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A bromine catalysed dimerisation of α,α′-dihalomonopyrrolo-TTF†

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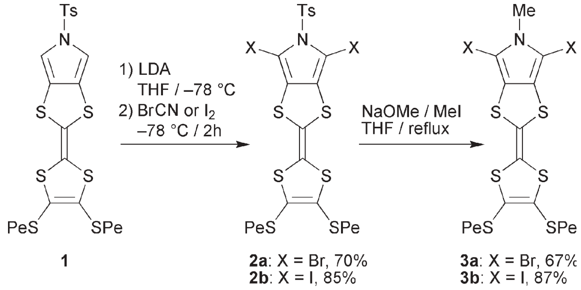
Received (in Cambridge, UK) 30th May 2007, Accepted 28th June 2007
First published as an Advance Article on the web 30th July 2007
DOI: 10.1039/b708191j

Dihalomonopyrrolo-TTF undergoes a bromine catalysed dimerisation reaction to yield a novel type of extended TTF derivative.

In the race for new organic metals and superconductors,[1] the redox-active tetrathiafulvalene[2] (TTF) and its derivatives have been intensively studied in the past three decades because of their unique π-electron donor properties. During the past years, TTF and its derivatives have also been incorporated into elaborate molecular and supramolecular systems, such as chemical sensors,[3] charge-separating ligands,[4] shuttles,[5] switches,[6] springs,[7] non-linear optical (NLO) materials,[8,9] cyclophanes and cage molecules.[10] For some of these purposes, the extension of the π-electron conjugation in TTF by a spacer unit has proved to be crucial, and extended TTF derivatives[11] have been widely used in NLO active materials.[12] Vinylogous extended TTFs are normally prepared by either an intramolecular oxidative coupling of 1,4-dithiafulvenes or by a Wittig/Wittig–Horner reaction between a 1,3-dithiol-2-yl phosphonium salt/phosphonate ester and an appropriate aldehyde/ketone.[13,14] Most recently, it has been discovered[14] that 4,5-dicyano-1,3-dithiole-2-one upon heating with trialkyl phosphite produces dicyanoacetylene which undergoes a [2 + 2] cycloaddition with different TTF derivatives to yield vinylogous extended TTF derivatives. However, most of these synthetic methods rely on multi-step procedures that often involve tedious separations. To the best of our knowledge, only very few reactions involving the direct dimerisation of TTF derivatives have been reported in the literature.[15]

Recently, we have described[16] the first examples of functionalisation of the monopyrrolotetrathiafulvalene[17] (MPTTF) building block with halogen atoms at the α-positions on the pyrrole ring. These dihalo-MPTTF derivatives are being used extensively for the preparation of new materials. During the synthesis of the dihalo-MPTTFs **3a**–**b**, we discovered that they undergo a hitherto unknown type of dimerisation reaction, producing a novel type of extended TTF derivative. Here, we describe the synthesis and characterisation of the dihalo-MPTTFs **3a**–**b** and their subsequent bromine catalysed dimerisations into the extended MPTTFs **4a**–**b**, together with a discussion of the mechanism leading to the formation of dimers **4a**–**b**.

The synthetic approach to **3a**–**b** is outlined in Scheme 1. In the first step, MPTTF[17b] **1** was treated with 3 equiv. of lithium diisopropylamide (LDA) and subsequently reacted with either cyanogen bromide or iodine, providing the dibromo derivative **2a** or diiodo derivative **2b** in yields of 70% and 85%, respectively. Subsequently, in a one-pot reaction, the tosyl group in **2a**–**b** was removed using sodium methoxide and the resulting pyrrole nitrogen was methylated using iodomethane, affording **3a** and **3b** in 67% and 87% yield, respectively.§



Scheme 1 Synthesis of the dihalo-MPTTFs **3a**–**b**.

