New Bis(ethylenedithio)tetrathiafulvalene Derivatives with Low Oxidation Potentials

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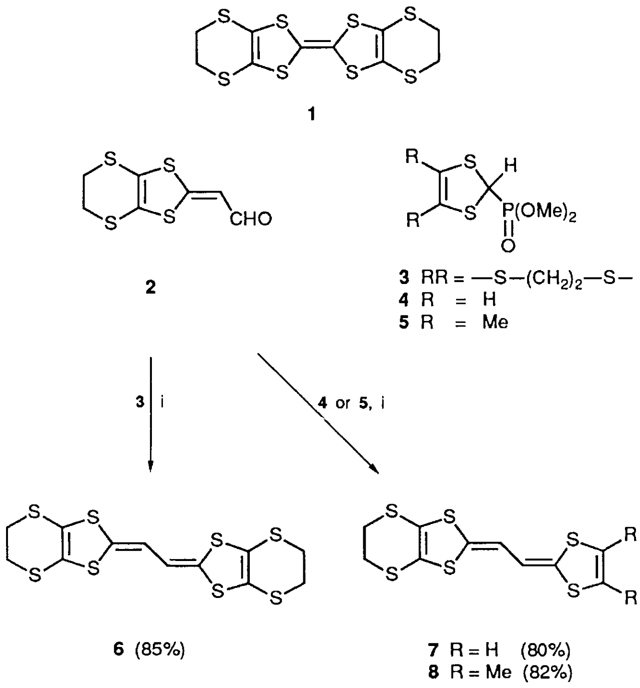
The efficient synthesis of three new vinylogous derivatives **6–8** of bis(ethylenedithio)tetrathiafulvalene (BEDT–TTF) is described; cyclic voltammetry establishes that the new donors have significantly lower solution oxidation potentials than that of BEDT–TTF, and the single crystal X-ray structure of compound **8** is described.

Cation radical salts formed by bis(ethylenedithio)tetrathiafulvalene (BEDT–TTF) **1** are the focus of intense interest within the arena of organic superconductors; several salts with T_c values ranging from 1 to 12 K at ambient pressure are known.[1] The synthesis of new π-donors related to BEDT–TTF **1** is central to understanding the solid-state properties of this fascinating class of materials.[2] In particular, derivatives with oxidation potentials which are lower than that of the parent compound **1** are prime targets.[2c,f,3] Herein we report the high-yielding synthesis of the symmetrical vinylogue **6** and the unsymmetrical analogues **7** and **8** *which have lower solution oxidation potentials than BEDT–TTF* **1**. Japanese workers have recently identified compound **6** as a desirable target.[4]

The synthesis of the new donors is outlined in Scheme 1. Aldehyde **2**[5] reacted cleanly in a Wittig–Horner reaction with the carbanion generated from reagents **3**,[5] **4**[6] and **5**[6,7] to afford the vinylogous donors **6–8**, respectively, which were isolated as air-stable solids (80–85% yield after purification).† These reactions, which are typically performed on a *ca.* 0.5 mmol scale, affording 100–150 mg batches of product, are readily amenable to scale-up.



Scheme 1 *Conditions*: i, n-butyllithium (1.1 equiv.), dry tetrahydrofuran, −78 °C

The X-ray crystal structure of compound **8** has been determined,‡ and bond lengths are given in the caption to Fig. 1. Molecule **8** is essentially planar, with a small amount of puckering at the ethylene bridge, C(11)–C(12), similar to that observed in BEDT–TTF **1**.[10] The molecule is in the *transoid* conformation, which was expected for steric reasons; this

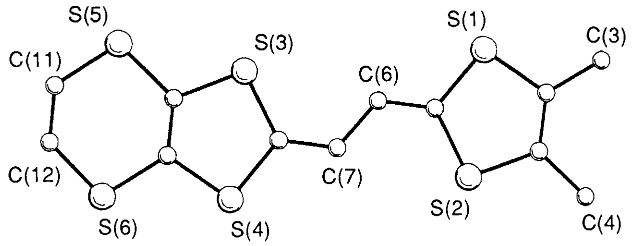


Fig. 1 Structure of compound **8**; bond lengths (Å): C(1)–S(1), 1.753(11); C(5)–S(1), 1.750(12); C(2)–C(1), 1.335(13); C(3)–C(1), 1.496(13); S(2)–C(2), 1.739(10); C(4)–C(2), 1.494(13); C(5)–S(2), 1.735(11); C(6)–C(5), 1.340(13); C(7)–C(6), 1.431(13); C(8)–C(7), 1.351(13); S(3)–C(8), 1.751(12); S(4)–C(8), 1.759(12); C(9)–S(3), 1.753(11); C(10)–C(9), 1.303(13); S(5)–C(9), 1.754(11); S(4)–C(10), 1.756(11); S(6)–C(10), 1.750(11); C(11)–S(5), 1.742(14); C(12)–C(11), 1.311(17); S(6)–C(12), 1.710(16)

