methylenethio)]tetrathiafulvalene (**4b**; BTBMT-TTF), both formally derived from BTMDT-TTF by replacing the middle methylene groups of the dihydrodithiepin rings with heteroatoms (O, S) (cf. Scheme 1).

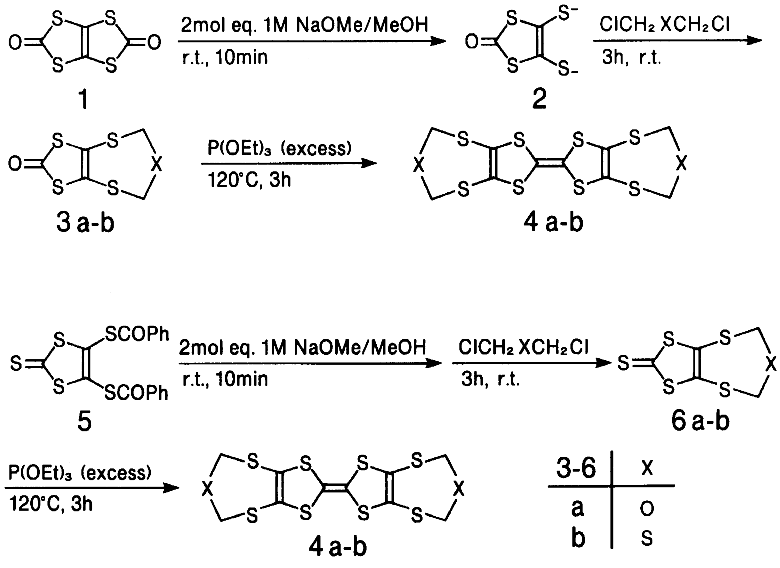


Scheme 1.

Results and Discussion

Synthesis of BOBMT-TTF and BTBMT-TTF. Both compounds were prepared in a novel two step procedure following a protocol recently developed for the synthesis of BEDT-TTF.[10] Treatment of 1,3,4,6-tetrathiapentalene-2,5-dione (**1**) with NaOMe/MeOH and subsequent alkylation of the in situ generated dianionic intermediate **2** with bis(chloromethyl) ether or bis(chloromethyl) sulfide provided the corresponding 4, 5-alkylenedithio-1,3-dithiol-2-ones **3a** and **3b** in yields of 45%. Coupling of **3a** and **3b** in triethyl phosphite furnished the desired donors **4a** and **4b** in yields of around 80% (cf. Scheme 2). A more common approach to **4a,b** (cf. Scheme 2),[6,7] employing 4,5-bis(benzoyldithio)-1,3-dithiole-2-thione (**5**) as starting compound gave the corresponding thiones **6a,b** in yields comparable to those of our route. However, the phosphite coupling of **6a,b** afforded the donors **4a,b** in only modest yields (≤30%), thus resulting in unsatisfactory overall yields (≤15%). Therefore, the latter route seems to be disadvantageous even though a desulfurization of **6a,b** in an additional reaction step is possible.[11]

Electrochemical Properties of BOBMT-TTF and BTBMT-TTF. The electrochemical behavior of **4a** is characterized by two ideally reversible redox waves, which correspond to the formation of the mono- and dications $\mathbf{4a}^{+}$ and $\mathbf{4a}^{2+}$, respectively. Compared with BTMDT-TTF and BEDT-TTF the first oxidation peak potential of **4a** is shifted anodically by more than +100 mV, whereas this effect is less pronounced for the second redox step. As the corresponding values of BTMDT-TTF and BEDT-TTF lie close together, the observed shift is caused by the substitution of two methylene groups with more electronegative oxygen atoms in the trimethylene bridges of BTMDT-TTF. The relatively high oxidation potentials of BOBMT-TTF confine the selection of anions suitable for prospective electrocrystallization experiments: The oxidation potential for the redox couple $\mathrm{I_3^-/I_2}$ was determined to be +716 mV vs. Ag/Ag$^+$, a value slightly lower than that found for $\mathbf{4a}/\mathbf{4a}^{+}$ under identical conditions. Accordingly, the preparation of radical cation salts of **4a** with oxidation-sensitive counterions like $\mathrm{I_3^-}$, $\mathrm{IBr_2^-}$ etc. might prove difficult, if not impossible.[12] It should also be noted that the difference ΔE between E_1 and E_2 is markedly smaller for **4a** than the corresponding values measured for BEDT-TTF and BTMDT-TTF (cf. Table 1); this points to a reduced on site Coulombic repulsion between the positive charges in the BOBMT-TTF dication. The virtual insolubility of **4b** in common organic solvents precluded the electrochemical determination of its redox potentials. However, taking into account that **4b**



Scheme 2.