Compound **3b** was easily purified by column chromatography and was isolated as a stable compound in the shape of yellow needles after diffusion of MeOH into a solution of **3b** in CH_2Cl_2. An X-ray crystal structure was obtained and the molecular structure is depicted in Fig. 1.¶ However, in the case of **3a**, some problems were encountered during purification. Compound **3a** was obtained as a yellow solid after purification by column chromatography, but surprisingly, the surface of the isolated solid turned black on standing. For the purposes of obtaining crystals suitable for X-ray diffraction, a sample of **3a** was dissolved in CH_2Cl_2–MeOH. After standing for a few days, it was noticed that the initially yellow solution had turned black. Inspection of the black solution by means of TLC revealed the presence of another material having an R_f value lower than that of **3a**, whereas a MALDI-MS spectrum recorded from the black solution showed a peak having exactly twice the molecular mass of **3a**, suggesting that the new material could be the dimer **4a** (Scheme 2). After five days, the black solution was filtered, affording yellow crystals of **3a**

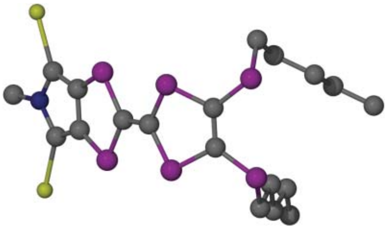


Fig. 1 Molecular structure of **3b** obtained using X-ray crystallography (H atoms omitted).

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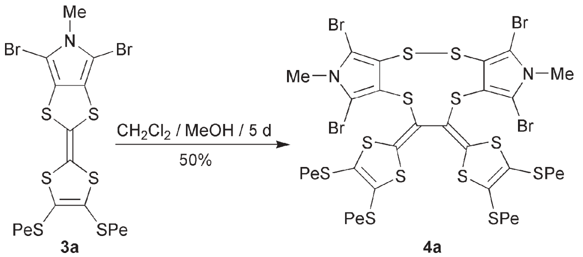
† Electronic supplementary information (ESI) available: Experimental details on the syntheses and characterisation of compounds **2a**–**b**, **3a**–**b** and **4a**–**b**. See DOI: 10.1039/b708191j

‡ Authors Gopee and Petersen contributed equally to the work described in this communication.



Scheme 2 Dimerisation of the dibromo-MPTTF derivative **3a**.

suitable for X-ray diffraction.¶ Subsequently, the filtrate was concentrated and the new compound formed during the crystallisation experiment was isolated (50% yield) as a yellow-orange solid by means of column chromatography. Further support for the proposed dimeric structure of **4a** came from ^{1}H NMR spectroscopy (300 MHz, 298 K, $CDCl_3$) of the isolated material. For example, the pentyl CH_3 protons are separated into two triplets ($J = 7$ Hz) resonating at $\delta = 0.92$ and 0.94 ppm and each integrating to 6H, while the CH_3 protons attached to the pyrrole rings appear as one singlet resonating at $\delta = 3.67$ ppm, integrating to 6H. On this basis, it can be concluded that the molecular structure of the isolated material contains two chemically none-quivalent thiopentyl substituents and consequently must have a lower degree of symmetry in its structure as compared to compound **3a**.

Although ^{1}H NMR spectroscopy supported the dimeric structure **4a**, other possible dimeric structures could not be ruled out at this stage. Diffraction quality single crystals of **4a** were obtained as yellow laths by slow diffusion of MeOH into a solution in CH_2Cl_2. The resulting X-ray structure (Fig. 2) revealed unequivocally the proposed dimeric structure of **4a**.¶ In the solid state, the molecule exhibits approximate C_2 point symmetry, with the 2-fold rotation axis passing through the midpoints of the S–S and C–C bonds in the central 10-membered ring. The planes through the pyrrole groups on either side of the 10-membered ring are twisted slightly with respect to each other (dihedral angle 28°), while the 1,3-dithiole-2-ylidene groups bound to the C–C bond are twisted more significantly (dihedral angle 70°), presumably to minimise steric repulsion.

