

The Vinylogue of Bis-4,5-methylenedithiotetrathiafulvalene: A New Electron Donor

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A new electron donor vinylogue-BMDT-TTF **5** [2,2'-ethanediylidenebis(1,3,4,6-tetrathiapentalene)] has been synthesized (overall yield from **8** 16%). The compound represents a structural modification of the molecular framework that has led to highly conducting, even superconducting, organic charge transfer (CT) complexes. Like other tetrathiafulvalene (TTF)-based donors **5** undergoes a reversible two-electron oxidation as shown by cyclic voltammetry.

Since the discovery of high, one dimensional conductivity in a tetrathiafulvalene (TTF) **1** complex with tetracyanoquinodimethane (TCNQ), tremendous progress has been made within the fields of synthetic organic, physical and theoretical chemistry towards designing and explaining the features of 'organic metals'.¹

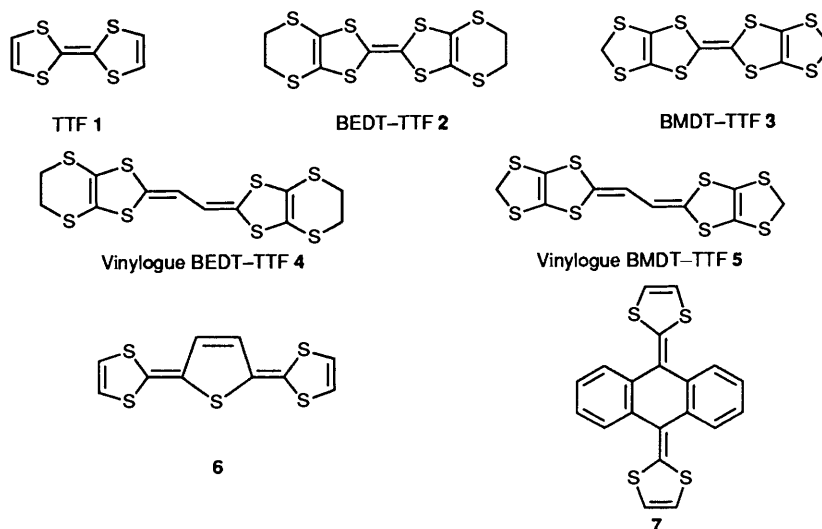
In the most investigated and successful case so far, BEDT-TTF **2**, a whole family of superconducting CT salts has been characterized and investigated.² It has been shown that the anion has a determining effect on the electrical properties, indicating extremely high sensitivity to minor changes in the molecular features. In the BEDT-TTF **2** case, it has been possible to identify up to four different crystal phases using the same anion and with very different electrical data, again indicating that solid state properties are dependent on subtle interactions between the molecules.³

The concept of dimensionality in organic metals is very important for suppression of Peirls instability and the achievement of superconductivity at low temperature.⁴ Given the tetrathio-TTF-framework, the coupling with methylene **3**, ethylene **2** or even propylene (BPDT-TTF) will affect the interstack interactions and thereby influence the 'dimensionality' of the CT complex. BPDT-TTF has very little possibility of interstack S...S contacts due to the bulky propylene groups and has yielded only one-dimensional conductors and semiconductors.⁴

The two-dimensional conductivity and superconductivity in BEDT-TTF is well known.⁵ Comparison of **2** and **3** shows that **3** is a more planar molecule.⁶ Also, compared to ethylene, the less bulky methylene group should presumably increase the ability of the molecule to form segregated stacks with strong interstack interactions. Surprisingly, this system has yielded mainly 1:1 and 3:1 insulators and semiconductors due to crystallization modes with charge separation,⁷ the only exception being the (BMDT-TTF)₂AuCN₂ complex⁷ which is a two-dimensional metal between 300 and 80 K.

Williams *et al.*⁸ have attempted to fine tune the molecular features by making the mixed methylene-propylene and methylene-ethylene donors assuming that between the two extremes, BMDT-TTF **3** and BPDT-TTF there might be an intermediate regime where molecular properties resemble those of BEDT-TTF **2**.