Table 1 Cyclic voltammetric data[a]

Donor	$E_1^{\frac{1}{2}}$/V	$E_2^{\frac{1}{2}}$/V	$\Delta E^{\frac{1}{2}}$/V
TTF	0.340	0.780	0.440
BEDT-TTF **1**	0.585	0.992	0.407
6	0.480	0.710	0.230
7	0.432	0.690	0.258
8	0.356	0.619	0.263

[a] Experimental conditions: donor (*ca.* 1 × 10^{-5} mol dm^{-3}), electrolyte $Et_4N^+PF_6^-$ (*ca.* 1 × 10^{-1} mol dm^{-3}) in dry dichloromethane under argon, 20 °C, *vs.* Ag/AgCl, Pt electrode, scan rate 100 mV s^{-1} using a BAS 100 Electrochemical Analyser.

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† Compound **6**, 85% yield, m.p. 239–240 °C (from carbon disulphide–hexane, 2 : 1 v/v); *m/z* (CI) 411 ($M^+ + 1$); λ_{max}/nm (CH_2Cl_2) 429, 403, 261, 230 and 197; δ_H (CD_3SOCD_3) 5.9 (2H, s) and 3.36 (8H, s): Compound 7, 80% yield, m.p. 161–162 °C (from dichloromethane–cyclohexane, 1 : 3 v/v); *m/z* (EI) 320 (M^+); λ_{max}/nm (CH_2Cl_2) 415, 401, 237 and 197; δ_H ($CDCl_3$) 6.20 (2H, d), 5.83 (2H, s) and 3.29 (4H, s). Compound **8**, 82% yield, m.p. 201–202 °C (from dichloromethane–cyclohexane, 1 : 3 v/v); *m/z* (EI) 348 (M^+); λ_{max}/nm (CH_2Cl_2) 423, 401, 233 and 197; δ_H ($CDCl_3$) 5.76 (2H, AB, *J* 11.22 Hz), 3.29 (4H, s), 1.90 (3H, s) and 1.89 (3H, s). Satisfactory elemental analyses were obtained.

‡ *Crystal data* for **8**: $C_{12}H_{12}S_6$, monoclinic space group $P2_1/n$, a = 6.680(1), b = 30.961(2), c = 7.643(1) Å, β = 113.20(1)°, U = 1452.85 Å^3, Z = 4, $F(000)$ = 720, Mo-Kα radiation, λ = 0.71069 Å. The structure was solved by direct methods (SHELXS 86)[8] and refined by least-squares analysis[9] (anisotropic for non-hydrogens) to R = 0.057 for 1216 observed ($F_o > 4\sigma F_o$) reflections from 2446 unique data. The data were collected on an Enraf-Nonius FAST area detector diffractometer positioned at the window of a rotating anode generator, equipped with a molybdenum target and graphite monochromator. The detector swing angle was 18° and the crystal-to-detector distance was 40 mm. Using steps of 0.15° in ω, reciprocal space was scanned to the extent of 190° with the crystal set at χ = 0, and 140° with the crystal set at χ = 90°, giving measurement of all reflections in slightly more than one-half of the hemisphere with $2\theta_{max}$ of at least 51°. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

