Synthesis and Properties of Bis-(phenylenedithio)-tetrathiafulvalene (BPhDT-TTF): a New π-Donor for Organic Metals

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Tetrathiafulvalene, Organic Metals, Electrocristallization

The new π-donor bis-(phenylenedithio)-tetrathiafulvalene (BPhDT-TTF), synthesized via phosphite coupling of 2-oxo-1,3-dithiolo-[4,5-b][1,4]-benzodithin (4), has been prepared in 5 steps starting from 1,2-dimercaptobenzene and chloroacetyl chloride. Spectroscopic and electrochemical data point to a close similarity of 5 and dibenzo-tetrathiafulvalene (DB-TTF). 5 forms a highly conducting radical-cation salt ($\rho_{RT} = 100$ S/cm) with AsF$_6$ as counter ion.

Introduction

The discovery of interesting solid state properties in the radical-cation salts of tetrathiafulvalene (TTF) and related compounds has attracted considerable interest in the last two decades. Among the alkylthio-substituted tetrachalcogenafullerenes, bis-(ethylenedithio)-tetrathiafulvalene (BEDT-TTF or ET) has emerged as the most promising donor molecule since more than thirty superconducting radical cation salts have been derived from it [1]. Recently, the isostructural radical cation salts $\pi$-(BEDT-TTF)$_2$Cu(NCS)$_2$ [2] and $\pi$-(BEDT-TTF)$_2$[Cu(NCN)$_2$Br] [3] were found to be ambient pressure superconductors with transition temperatures $T_c$ as high as 10.3 and 11.5 K, respectively.

The observation that $T_c$ decreases very rapidly under applied pressure in these materials has led to the suggestion that enlarging the unit cell (within a series of isostructural salts) could be the method of choice for further raising $T_c$ [4]. While the use of larger anions has become quite common in the pursuit of this aim, less effort has been devoted to the synthesis of new donor molecules that are based on the ET skeleton, but extended in length.

In this alternative approach toward the preparation of new organic (super)conductors one must, however, be careful not to introduce additional disorder into the crystal, because of its detrimental effect on superconductivity. In particular the use of simple alkyl- or alkylthio-substituents appears to be quite unfavourable in this respect.

Following this line of reasoning, we have replaced the terminal ethylene bridges of BEDT-TTF with benzene rings in order to study the influence of a longer molecular axis on the electrochemical behaviour of the title compound as well as on the structure and properties of its radical cation salts.

Experimental

DB-TTF and BEDT-TTF were prepared according to literature procedures [5, 6]. K-isopropyldithiocarbonate was obtained as described in ref. [7] and recrystallized from i-PrOH prior to use.

$n$-Bu$_2$NaAsF$_6$ was synthesized according to ref. [8] and dried at 150 °C/10$^{-4}$ Torr prior to use in electrocristallization experiments.

Solvents used for electrochemical purposes were of spectroscopic grade, dried and pretreated as described in ref. [9].

$^1$H and $^{13}$C NMR spectra were run on a Jeol C-60 HL, mass spectra on a Varian MAT 311 A spectrometer. IR and UV/VIS spectra were recorded with a Nicolet DX 5 and a Perkin-Elmer Lambda 5 spectrometer, respectively. Backscattering Raman spectra were measured with a Jarell-Ash double monochromator with single channel detection. For excitation the Ar⁺-laser line at 476 nm was selected. The equipment used for
cyclic voltammetry was identical to that described previously [10].

**Donor synthesis**

**2-Oxo-1,4-benzodithian (1)**

Chloroacetyl chloride (11.5 g, 0.105 mol) is added dropwise and with cooling (ice/salt, −3 °C) to a stirred solution of 1,2-dimercaptobenzene (15 g, 0.105 mol) and triethylamine (21.34 g, 0.21 mol) in dry CH₂Cl₂ (250 ml) under an atmosphere of argon. After the addition (1 h) the solution is stirred for another 3 h at room temperature. The precipitate of NH₄Cl is filtered off and washed with EtOH (3 × 15 ml). The combined organic phases are washed with water (3 × 50 ml) and dried over Na₂SO₄. After evaporation of the solvent, the crude product remains as a clear light-yellow oil. Short-path vacuum distillation separates desired 1 (b.p. 95 °C/0.02 Torr) from the by-product benzodithieno[4,5-b][1,4]-benzodithiin (5). A sample of analytically pure 1 is obtained by recrystallization from hexane. Yield: 12.43 g (65%); m.p. 115–120 °C for 3 h at room temperature. The precipitate of KCl is filtered off and washed with acetone (2 × 30 ml). The organic phases are combined and the solvent is removed at reduced pressure to give 1 in quantitative yield as a red oil which is used in the next step without further purification.