A somewhat different approach could be the addition of a spacer group between the dithiole units. This will obviously change the molecular features and crystal packing. Many papers have been published recently, that describe the synthesis and properties of various extended systems. Some very recent examples are shown here, **4-7**. The thiophene based system **6** of which derivatives have been made by Takahashi *et al.*,⁹ is one way of introducing new features to the well-known TTF-system. A somewhat similar approach has been published by Bryce *et al.*,¹⁰ who reported **7** made from anthraquinone via

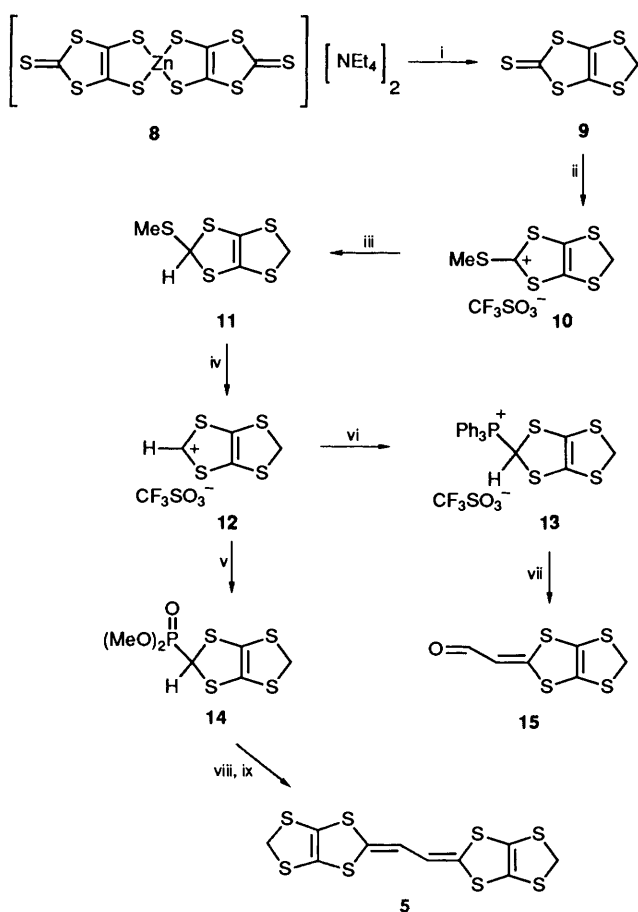


a Horner–Wittig reaction. A highly conducting 4:1 TCNQ complex of **7** has also been reported.¹⁰ However the simplest way to add a spacer group is exemplified in **4**, the 'vinylogue' of BEDT–TTF. This molecule has been synthesized recently by us^{11a} and two other groups^{11b,c} independently. Several 'vinylogues' of TTF-based systems have also been published.¹² Typically the introduction of spacer units adds conjugation to the system and causes a desirable lowering of the oxidation potential.

Given this information, we found the vinylogue of BMDT–TTF **5** to be a good target because the donor retains planarity and has a good potential for interstack interactions. This, together with lower symmetry, was expected to suppress Peirls distortions in CT complexes. We assumed that a similar synthetic strategy to that used in the product of **4** would also apply to **5**.

Results and Discussion

Our key starting material was the zincate¹³ **8** (see Scheme 1)

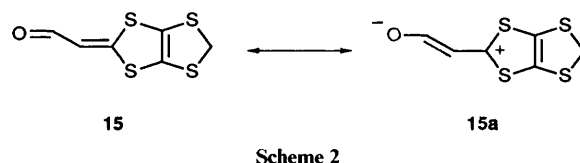


Scheme 1 Reagents and conditions: i, CH_2Br_2 ; acetone; ii, $\text{CF}_3\text{SO}_3\text{Me}$; iii, NaBH_4 ; iv, $\text{CF}_3\text{SO}_3\text{H}$; v, $\text{P}(\text{OMe})_3$, NaI ; vi, Ph_3P ; vii, $(\text{CHO})_2$, $\text{N}(\text{Et})_3$; viii, BuLi , THF, -78°C ; ix, **15**

which was found to react rather sluggishly with dibromomethane. Surprisingly, reaction with the much more reactive sodium salt of **8** yielded only a trace amount of **9**. This is in contrast to the similar reaction with dibromoethane in the synthesis of **4**. The zincate has been reported¹³ to react faster with diiodomethane, but we preferred dibromomethane because the yield was higher. The thione **9** reacted with methyl trifluoromethanesulphonate in 98% yield in a very convenient reaction to give the methylthio-substituted salt **10**. This salt **10** was reduced with sodium borohydride to a white solid **11**

that could be converted into the dithiolium salt **12** with trifluoromethanesulphonic acid in diethyl ether. This new procedure generates fewer work-up problems than the previously used procedure (for synthesising **4**) using hydroboric acid in acetic anhydride.¹⁴ However, it was necessary to work fast and with very clean solvents to avoid decomposition of the product to highly coloured by-products.

The Wittig-type condensation with glyoxal¹⁵ was carried out stepwise because the commercially available glyoxal is an aqueous solution (40%). The water does not interfere with the phosphorane generated from the phosphonium salt **13** and base. The reaction works cleanly to give the aldehyde **15**,* but we have never observed the reaction to go any further, *i.e.* to react with two aldehyde groups.¹⁵ The low reactivity of aldehyde **15** can be explained by resonance structures of **15a** (Scheme 2).