Table 1. Electrochemical Oxidation Peak Potentials [mV][a)]

	E_1	E_2	ΔE
BOBMT-TTF	754	1109	355
BTMDT-TTF	644	1055	411
BEDT-TTF	631	1043	412

a) Measured at Pt electrodes in CH_2Cl_2/n-Bu_4NPF_6 (0.1 M) vs. Ag/Ag^+ in CH_3CN/n-Bu_4NClO_4 (0.1 M); substrate concentration ca. 5×10^{-4} mol dm^{-3}; scan rate: 100 mV s^{-1} (all potential values ±20 mV).

is easily oxidized by iodine (vide infra), the first anodic peak potential E_1 can be estimated to be around or smaller than +700 mV vs. Ag/Ag^+. A value halfway between those found for BOBMT-TTF and BTMDT-TTF would be expected with regard to the decreasing electronegatvities of the substituents. The anodic peak potentials of BOBMT-TTF, BTMDT-TTF, and BEDT-TTF measured under identical conditions are summarized in Table 1.

Donor Properties of BOBMT-TTF and BTBMT-TTF. BOBMT-TTF and tetracyanoquinodimethane (TCNQ) reacted in chlorobenzene under formation of a black, microcrystalline charge-transfer (CT) complex **7** which comprises donor and acceptor in a 1 : 1 ratio according to elemental analyses; attempts to obtain single crystals of suitable size and quality for X-ray diffraction and physical investigations (vide infra) were unsuccessful so far. IR spectra of **7** exhibit a strong electronic absorption stretching from ≅4000 to 1500 cm^{-1} (cf. Fig. 1). Moreover, the IR absorption of the CN stretch vibration of TCNQ in **7** is shifted from 2224 cm^{-1} (neutral TCNQ) to 2204 cm^{-1}. These findings indicate a *fractional* charge transfer from the donor **4a** to the acceptor TCNQ. According to previous work,[13)] the degree of charge transfer, Z, in **7** corresponds approximately to a value around 0.5 which comes close to that reported for TTF-TCNQ (Z=0.59).[14)] In contrast to the symmetrical Lorentzian ESR signals of Li^+TCNQ^- or TTF-TCNQ, ESR spectra of **7** exhibit an asymmetric, splitted (Dysonian ?) feature with a (maximum) linewidth ΔH of approximately 0.7 mT at room temperature (cf. Fig. 2). The (averaged) g-factor (2.007) and the relatively high spin density (2.4×10^{23} spins/mol) indicate the presence of a considerable number of delocalized electrons and thus corroborate the interpretation of the IR data. The splitting of the ESR signal could either be due to an anisotropic g-tensor or to the presence of *two* types of radical ions with differing g-factors in the solid, such as radical cations (e.g. **4a**$^+$) and anions (e.g. $TCNQ^-$). Hence, assuming the latter case, the signal shape could originate in a superposition of two signals with similar linewidths (ΔH≅0.3 mT), but different g-values: 2.0074 for the intensive, 2.0044 (estimated) for the weak signal, respectively. Data for

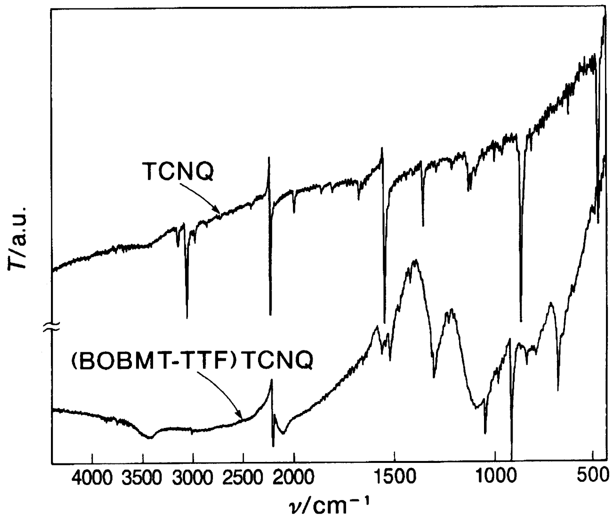


Fig. 1. FT-IR spectra of TCNQ (upper part) and (BOBMT-TTF) TCNQ (**7**) (lower part).

