Preparation of Mono- and 1,2-Di-bromotetrathiafulvalenes (TTFBr and 1,2-TTFBr$_2$)

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The synthesis and characterization of mono- and 1,2-di-bromotetrathiafulvalenes, important precursors to more complex tetrathiafulvalene systems, is described; the X-ray crystal structure of the dibromo derivative is presented.

In spite of the importance of tetrathiafulvalene (TTF) **1** as a π-electron-donor in organic conductors, its chemistry has been severely limited by the lack of suitable intermediates for the preparation of substituted derivatives,[1] oligomers and polymers directly from TTF precursors. We report the preparation of the monobromo-derivative **2** and specifically one of the three possible isomeric dibromo derivatives, 1,2-dibromotetrathiafulvalene **3**.

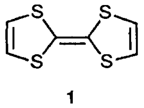
Compounds **2** and **3** were prepared *via* metallation and bromination according to Scheme 1. They were obtained together in all reaction mixtures.[2] We used a variety of metallating agents, but none led to the formation of only one of the compounds. This is probably due to the tendency of TTF^{1-} to undergo disproportionation[3] [see eqn. (1)].

$$2\mathrm{TTF}^{1-} \rightarrow \mathrm{TTF} + \mathrm{TTF}^{2-} \qquad (1)$$

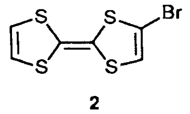
Identical conditions were used for all reactions. To a solution of 204 mg (1 mmol) of TTF in dry THF (30 ml) was added 1 mmol of the metallating agent at −78 °C. The resulting solution was stirred for 45 min under argon and then 326 mg (1 mmol) of 1,2-dibromotetrachloroethane (with which tetrabromotetrathiafulvalene was prepared[4]) in THF (5 ml) was added dropwise. The solution turned gradually from lemon-yellow to orange-red. After 2 h, water and diethyl ether were added and the crude mixture of the bromides (300–400 mg) was recovered from the organic phase.

$$\begin{array}{l} \mathrm{TTF} + \mathrm{RLi} \rightarrow \mathrm{TTF}^{1-} + \mathrm{TTF}^{2-} \\ \qquad\qquad\qquad \big\downarrow \ \mathrm{BrCl_2C{-}CCl_2Br} \\ \qquad\qquad \mathrm{TTFBr} + \mathrm{TTFBr_2} \end{array}$$

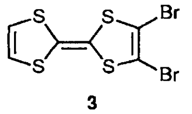
Scheme 1



1



2



3

The brominated TTF compounds were separated by silica gel column chromatography (CS$_2$–light-petroleum as eluent) and identified by ^{1}H NMR and mass spectrometry.† The results of four procedures are summarized in Table 1. In a

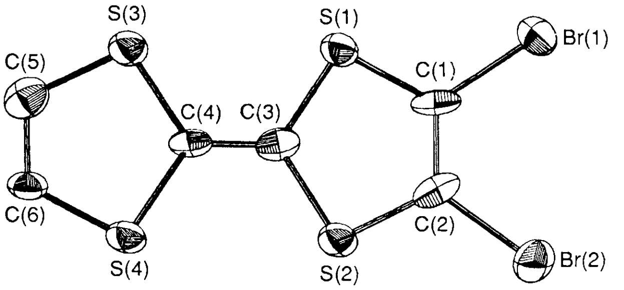


Fig. 1 ORTEP drawing of 1,2-dibromotetrathiafulvalene

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† All ^{1}H NMR spectra (in ppm) were measured in CS$_2$–CDCl$_3$ mixtures. TTFBr [6.33 (s, 2H); 6.26 (s, 1H). MS (CI): M + 1, 284 (65%)]. TTFBr$_2$ [6.35 (s, 2H)]. TTFBr$_3$ [6.29 (s, 1H); MS (EI): M$^+$, 442 (75%)]. TTFBr$_4$ [MS (EI): M$^+$, 520 (92%)].