However the anion generated from the corresponding phosphonate **14**¹⁵ and BuLi at -78°C in THF reacted smoothly to give the vinylogue of BMDT–TTF **5** when treated with aldehyde **15**.

The new donor **5** showed a reversible two-electron oxidation by cyclic voltammetry, $E_1 = 0.41\text{ V}$, $E_2 = 0.60\text{ V}$ ($0.1\text{ mol dm}^{-3}\text{ Bu}_4\text{NPF}_6$ in dichloromethane, calomel ref, platinum electrode). These values are significantly lower than the values for BEDT–TTF obtained by us under similar conditions (0.49 V vs. 0.74 V) and the difference between E_1 and E_2 is also lower.† However the difference compared to **4** is insignificant ($0.40\text{ vs. }0.57$) as expected.

Our data does not provide information on the conformation of **5**. In the recently published X-ray structure^{11c} of a very similar compound the molecule is obviously in a transoid conformation. The ^1H NMR data^{11c} also support a conformationally locked structure in solution, in view of the coupling constant (11.22 Hz) reported between the two central ethylene protons.

Experimental

Melting points are uncorrected. Elemental analyses were carried out by Atlantic Microlabs, Norcross, GA or Micro-analytical Lab. Copenhagen University. NMR spectra were recorded at 200 MHz. Chemical shifts are quoted in ppm downfield from tetramethylsilane, and coupling constants are in Hz.

1,3,4,6-Tetrathiapentalene-2-thione 9. The zinc complex **8**¹³ (50 g) was stirred for 4 days in acetone–dibromomethane (1600 ml; 5:1) at room temperature. The solvent was evaporated (dibromomethane can be recovered) leaving a brown salt cake. This was thrice triturated with hot dichloroethane (400 ml). The combined extracts were treated with Norit to give a yellow solution. The solvent was evaporated to crystallization point to give thione **9** (8.6 g). Addition of hexane gave a second crop of product (total 15.4 g, 53%), m.p. 157°C (lit.,^{13b} = 159°C); $\delta_{\text{H}}(\text{CDCl}_3)$ 4.97 (s, CH_2).

* In contrast to the case of the aldehyde **15** the presence of electron-withdrawing groups on the dithiole units of the phosphonium salts (see ref. 12a, b, c) suppresses the deactivation of the intermediate aldehydes, leading to the vinylogues directly in one step.

† For a discussion of the on-site Coulomb repulsion see ref. 1c.

2-Thiomethyl-1,3,4,6-tetrathiapentalen-2-ylum trifluoromethanesulphonate **10**. A suspension of thione **9** (3.25 g, 15.5 mmol) in CH_2Cl_2 (50 ml) was treated with methyl trifluoromethanesulphonate (2.6 g, 15.8 mmol) and the mixture was stirred for 6 h. The stirring was discontinued as a layer of diethyl ether (50 ml) was added. The following day **10** (5.63 g, 97.3%) appeared as a red, crystalline salt which was filtered off and washed with more dry diethyl ether, m.p. 149 °C, $\delta_{\text{H}}(\text{CD}_3\text{CN})$ 3.10 (3 H, s, SMe) and 5.4 (2 H, s, CH_2); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1255 (triflate) (Found: C, 19.45; H, 1.15; S, 51.05. $\text{C}_6\text{H}_5\text{F}_2\text{O}_3\text{S}_6$ requires C, 19.25; H, 1.34; S, 51.34).

Methyl 1,3,4,6-tetrathiapentalen-2-yl sulphide **11**. To an ice-cold suspension of finely divided sodium borohydride (0.3 g, 8.1 mmol) acetonitrile–isopropyl alcohol (1:1, 100 ml) under N_2 , was added portionwise **10** (3 g, 8 mmol). The mixture was stirred for 1 h and then diluted with water (50 ml). The resulting solid (1.72 g) was filtered off and crystallized from chloroform–pentane to give **11** (1.34, 70.0%) as off-white crystals, m.p. 72 °C; $\delta_{\text{H}}(\text{CDCl}_3)$ 6.43 (1 H, s), 4.96 (1 H, d, J 10), 4.64 (1 H, d, J 10) and 2.27 (3 H, s); m/z 226 (M^+ , 39%), 210 (15), 179 (100) and 135 (15) (Found: C, 26.6; H, 2.40; S, 70.1. $\text{C}_5\text{H}_6\text{S}_5$ requires C, 26.55; H, 2.65; S, 70.80%).