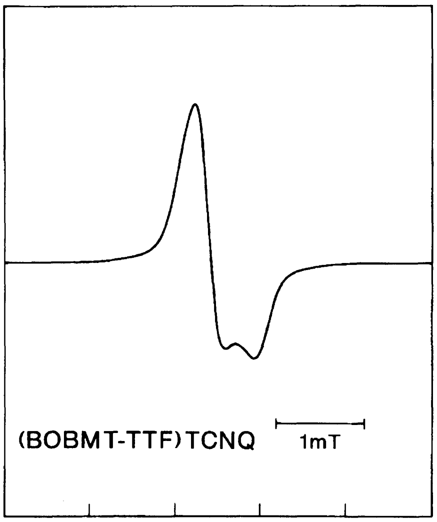


Fig. 2. ESR spectrum of (BOBMT-TTF) TCNQ (**7**) at 297 K.

typical TCNQ derivatives such as Li^+TCNQ^- ($\Delta H=0.35$ mT; $g=2.004$) or TTF-TCNQ ($\Delta H=0.8$ mT; $g=2.004$) as well as those for radical cation salts of **4a** would be consistent with this view.[15—17] With respect to the well-known, highly anisotropic properties of low-dimensional TCNQ complexes,[17] however, the observed feature could also be due to an anisotropy of the *g*-value of a single radical species, as it was found for *p*-phenylenediamine–chloranil.[18] Though a final clarification of this question requires a detailed ESR study of oriented single crystals, it may be concluded from the ESR and IR data available, that **7** comprises a large fraction of radical species with mobile electrons and thus should exhibit a certain electrical conductivity. Indeed, the room temperature conductivity σ_{RT} of compaction samples amounts to the relatively high value of 10 S cm^{-1} (resistance $\rho_{RT}\cong110$ m Ω cm), as determined by four probe measurements; the temperature dependence of the resistivity shows simply activated behavior in the range from 290 to 70 K ($E_{Gap}\simeq47$ meV). This result is surprising, since the corresponding CT complex (BTMDT-TTF)TCNQ is a rather poor conductor ($\sigma_{RT}=0.06$ S cm^{-1}; $\rho_{RT}=16$ Ω cm).[19] A similar reaction of **4b**, the sulfur analog of BOBMT-TTF, with TCNQ could not be achieved, even in boiling chlorobenzene no CT complex was formed. This is most likely due to the insolubility of BTBMT-TTF in common organic solvents. However, **4b** reacted with excess iodine in chlorobenzene at ambient temperature to give a black, microcrystalline salt **8** of the composition $(BTBMT\text{-}TTF)_2I_3$. IR spectra show only a very weak, if any electronic absorption superimposed to the skeletal vibrations of **4b**. The appearance of a new IR active mode at 1423 cm^{-1} as a result of the oxidation is typical for tetrathiafulvalene-based radical cation salts; all other bands remained unchanged within experimental error. ESR spectra of **8** show a symmetric, single line with a linewidth of 18 mT; *g*-value and spin density amount to 1.9958 and 1.49×10^{23} spins/mol, respectively. The room temperature conductivity of **8** (compaction samples) was determined to be 4×10^{-7} S cm^{-1}.

In conclusion, we have presented a new, facile synthetic access to the donor molecules BOBMT-TTF and BTBMT-TTF. The ability of **4a** to form stable radical cation salts in solution as well as a highly conducting CT complex with TCNQ encourages further studies, whereas **4b** seems to be — mainly due to its insolubility — a less promising candidate. The results of electrocrystallization experiments which are actively being carried out in this laboratory will be reported in a separate communication.

Experimental

The compounds **1**, **5**, bis(chloromethyl) sulfide and NaOMe (1 molar in MeOH) were used as purchased (Kanto Chemicals and Tokyo Kasei); bis(chloromethyl) ether was prepared according to the literature procedure.[20] MeOH was dried with MgOMe, distilled under argon and stored with molecular sieves. All experiments were carried out in an Ar atmosphere. IR spectra were run on a Perkin–Elmer FT-IR 1600, NMR (^1H and ^{13}C) and ESR spectra on JNM-EX 400 (JEOL) and REI-X (JEOL) spectrometers, mass spectra on a Perkin–Elmer GC-MS X 30 system, respectively. For cyclic voltammertry a BAS 100B electroanalytical system (Bioanalytical Systems) was used. All electrochemical measurements were performed in Ar atmosphere with dried and degassed CH_2Cl_2. The peak potentials of the redox system ferrocene/ferricinium amounted to 585/513 mV vs. Ag/Ag^+, respectively. Compaction samples of **7** and **8** in the shape of rectangular bars were manufactured with a hydraulic press ($p\cong5$ kbar). Four probe conductivity measurements were performed with gold wires ($\phi=20\mu m$) attached with silver paint to previously evaporated gold pads.

