Bis(dihydro-1,4-oxathiino)tetrathiafulvalene, a New Donor for Cation Radical Salts

Jonas Hellberg,*[a] Mikael Moge,[a] Dagmar Bauer[b] and Jost-Ulrich von Schütz[b]

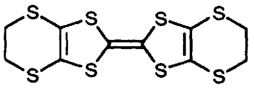
[a] *Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden*
[b] *Physikalisches Institut teil III, Universität Stuttgart, D-70550 Stuttgart, Germany*

The synthesis, characterization and electrochemical properties of the title molecule, a hybrid of bis(ethylenedioxy)tetrathiafulvalene and bis(ethylenedithio)tetrathiafulvalene, are presented.

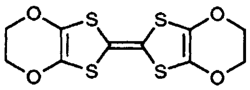
Among the organic donors for conducting cation radical salts so far synthesized, bis(ethylenedithio)tetrathiafulvalene (BEDT–TTF, or ET), takes a leading position in the race for new organic superconductors, with T_c reaching over 10 K.[1] A prerequisite for molecular engineering of these systems is that the donor structure can be varied and the effect upon the properties of the cation radical salts thereafter studied. A small but important modification is to vary the chalcogen substitution on the TTF-skeleton, and in this series bis(ethylenedioxy)tetrathiafulvalene (BO)[2] and 4,5-ethylenedioxy-4′,5′-ethylenedithiotetrathiafulvalene (EOET)[3] are two recent examples.

We now report the synthesis of a new substituted TTF; namely bis(dihydro-1,4-oxathiino)tetrathiafulvalene, OXTTF, its characterization and electrochemical behaviour.

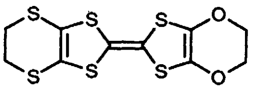
The synthesis of OXTTF is outlined in Scheme 1, and is a variation of a popular ET-synthesis.[4] 2-Mercaptoethanol reacted conveniently with ethylbromoacetate to give 2-(2-hydroxyethylthio)ethylacetate **2**, which underwent ring closure in the presence of toluene-*p*-sulfonic acid, to give 1,4-oxathiane-2-one **3**.[5] Treatment with NBS gave the brominated adduct **4**, which underwent smooth alkylation with sodium *O*-isopropoxylxanthate to give **5**. Ring closure in sulfuric acid gave (dihydro-1,4-oxathiino)-1,3-dithiole-2-one **6**† in 10% yield (from **2**). Dimerization was achieved in refluxing trimethylphosphite to give **1** as a mixture (*vide infra*) of diastereoisomers (*E*-**1** and *Z*-**1**) in 22–26% yield after chromatography.‡



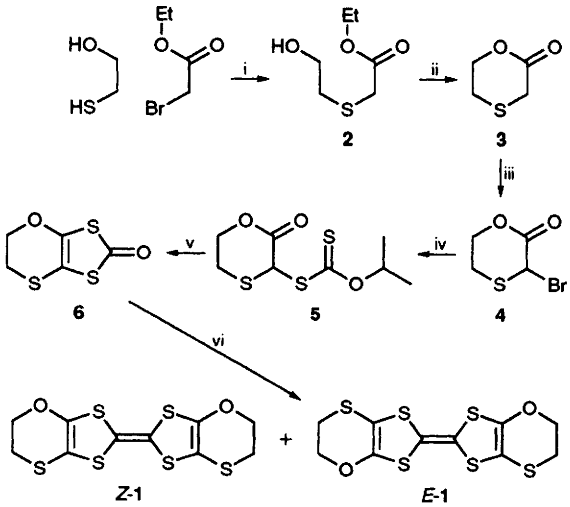
ET



BO



EOET



Scheme 1 *Reagents*: i, K_2CO_3, MeCN, room temp., overnight; ii, *p*-TsOH, PhCl, 130 °C, 20–30 h; iii, NBS, PhCl, 120 °C, 1 h; iv, sodium *O*-isopropylxanthate, PhCl/acetone, room temp., 2–3 h; v, H_2SO_4 0 °C, 2 h, 10% (5 steps); vi, $(MeO)_3P$, reflux, 3 h, 22–26%

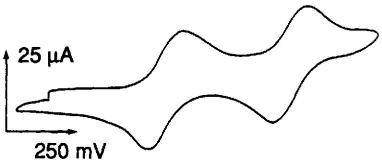


Fig. 1 CV-trace for the mixture of *E* and *Z*-**1**

Cyclovoltammetry§ (Fig. 1) of the diastereoisomeric mixture revealed two nicely reversible oxidation waves, at 0.39 and 0.81 V (*vs.* SCE), respectively (Fig. 1). This is slightly lower than ET measured in the same system (0.46, 0.89 V), but with roughly the same difference between the waves, indicating an on-site coloumbic repulsion of the same magnitude in the two donors.