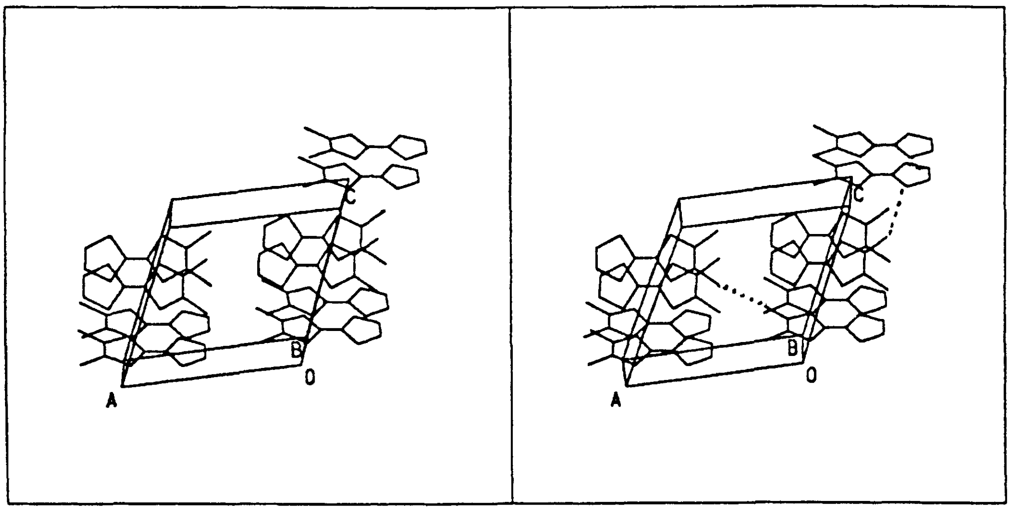

Fig. 2 Stereoview of the structure of **3** showing the stacking along the *b* axis and Br · · · Br and Br · · · S interactions as broken lines

typical experiment, for instance when the metallation was carried out with phenyllithium, the yield of isolated products (based on the weight of the crude products, 416 mg) was 13% of **2** and 41% of **3**.

While **2** can be uniquely characterized by ^{1}H NMR, the unambiguous identity of the structure of **3** as the 1,2-isomer required a crystal structure determination. It is important to note that no other isomer of **3** was identified in the reaction mixture. This may indicate either the preference of coordination in the Li$^+$ salt of TTF^{2-}, or the increased acidity of the hydrogen adjacent to Br in **2**. Crystals of **3** were precipitated by slow evaporation at room temperature from a light petroleum–CS$_2$ solution. They are red transparent needles, m.p. 128.5–130.4 °C and the structure determination[‡] indeed verified the product to be **3**.

The introduction of two bromine atoms into **1** leads to a slight elongation of the exocyclic C=C bonds from 1.314(3) Å in **1**[6] to 1.37(2), in **3**. The 1,2 mode of disubstitution of bromine also results in an important change in the space group from a centrosymmetric $P2_1/c$ (Z = 2) in **1** to a chiral one, $P2_1$ (Z = 2) in **3**. This packing mode, Fig. 1, results from screw-related interactions Br(1) · · · Br(1) 3.699(3) Å and Br(2) · · · S(4) 3.646(6) Å.

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Table 1 Summary of results for different metallating agents in Scheme 1

Reaction Number	Metallating Agent	TTFBr$_2$: TTFBr Ratio in crude[a]	Other compounds found in the reaction mixture
1	LDA[b]	3.8 : 1	~40% of crude mass contained TTFBr$_3$ and TTFBr$_4$ and an unidentified dark material
2	LiPh	2.1 : 1	~10% of crude mass contained TTFBr$_3$ and TTFBr$_4$
3	LiHMDS[c]	1.6 : 1	Crude mass contained traces of TTFBr$_4$ and TTFBr$_3$
4	LiMe	1 : 2.7	None

[a] Mole ratio based on ^{1}H NMR. [b] Lithium diisopropylamide. [c] Lithium hexamethyldisilazane.

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[‡] The compound is monoclinic, space group $P2_1$ $C_6H_2S_4Br_2$, M_r = 362, a = 11.410(3), b = 4.049(2), c = 11.819(3) Å, β = 114.28(5)°, V = 497.7(8) Å^3, Z = 2, D_c = 2.402 g cm^{-3}, Mo-Kα radiation (λ = 0.71073 Å), μ = 87.0 cm^{-1}, F(000) = 344. The structure was solved by direct methods; least-squares refinement with anisotropic temperature factors for non-hydrogen atoms. No absorption corrections were applied. R_f = 0.0526 R_w = 0.0576, for 807 observed reflections out of 1006 measured with $F > 4\sigma(F)$ on a four-circle diffractometer. Five peaks of height ~1.0 e Å^{-3} appeared on a final difference map in the vicinity of the bromide atoms. All calculations were carried out with SHELX76 or SHELX86.[5] 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.

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