A possible mechanism for the formation of **4a** from **3a** is outlined in Scheme 3 and involves initially elimination of Br_2 from a small amount of **3a**.‖ In the next step, an electrophilic addition of Br_2 to **3a** affords the bromonium ion **5**, which subsequently reacts with another molecule of **3a** to give the positively charged intermediate **6**. Finally, **6** reacts with bromide to regenerate Br_2, and rearrangement of the bonds produces the neutral dimer **4a**.**

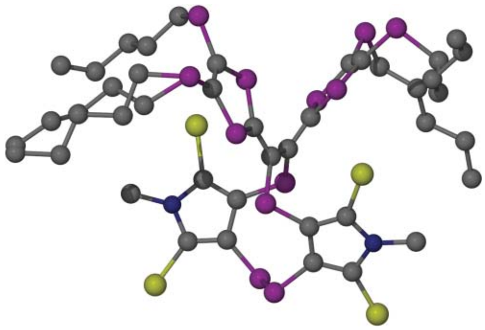
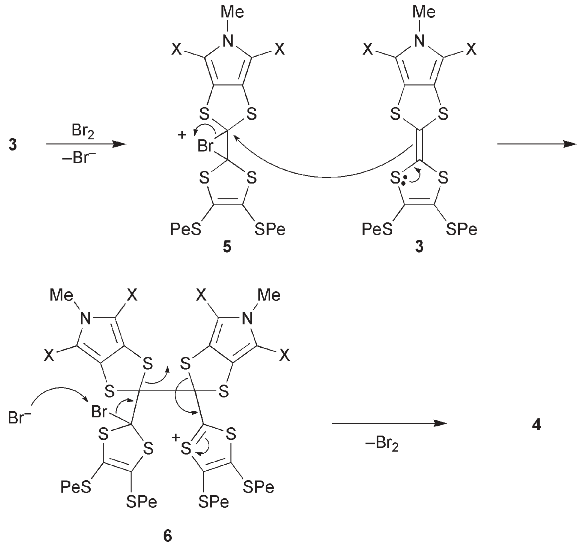


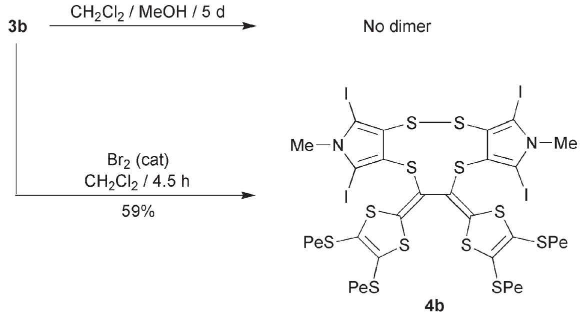
Fig. 2 Molecular structure of **4a** obtained using X-ray crystallography (H atoms omitted). One pentyl chain is modelled as disordered, with both orientations shown.



Scheme 3 Proposed reaction mechanism for formation of the dimers **4**.

In contrast to the low stability observed for the dibromo-MPTTF derivative **3a**, the diiodo-MPTTF derivative **3b** is rather more stable.¶ Even after standing for an extended period, a solution of **3b** in CH_2Cl_2–MeOH did not show any evidence (TLC analysis and MALDI-MS) for the formation (Scheme 4) of the dimer **4b**. However, upon addition of a catalytic amount of Br_2 to a solution of **3b** in CH_2Cl_2, the dimer **4b** was formed (Scheme 4) within 4.5 h in 59% yield. Furthermore, addition of a catalytic amount (1 mol%) of Br_2 to a solution of **3a** in CH_2Cl_2 gave the corresponding dimer **4a** in a 68% yield within 24 h.† These observations clearly support the hypothesis that the dimerisation reaction is catalysed by Br_2. Compound **4b** was characterised using standard methods,† including X-ray crystallography.¶

Electrochemical characterisation of the new dimers **4a** and **4b** was carried out using cyclic voltammetry (CV). For comparison, the electrochemical behaviour of the monomers **3a** and **3b** was investigated under similar conditions. As expected, the CVs of compound **3a** and **3b** showed (Table 1) two reversible mono-electron redox processes, which can be associated with the first and second oxidation of the MPTTF unit. By contrast, the CVs of the dimers **4a** and **4b** showed one reversible two-electron redox



Scheme 4 Bromine catalysed formation of the dimer **4b**.