4-Oxa-2,6,8,10-tetrathiabicyclo[5.3.0]dec-1(7)ene-9-one (3a). To **1** (3.12 g; 15 mmol) was added 1 M NaOMe/MeOH (30 ml; 30 mmol) (1 M=1 mol dm^{-3}) in one portion via a syringe/rubber septum. The resulting reaction mixture was stirred for 10 min, then bis(chloromethyl) ether (1.72 g; 15 mmol) dissolved in MeOH abs (30 ml) was added dropwise. After stirring for another 3 h at room temperature, the reaction mixture was poured into water (200 ml), extracted with CH_2Cl_2 (3×100 ml), dried over $MgSO_4$ and the solvent evaporated to give crude **3a**. The crude product was dissolved in boiling MeOH with charcoal added as decolorizing agent and the hot solution filtered into distilled water. After standing overnight in a refrigerator, the white precipitate was filtered by suction, washed with pentane and finally dried in vacuo to give **3a** as a white solid (1.48 g; 44%). Mp (decomp) 159—160 °C. Found: C, 26.85; H, 1.69%. Calcd for $C_5H_4O_2S_4$: C, 26.77; H, 1.79%. MS *m/z* 224 (M^+), 194, 166, 120, and 88. IR (KBr) 3003, 2914, 1670, 1569, 1421, 1299, 1226, 1051, 976, 911, 751, and 676 cm^{-1}. ^1HNMR ($CDCl_3$) $\delta=4.89$. ^{13}CNMR (d_6-DMSO) $\delta=75.60$ (s, CH_2), 129.52 (s, C=C), and 189.55 (C=O).

2,4,6,8,10-Pentathiabicyclo[5.3.0]dec-1(7)ene-9-

one (3b). The reaction and the work-up were carried out exactly as described for **3a**, however, bis(chloromethyl) sulfide (1.96 g; 15 mmol) was used as alkylating agent. After a recrystallization as described above, **3b** was obtained as a white powder (1.62 g; 45%). Mp (decomp) 197—198 °C. Found: C, 25.02; H, 1.59%. Calcd for $C_5H_4OS_5$: C, 24.98; H, 1.68%. MS *m/z* 240 (M^+), 207, 194, 180, 166, 134, and 88. IR (KBr) 2989, 2970, 2914, 1682, 1651, 1611, 1366, 1223, 1162, 1128, 886, 856, 792, 745, and 720 cm^{-1}. ^{1}H NMR ($CDCl_3$) $\delta=4.00$.$^{21)}$

4-Oxa-2,6,8,10-tetrathiabicyclo[5.3.0]dec-1(7)ene-9-thione (6a). To **5** (6.1 g; 15 mmol) was added 1 M NaOMe/MeOH (30 ml; 30 mmol) in one portion via a syringe/rubber septum. The resulting deep red reaction mixture was stirred for 10 min, then bis(chloromethyl) ether (1.72 g; 15 mmol) disolved in MeOH abs (30 ml) was added dropwise. After stirring for another 3 h at room temperature, the reaction mixture was worked up as described for **3a**. The crude product was dissolved in hot $CHCl_3$ and filtered into MeOH to give **6a** as yellow crystals (1.62 g; 45%). Mp (decomp) 185—186 °C. Found: C, 24.95; H, 1.38%. Calcd for $C_5H_4OS_5$: C, 24.98; H, 1.68%. MS *m/z* 240, 210, 166, 146, 134, 105, 88, and 76. IR (KBr) 2910, 1471, 1303, 1052, 906, 672, and 516 cm^{-1}. ^{1}H NMR (d_6-DMSO) $\delta=5.17$ (s, CH_2). ^{13}C NMR (d_6-DMSO) $\delta=65.09$ (s, CH_2), 129.43 (s, C=C), and 201.29 (s, C=S).