**3-Chloro-2-oxo-1,4-benzodithian (2)**

A suspension of 1 (5.65 g, 0.031 mol) and N-chlorosuccinimide (4.14 g, 0.031 mol) in dry CCl₄ (80 ml) is refluxed for 3 h. The residue of succinimide formed is filtered off and washed with CCl₄ (3 × 50 ml). The organic phases are combined and the solvent is removed under reduced pressure to yield a clear yellow oil which crystallizes spontaneously. The crude product consists of 3 (= 65%) and of unreacted 2 (= 35%) as determined by 1H NMR assay. Double recrystallization from hexane gives pure 2 (3.69 g, 55%); m.p. 102–103 °C.

**2-Oxo-3-(i-propoxythiocarbonylthio)-1,4-benzodithian (3)**

Compound 2 (1.95 g, 8.99 mmol) and potassium O-(i-propylthiocarbamate (1.56 g, 8.99 mmol) are dissolved in dry acetone (100 ml) and stirred for 1 h at room temperature. The precipitate of KCl is filtered off and washed with acetone (2 × 30 ml). The organic phases are combined and the solvent is removed at reduced pressure to give 3 in quantitative yield as a red oil which is used in the next step without further purification.

**2-Oxo-1,3-dithiolo-[4,5-b][1,4]-benzodithiin (4)**

Compound 3 (2.84 g, 8.99 mmol) is added, with stirring and cooling (−5 °C), to concentrated H₂SO₄. After the addition (1.5 h) the reaction mixture is kept at 0 °C while stirring for another 2 h. Small portions of ice (total = 250–300 ml) are added cautiously to the reaction mixture to keep the temperature below +5 °C. The resulting dark-red suspension is passed through a Büchner-funnel, the residue is carefully washed with water (4 × 30 ml). The water-phase is extracted with toluene (3 × 50 ml). The residue is also dissolved in toluene (100 ml), the combined organic extracts are filtered and dried over Na₂SO₄. After evaporation of the solvent, the crude product is recrystallized from isopropanol to give dark red crystals.

Yield: 0.305 g (13%); m.p. 169 °C.

**C₅H₄OS₄ (256.3)**

Calcd C 42.16 H 1.57,
Found C 42.60 H 1.96.

1H NMR (CDCl₃/TMS): δ = 7.1 (m, 4H). − IR (KBr): ν = 3030, 1675 (vs, br), 1630, 1505, 1450 (s), 1430, 1265, 915, 885, 740, 440 cm⁻¹. − MS (EI, 70 eV): m/z (% ) = 256 (100) [M⁺], 228 (65), 184 (31), 152 (90), 140 (24), 120 (10), 108 (71), 96 (23), 88 (19), 76 (7).

**2-(1,3-Dithiolo-[4,5-b][1,4]-benzodithiin-2-ylidene)-1,3-dithiolo-[4,5-b][1,4]-benzodithiin (5)**

Compound 4 (0.2 g, 0.78 mmol) is dissolved in freshly distilled P(OEt)₃ (15 ml) and heated to 115–120 °C for 3 h in an atmosphere of Ar. After cooling to room temperature the yellow precipitate is filtered off, washed with EtOH (3 × 15 ml) and...
dried in vacuo. Recrystallization from CCl₄ affords 5 as yellow microcrystals.
Yield: 0.14 g (75%); m. p. (dec.) 286 – 287 °C.

C₁₈H₈S₈ (480.7)
Calcd C 44.97 H 1.67, Found C 44.58 H 1.80.