The diastereoisomers have so far been impossible to separate by chromatography but their presence is indicated by doubling of two of the ^{13}C-signals. However, since it can be anticipated that these diastereoisomers exist in equilibria in solution, as previously shown for another substituted TTF system,[6] every transformation requiring dissolved **1** (*i.e.* electrocrystallization) will provide this mixture of isomers, which should make isolation unnecessary. Whether the corresponding cation radical is more easy to isomerize or not, is an open question since the cation radical should be less protophilic (= more difficult), but the charge resides partly on the central double bond, which could facilitate isomerization.

Constant-current electrocrystallization in the presence of ClO_4^- or PF_6^- yields black shiny crystals with the composition 2:1 according to elemental analyses. Only one morphology could be observed in both cases. Preliminary results from ESR measurements of the ClO_4^--salt (single crystal) show an intensive (0.4 spins per molecular unit) Lorentzian ESR-line, with ≈25 G linewidth and a *g* value close to the free electron. The room temp. conductivity for a compressed pellet is ≈5 S cm^{-1}, a rather high value.

Financial support from the Swedish National Science Research Council and Carl Tryggers Stiftelse is gratefully acknowledged.

Received, 11th November 1993; Com. 3/06766A

Footnotes

† *Data* for **6**: ^1H NMR: δ 3.28 (m, 2H), 4.57 (m, 2H); ^{13}C NMR: δ 27.30, 68.65, 91.88, 134.74, 185.33; MS (70 eV): 192 (100%, M^+), 164 (62%, $M^+ - C_2H_4$); satisfactory elemental analyses were obtained.

‡ *Data* for the mixture of *E*-**1** and *Z*-**1**; ^1H NMR: δ 3.13 (m, 4H), 4.45 (m, 4H); ^{13}C NMR: δ 25.86, 68.06, 90.73, 90.94, 107.05, 135.76, 136.02; MS (70 eV): 352 (13%, M^+), 324 (12%, $M^+ - C_2H_4$), 220 (38%), 192 (47%), 88 (100%), 76 (37%); satisfactory elemental analyses were obtained.

§ Performed in dichloromethane with Bu_4NPF_6 as electrolyte, scan rate 100 mV s^{-1}.

References

1 K. Nozawa, T. Sugano, H. Urayama, H. Yamochi, G. Saito and M. Kinoshita, *Chem. Lett.*, 1988, 677; A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlsson, J. M. Williams, W. K. Kwok, K. G. Vandervoort, J. E. Thompson, D. L. Stupka, D. Jung and M.-H. Whangbo, *Inorg. Chem.*, 1990, **29**, 2555; J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlsson, U. Geiser, L. K. Montgomery, G. J. Pyrka, D. M. Watkins, J. M. Kommers, S. J. Boryschuk, A. V. Strieby Crouch, W. K. Kwok, J. E. Schirber, D. L. Overmyer, D. Jung and M.-H. Whangbo, *Inorg. Chem.*, 1990, **29**, 3262.

2 T. Suzuki, H. Yamochi, G. Srdanov, K. Hinkelmann and F. Wudl, *J. Am. Chem. Soc.*, 1989, **111**, 3108; S. Kahlich, D. Schweitzer, I. Heinen, S. E. Lan, B. Nuber, M. J. Keller, K. Winzer and H. W. Helberg, *Solid State Chem.*, 1991, **80**, 191; M. A. Beno, H. H. Wang, A. M. Kini, K. D. Carlson, U. Geiser, W. K. Kwok, J. E. Thompson and J. M. Williams, *Inorg. Chem.*, 1990, **29**, 1601.

3 A. M. Kini, T. Mori, U. Geiser, S. M. Budz and J. M. Williams, *J. Chem. Soc., Chem. Commun.*, 1990, 647.

4 J. Larsen and C. Lenoir, *Synthesis*, 1989, 134; J. Larsen and C. Lenoir, *Org. Synth.*, 1993, **72**, 265.

5 J. Koskimies, *Acta Chem. Scand.*, 1984, **B38**, 101.

6 A. Suizi, A. Robert, P. Batail and L. Ouahab, *J. Org. Chem.*, 1987, **52**, 1610.