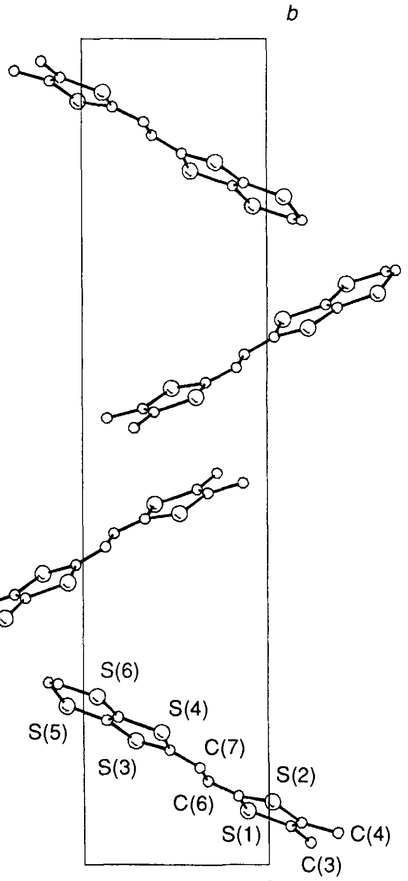

Fig. 2 Single crystal X-ray structure of compound **8**: view down the *a* axis

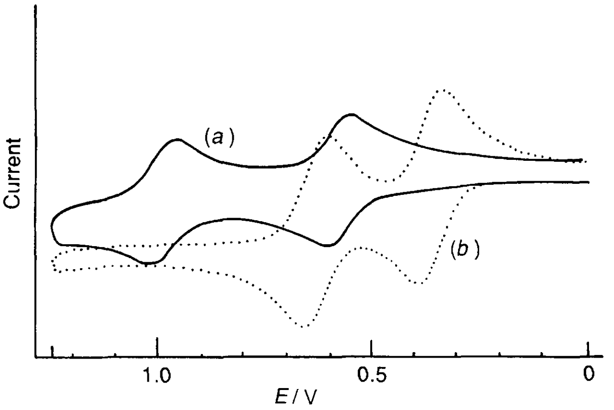

Fig. 3 Cyclic voltammograms of (*a*) BEDT-TTF **1** and (*b*) donor **8**

observation is consistent with the interpretation of spectroscopic data for other vinylogous TTF derivatives.[11] Fig. 2 shows a view of the unit cell along the *a* axis. Along the *b* axis there is overlap of the 4,5-dimethyl-1,3-dithiole rings of adjacent molecules, but there are no short (<4.0 Å) non-bonded S···S contacts in the structure.

Cyclic voltammetric data establish that both the first and second solution ionisation potentials of donors **6–8** are significantly *lower* than those of BEDT-TTF **1** (by *ca.* 0.1–0.2 V for $E_1{}^{\frac{1}{2}}$ and by *ca.* 0.3 V for $E_2{}^{\frac{1}{2}}$) (Table 1, Fig. 3). Indeed, $E_1{}^{\frac{1}{2}}$ for donor **8** is very similar to that of TTF measured under identical conditions. Another striking feature of the data in Table 1 is that the difference between the first and second ionisation potentials of the vinylogues is considerably less than that of BEDT-TTF **1**. This is clear evidence that 'stretching' the BEDT-TTF molecule stabilises the dication state, owing to reduction of on-site Coulombic repulsion; these new data are in agreement with those reported previously for other multistage redox systems.[11,12] The formation of charge-transfer complexes and ion radical salts of these new donors is in progress.

Addendum: Since completion of this work we have learned that compound **6** has been prepared by two other groups using similar methodology.[13] We thank Profs Cava, Metzger and Becher for a preprint of their work and correspondence.

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References

1 (*a*) *The Physics and Chemistry of Organic Superconductors*, ed. G. Saito and S. Kagoshima, Springer-Verlag, London, 1990; (*b*) Proceedings of the International Conference on Science and Technology of Synthetic Metals, Tübingen, September 1990, to be published in *Synthetic Metals*, 1991.

2 (*a*) H. Tatemitsu, E. Nishikawa, Y. Sakata and S. Misumi, *J. Chem. Soc., Chem. Commun.*, 1985, 106; (*b*) A. M. Kini, S. F. Tytko, J. E. Hunt and J. M. Williams, *Tetrahedron Lett.*, 1987, **28**, 4153; (*c*) W. Chen, M. P. Cava, M. A. Takassi and R. M. Metzger, *J. Am. Chem. Soc.*, 1988, **110**, 7093; (*d*) A. M. Kini, B. D. Gates, M. A. Beno and J. M. Williams, *J. Chem. Soc., Chem. Commun.*, 1989, 169; (*e*) K. S. Varma, J. Evans, S. Edge, A. E. Underhill, G. Bojensen and J. Becher, *J. Chem. Soc., Chem. Commun.*, 1989, 257; (*f*) T. Suzuki, Y. Yamochi, G. Srdanov, K. Hinkelmann and F. Wudl, *J. Am. Chem. Soc.*, 1989, **111**, 3108; (*g*) A. M. Kini, T. Mori, U. Geiser, S. M. Budz and J. M. Williams, *J. Chem. Soc. Chem. Commun.*, 1990, 647.

3 D. L. Lichtenberger, R. L. Johnston, K. Hinkelmann, T. Suzuki and F. Wudl, *J. Am. Chem. Soc.*, 1990, **112**, 3302.

4 Z. Yoshida and T. Sugimoto, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1573.

5 A. J. Moore and M. R. Bryce, *Synthesis*, 1991, 26.

6 M. R. Bryce and A. J. Moore, *Synth. Metals*, 1988, **27**, B557.

7 K. Akiba, K. Ishikawa and N. Inamoto, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2674.

8 G. M. Sheldrick, University of Göttingen, 1986.

9 G. M. Sheldrick, SHELX 76, University of Cambridge, 1976.

10 H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 301.

11 T. Sugimoto, H. Awaji, I. Sugimoto, Y. Misaki, T. Kawase, S. Yoneda, Z. Yoshida, T. Kobayashi and H. Anzai, *Chem. Mater.*, 1989, **1**, 535.

12 K. Deuchert and S. Hünig, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 875.

13 V. Yu. Khodorkovskii, L. N. Veselova and O. Ya. Neiland, *Khim. Geterotsikl. Soedin.*, 1990, 130; *Chem. Abstr.*, 1990, **113**, 22868; T. K. Hansen, M. V. Lakshmikantham, M. P. Cava, R. M. Metzger and J. Becher, *J. Org. Chem.*, in the press.