IR (KBr): v = 3051, 1560, 1447 (s), 1426 (s), 1251, 737 (vs, br), 660, 519, 456, 400. – UV/VIS (CCl₄) (absorb. a.u.): λ_max = 302.8 (0.544), 346.8 (0.492). – MS (EI, 70 eV): m/z (% ) = 480(100) [M +], 340(4), 284(17), 240(11), 208(32), 196(50), 164(16), 152(28), 120(41), 108(33), 88(6).

Electrocrystallization
An amount of 5 (typically: 10 mg/2.8 × 10⁻⁵ mol) is deposited in the anodic compartment of a standard H-cell (volume: 25 ml), then methylene chloride containing dissolved n-Bu₄NAsF₆ (161.7 mg, 3.75 × 10⁻⁴ mol) is added. To achieve saturation of the solution with 5, the cell is kept in an incubator at 30 °C during the whole experiment. After thermal equilibration (12 h), electrocrystallization is performed at Pt electrodes with a current density of 0.5 – 1 //A/cm² for a period of 14 – 20 days. After harvesting, the products are washed thoroughly with CH₂Cl₂, CCl₄ and petroleum/ether, then finally dried in vacuo.

Calcd¹ C 39.14 H 1.45 Cl 12.12, Calcd² C 36.75 H 1.44 Cl 2.97,
Found C 40.06 H 1.44 Cl 2.97.

IR (KBr): v = 1560, 1447, 1426 (m), 1250 (br, s), 1110 (sh), 906 (w), 751, 702, 660, 400 (s) cm⁻¹.

Resistivity measurements
D. C. four-probe resistivity measurements were performed with gold wires attached directly to the samples with gold or platinum paste. The typical contact resistance was less than 1 kΩ at room temperature. The temperature dependence of the electrical resistivity was determined with the help of a ⁴He-cryostat. The pressure dependence of the resistivity at room-temperature was measured in a He gas pressure cell.

Results and Discussion

Synthesis of 5
Earlier attempts to prepare 5 by thermal reaction of tetrakis-(trimethylsilyl)-tetrathiafulvalene and phenylsulfinyl-chloride were unsuccessful [12]. Hence, as outlined below (Scheme 1), a synthetic approach was chosen which had been successfully employed previously for the preparation of BEDT-TTF and its homologues [7, 13].

Compound 1 had been prepared earlier by a multistep procedure [11], which was circumvented here by starting from commercially available 1,2-dimercaptobenzene and chloroacetyl chloride. α-Chlorination of 1 was achieved by N-chloro-succinimide (NCS) in dry carbon tetrachloride [14]. Reaction of 2 and potassium O-(i-propyl)-dithiocarbonate in dry acetone gave 3. Subsequent cyclization of 3 in concentrated sulphuric acid produced 4 in moderate yield. Coupling of 4 in neat triethylphosphite afforded the desired product 5 as an extremely insoluble, yellow substance.

Spectroscopic and electrochemical properties of 5
The unusually low solubility of 5 (≈ 20 mg/l CCl₄ at room temperature) impeded spectroscopic characterization as well as electrochemical studies.

Scheme 1.
The annellation of benzene rings causes a hypsochromic shift of the longest wavelength absorptions as compared with ET (orange), which also explains the yellow colour of 5. A similar shift is observed when going from TTF (orange) to DB-TTF (yellow) [6] (cf. Scheme 2).

Scheme 2.

IR spectra of 5 and DB-TTF are almost superimposable; the mass-spectroscopic fragmentation pattern resembles data obtained for DB-TTF and other annellated tetrathiafulvalenes [15] rather than those found for BEDT-TTF [16].

The electrochemical behaviour of 5 is characterized by two one-electron redox-couples which correspond to the formation of the mono- and dications $5^+$ and $5^{2+}$, respectively. Compared with BEDT-TTF, the oxidation peak potentials of 5 are shifted anodically amounting to values found for DB-TTF under identical conditions (see table); an analogous effect has been observed for the reference system DB-TTF/TTF [6]. Obviously, the annellation of benzene-rings to the TTF- or BEDT-TTF skeleton alters the electronic structure of the parent molecules tremendously and results in a significant destabilization of the corresponding radical cations. These experimental findings point to a close similarity of 5 and DB-TTF.