2, 4, 6, 8, 10- Pentathiabicyclo[5.3.0]dec- 1(7)ene- 9-thione (6b). The reaction and the work-up were carried out as described for **6a**, however, bis(chloromethyl) sulfide (1.96 g; 15 mmol) in MeOH (30 ml) was used as alkylating agent. After recrystallization as described above, **6b** was obtained as bright yellow crystals (2.30 g; 60%). Mp (decomp) 206—208 °C. Found: C, 23.42; H, 1.41%. Calcd for $C_5H_4S_6$: C, 23.42; H, 1.57%. MS *m/z* 256, 180,134, 88, and 76. IR (KBr) 2955, 2907, 1363, 1221, 1166, 1128, 1035, 854, and 782 cm^{-1}. ^{1}H NMR ($CDCl_3$) $\delta=4.03$ (s, CH_2).$^{21)}$

Bis[oxybis(methylenethio)]tetrathiafulvalene (4a). Method A. Compound **3a** (1.08 g; 4.81 mmol) was dissolved in $P(OEt)_3$ (100 ml) and heated to 120 °C (oil-bath temperature) for 3 h. After cooling, the yellow precipitate was collected, washed with MeOH, EtOH, and pentane, and finally recrystallized from $CHCl_3$ to give **4a** as a bright yellow powder (0.78 g; 78%). Mp (decomp) 247—248°C. Found: C, 28.86; H, 1.82%. Calcd for $C_{10}H_8O_2S_8$: C, 28.83; H, 1.93%. MS *m/z* 416 (M^+), 386, 356, 222, 178, 158, and 88. IR (KBr) 2921, 2908, 1423, 1288, 1225, 1040, 993, 974, 909, 773, 690, and 664 cm^{-1}. UV-vis ($CHCl_3$) λ (log ε) 394 (2.380), 336 (2.975), 300 (2.623), and 258 (2.908).

Method B. Compound **6a** (0.3 g; 1.24 mmol) was heated in $P(OEt)_3$ (30 ml) to 120 °C for 3 h. The yellow precipitate was worked up as described for Method A. Yield: 80 mg (31%).

Bis[thiobis(methylenethio)]tetrathiafulvalene (4b). Method A. Compound **3b** (1 g; 4.16 mmol) was suspended in $P(OEt)_3$ (80 ml) and heated to 120 °C (oil-bath temperature) for 3 h. After cooling, the precipitate formed was collected, washed and dried as described for **4a**, to yield **4b** as a bright yellow-orange solid (0.76 g; 81%). Mp≥300°C (at $T\geq240$°C color changes from yellow-orange to brown). Found: C, 26.94; H, 1.69%. Calcd for $C_{10}H_8S_{10}$: C, 26.76; H, 1.79%. MS *m/z* 448 (M^+), 370, 268, 222, 180, 148, and 88. IR (KBr) 2958, 2901, 1364, 1218, 1164, 1125, 878, 852, 770, and 722 cm^{-1}.

Method B. Compound **6b** (0.3 g; 1.17 mmol) was suspended in $P(OEt)_3$ (20 ml) and kept at 115 °C for 3 h. After work-up as described above, **4b** was obtained (71 mg; 27%).

(BOBMT-TTF)TCNQ (7). A mixture of solid **4a** (50 mg; 0.12 mmol) and TCNQ (24.5 mg; 0.12 mmol) in chlorobenzene (20 ml) was heated to reflux temperature for 10 min. After cooling, the black precipitate was collected, washed with dichloromethane and pentane and dried in vacuo. Yiled (58.6 mg; 79%). Found: C, 42.71; H, 1.95; N, 8.84%. Calcd for $C_{22}H_{12}N_4O_2S_8$: C, 42.56; H, 1.95; N, 9.02%. IR (KBr) 2204, 1560, 1522, 1302, 1046, 913, 833, 675, and 468 cm^{-1}.

$(BTMT\text{-}TTF)_2I_3$ (8). To a stirred suspension of **4b** (50 mg; 0.11 mmol) in chlorobenzene (10 ml) was added a solution of iodine (71 mg; 0.56 mmol) in chlorobenzene. After stirring overnight, the black precipitate was collected, washed iodine-free with CCl_4 and finally dried in vacuo to give analytically pure **8** (60 mg; 85%). Found: C, 18.78; H, 1.00%. Calcd for $C_{20}H_{16}S_{20}I_3$: C, 18.66; H, 1.25%. IR (KBr) 1423, 1364, 1218, 1164, 1124, 877, 852, 810, 769, 720, 517, and 478 cm^{-1}.

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