1,3,4,6-Tetrapentalen-2-ylum trifluoromethanesulphonate **12**. To a suspension of dithiole **11** (1.0 g) in dry diethyl ether (20 ml), trifluoromethanesulphonic acid (2.5 ml) was added dropwise over 2–3 min while N_2 was bubbled through the suspension. The mixture was stirred for 5 min after which orange crystals of **12** (1.15 g, 83.4%) were filtered off and washed with dry diethyl ether (10 ml). The compound was dried without access to air, m.p. 118–120 °C; $\delta_{\text{H}}(\text{CD}_3\text{CN})$ 10.35 (1 H, s) and 5.40 (2 H, s); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1250 (triflate) (Found: C, 18.25; H, 0.75; S, 47.9. $\text{C}_5\text{H}_3\text{F}_3\text{O}_3\text{S}_5$ requires C, 18.29; H, 0.91; S, 48.78).

Dimethyl (1,3,4,6-tetrathiapentalen-2-yl)phosphonate **14**. The dithiolium salt **12** (2.05 g, 6.3 mmol) was added to a solution of trimethyl phosphite (0.78 g, 6.3 mmol) in dry MeCN (50 ml) under N_2 . Sodium iodide (0.95 g, 6.3 mmol) was then added and the mixture was stirred for 2 h at room temperature. After solvent evaporation the residue was chromatographed (silica) using ethyl acetate–dichloromethane (1:1) as mobile phase. This afforded the phosphonate **14** as an off-white solid (1.07 g, 59%), m.p. 122–124 °C; m/z 288 (M^+ , 50%) and 179 (100%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1052 (P–O–C) and 1247 (P=O); $\delta_{\text{H}}(\text{CDCl}_3)$ 5.31 (1 H, d, J_{p} 3), 5.02 (1 H, d, J 5), 4.72 (1 H, d, J 5) and 3.88 (6 H, d, J_{p} 8) (Found: C, 25.1; H, 2.9. $\text{C}_6\text{H}_9\text{O}_3\text{PS}_4$ requires C, 25.00; H, 3.13).

1,3,4,6-Tetrathiapentalen-2-ylideneacetaldehyde **15**. The dithiolium salt **12** (1.0 g, 30 mmol) was added to a solution of triphenylphosphine (0.8 g, 3.0 mmol) in dry THF–MeCN (1:1; 50 ml). This generated a pale yellow solution of the phosphonium salt **13** *in situ* to which aqueous glyoxal (40%; 5 ml) and triethylamine (1 ml) were added, while N_2 was bubbled through: a dark solution resulted. The solvent was evaporated and the residue was dissolved in dichloromethane, washed (water) and dried (MgSO_4). Part of the dichloromethane was evaporated and the remaining dark solution was chromatographed on silica using dichloromethane–hexane (1:2) as eluent. The clear yellow fractions were combined yielding **15** (0.42 g, 66%) as a yellow crystalline solid, m.p. 123–124 °C; m/z 220 (M^+ , 100%), 191 (8), 134 (12). $\delta_{\text{H}}(\text{CDCl}_3)$ 9.38 (1 H, d, J 1), 6.70 (1 H, d, J 1) and 5.05 (2 H, s); $\nu_{\text{max}}/\text{cm}^{-1}$ 1618 (CHO), 1610 (CH=C) and 1466 (CH_2). (Found: C, 32.75; H, 1.85. $\text{C}_6\text{H}_4\text{OS}_4$ requires C, 32.73; H, 1.81).

2,2'-Ethane-1,2-diylidenebis(1,3,4,6-tetrathiapentalene) **5**. The phosphonate **14** (100 mg, 0.35 mmol) was dissolved in dry

THF (25 ml) under N_2 in a three-necked flask with magnetic stirring. The solution was cooled to ca. –78 °C and BuLi (2.5 mol dm^{-3} ; 0.15 ml) in hexane was added, *via* a syringe to yield a yellow suspension. After 5 min, a solution of the aldehyde **15** (76 mg, 0.35 mmol) in dry THF (20 ml) was added *via* a syringe and the solution was warmed to room temperature. The yellow brownish solid was filtered off, washed with water and MeOH, and recrystallized from hot DMSO to give **5** (55 mg, 42%) as yellow crystals, m.p. 246–247 °C (decomp.); m/z 382 (M^+ , 100%), 247 (82) and 114 (54); $\delta_{\text{H}}(360 \text{ MHz}, (\text{CD}_3)_2\text{SO})$ 6.05 (2 H, s) and 5.14 (4 H, s) (Found: C, 31.4; H, 1.65. $\text{C}_{10}\text{H}_6\text{S}_8$ requires C, 31.42; H, 1.57).

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