It is interesting to note that a substitution of TTF or BEDT-TTF with phenyl-groups in 4 and 4' (or 5') position, as realized in the donor molecules diphenyl-tetrathiafulvalene [17] and bis-(phenylethylenedithio)-tetrathiafulvalene (BPhEDT-TTF) [18] hardly changes the electrochemical behaviour.

Besides these general trends, cyclic voltammograms of 5 are strongly dependent on the scan rate, which is in contrast to the ideal reversible redox behaviour of other TTF-derivatives [5, 6]. The ratios of peak currents as well as the peak potential separation of the two redox couples vary with scan rate, thus pointing to "kinetic complications" [19]: i.e. chemical reactions of the radical species formed follow the initial charge transfer reactions. The ratio of anodic/cathodic peak currents approaches unity and the potential separation narrows to approximately 70 mV (first redox couple) applying scan rates $\geq 250$ mV/s, thus indicating reversible or quasi-reversible behaviour. In contrast, the second redox couple is not fully reversible even at higher sweep rates.

Peak potentials of 5, DB-TTF [20] and BEDT-TTF measured under identical conditions are summarized in the table; a cyclic voltammogram of 5 is shown in Fig. 1.

![Cyclic voltammogram of 5](image)

**Fig. 1.** Cyclic voltammogram of 5 ($10^{-4}$ M) in CH$_2$Cl$_2$/n-Bu$_4$NP$F_6$ (0.1 M) vs. SCE, $v = 200$ mV/s.

<table>
<thead>
<tr>
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<th>Electrochemical peak potentials [mV]*</th>
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<tbody>
<tr>
<td>5</td>
<td>750 1130</td>
</tr>
<tr>
<td>DB-TTF</td>
<td>650 1140</td>
</tr>
<tr>
<td>BEDT-TTF</td>
<td>550 965</td>
</tr>
</tbody>
</table>

* Measured at Pt electrodes in CH$_2$Cl$_2$/n-Bu$_4$NPF$_6$ (0.1 M) vs. Saturated Calomel Electrode (SCE); sweep rate: 200 mV/s (all potential values $\pm 20$ mV).

**Synthesis and properties of radical-cation salts of 5**

Preliminary electrosynthetic experiments, performed with a variety of inorganic counterions, gave crystalline products only with the AsF$_6^-$ anion so far [21]. Surprisingly, numerous thin, greenish-brown fibers were formed in the anodic compartment instead of well-shaped single crystals (cf. Fig. 2). The fibers (max. dim. 
10000 x 40x10 μm²) show a rectangular cross-section and exhibit an unusual mechanical flexibility which contrasts the fragility of most other organic metals. The crystalline character of the products obtained was ascertained by Debye-Scherrer diffractograms.

The product stoichiometries of several batches, as determined by elemental and microprobe analyses, point to a general formula (BPhDT-TTF)_x AsF_6(CH_2Cl_2)_y (6), where x = 2–3 and y ≈ 0.5. Though the analytical data favour a 3:1-stoichiometry, this appears to be less likely than a 2:1-composition (vide infra). The intrinsic crystal properties (conductivity, microprobe analyses, spectral data) remained unchanged for all samples measured so far, which indicates the presence of a single phase. As crystal size has precluded a structure determination, Raman scattering experiments were performed for further characterization of 6; IR- and Raman spectroscopy have become important tools for the investigation of organic metals [22]. In the present case, however, the data obtained suffer from low quality due to the use of compaction samples instead of high quality single crystals; hence a discussion will be restricted to a tentative assignment of characteristic features. A typical spectrum is shown in Fig. 3. Backscattering Raman spectra of 6 consist of a few, broadened lines between 1700 and 200 cm⁻¹; no further signals could be detected in measurements up to 4000 cm⁻¹. Pronounced bands at 1565 and 1450 cm⁻¹, as well as the broad feature centered at 1260 cm⁻¹ might be attributed to various C=C-stretching vibrations (a₁, b₂) of the benzene substituents [23]. This assignment is corroborated by the appearance of the corresponding bands in IR-transmission spectra. Also the well-resolved signal at 1115 cm⁻¹ and the broad one centered at 1000 cm⁻¹ are characteristic of radial skeletal vibrations of o-disubstituted benzene rings. Besides the contributions of the aromatic substituents, several strong lines in the region between 1525 and 1450 cm⁻¹ remain unexplained. As results from a comparison of IR and Raman spectra, the bands at 1520, 1475 and 1448 cm⁻¹ are due to symmetric (IR-inactive) C=C-stretching vibrations of the internal TTF-core of 5.

A similar feature comprising three close-lying lines at 1510, 1470, 1450 cm⁻¹ has also been found for ⋅(BEDT-TTF)₂Cu(NCS)₂, where the latter two bands have been assigned to the symmetrical C=C-vibrations of the central double bond and the ring double bond of the TTF-skeleton [24], respectively. As the frequencies of the TTF core stretching vibrations are strongly dependent on the degree of oxidation, spectroscopic data allow to draw conclusions concerning the charge-distribution of the donor molecules [22]. Thus, the observed bands are rather in favour of a postulated 2:1 composition of 6, which implies a charge of +0.5 on the BPhDT-TTF molecules, than of a 3:1 stoichiometry. The latter would require either a
charge of 0.33 on every donor unit or an unequal charge distribution. Though the question of the correct composition of 6 cannot be clarified sufficiently based on the data available, the presence of donors bearing different charges appears to be less probable with respect to the Raman data.

The poor signal-to-noise ratio in the lower part of the spectrum did neither allow a clear observation of the three Raman-active modes of the AsF$_6^-$ counterion nor of the solvent incorporated whereas strong bands at 698 and 400 cm$^{-1}$ in IR spectra can be attributed unambiguously to the $v_3$ and $v_4$ modes of the anion [25], based on a comparison of spectra of 5, 6 and of $n$-Bu$_4$NASF$_6$ itself. In addition, Raman lines at 774 (C$-$S stretch) and 481 cm$^{-1}$ were found; while the former one is typical of the BEDT-TTF skeleton, the latter might be attributed to skeletal vibrations of the benzene rings.

Four-probe conductivity measurements revealed 6 to be highly conducting: the room temperature conductivity $\sigma_{RT}$ of single fibers along the fiber axis ranges typically around 100 S/cm. The temperature-dependence of the electrical resistivity $\varrho$ is depicted as Arrhenius plot in Fig. 4. Lowering the temperature from 290 to ca. 200 K results in a weak increase in resistivity which indicates semiconducting behaviour with a small band-gap ($E_{\text{GAP}} \approx 26$ meV, dotted line in Fig. 4) in this region. Around 190 K a broad phase transition might occur which is followed by a steep upturn in resistivity. The temperature dependence below 180 K corresponds to a semiconductor with a gap of $\approx 240$ meV (dashed line in Fig. 4). $\sigma_{RT}$ of 6 increases monotonously as a function of hydrostatic He gas pressure; at 4.5 kbar $\sigma_{RT}$ is larger by approximately 50% with respect to zero pressure.

In conclusion we have synthesized a new donor, BPhDT-TTF 6, which is identical to BEDT-TTF in its central part but about one third longer. We have demonstrated that its donor properties, despite of its relatively high oxidation potentials, are suitable for the formation of radical cation salts, whose conductivities are comparable to those of BEDT-TTF salts.

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[1] For recent reviews see:


[20] For DB-TTF a reversible redox-behaviour as described in [6] was only observed in acetonitrile but not in methylene chloride as solvent. The non-ideal shape of cyclic voltammograms in the latter solvent is due to the adjustment of the comproportionation equilibrium DB-TTF$^{2+}$ + DB-TTF $\rightarrow$ 2 DB-TTF$^+$.
[21] Electrocrystallization experiments with IBr$_2$ as counterion produced a salt of formal composition (BPhDT-TTF)$_n$IBr$_2$. However, Raman scattering experiments indicate the presence of two different anions in the fibrous crystal formed: i.e. I$_3^-$ and IBr$_2^-$. Thus, as a result of microprobe analyses the stoichiometry is rather described by the formula (BPhDT-TTF)$_n$(IBr$_2$)$_{0.9}$(I$_3$)$_{0.1}$. The compound exhibits a room-temperature conductivity of 1.5 S/cm (pressed sample) and shows semiconducting behaviour on cooling ($E_{\text{gap}} = 113$ meV).