Table 1 Electrochemical data[a] for compounds **3a**, **3b**, **4a** and **4b** determined using cyclic voltammetry in THF–MeCN (1 : 1)

Compound	$E_{1/2}{}^{1}$/V[b]	No. electrons[c]	$E_{1/2}{}^{2}$/V[b]	No. electrons[c]
3a	+0.27	1	+0.54	1
4a	+0.26	2		
3b	+0.23	1	+0.51	1
4b	+0.25	2		

[a] 298 K, n-Bu$_4$NPF$_6$ (0.1 M) as supporting electrolyte, all potentials were measured against a Ag/AgNO$_3$ reference, scan rate was 100 mV s^{-1}. [b] Reversible processes. [c] The number of electrons involved in each process was determined from differential pulse voltammetry.

process, a situation which is characteristic[13] for most extended TTF derivatives.

In summary, a new method for the dimerisation of monopyrrolo-TTF derivatives has been described. The electrochemical and physical characterisation of the resulting dimers were consistent with their structures. A mechanism for the formation of these dimers was postulated and verified by simple experiments. It was therefore proven that Br$_2$ is responsible for catalysing this dimerisation. Though dimerisation of TTF systems by long synthetic routes is well known, to our knowledge, these are the first examples of bromine catalysed reactions for the dimerisation of the monopyrrolo-TTF derivatives. Indeed, this could be an attractive tool in the synthesis of important materials based on TTF systems, especially extended TTF systems.

We gratefully acknowledge financial support provided by the Danish Strategic Research Council through the Young Researchers Programme (#2117-05-0115), and the Danish Technical Research Council (#2058-03-0036). We are grateful to the Danish Natural Science Research Council and the Carlsberg Foundation for provision of the X-ray equipment.

Notes and references

§ An attempt was made to isolate the intermediate detosylated compound of **2b**, but this proved to be impossible. The compound seemed to decompose abruptly on contact with water during the workup.

¶ Compounds **3a** and **3b** are isomorphous, and **4a** and **4b** are isomorphous. **Crystal data**. **3a**: $C_{19}H_{25}Br_2NS_6$, M = 619.58, monoclinic, a = 17.5630(9), b = 8.0200(4), c = 17.9855(9) Å, β = 94.597(2)°, U = 2525.2(2) Å^3, T = 180(2) K, space group $P2_1/c$, Z = 4, μ(Mo-Kα) = 3.714 mm^{-1}, 33 371 reflections measured, 4187 unique (R_{int} = 0.078), $R1[I > 2\sigma(I)]$ = 0.041, w$R2$(all data) = 0.098. **3b**: $C_{19}H_{25}I_2NS_6$, M = 713.56, monoclinic, a = 17.7967(6), b = 7.9872(3), c = 18.2265(6) Å, β = 93.503(1)°, U = 2585.98(16) Å^3, T = 180(2) K, space group $P2_1/c$, Z = 4, μ(Mo-Kα) = 2.924 mm^{-1}, 42 034 reflections measured, 5251 unique (R_{int} = 0.052), $R1[I > 2\sigma(I)]$ = 0.034, w$R2$(all data) = 0.077. **4a**: $C_{38}H_{50}Br_4N_2S_{12}$, M = 1239.16, triclinic, a = 11.6042(6), b = 14.9350(8), c = 16.0311(9) Å, α = 112.535(2), β = 90.490(2), γ = 106.707(2)°, U = 2435.6(2) Å^3, T = 180(2) K, space group $P\bar{1}$, Z = 2, μ(Mo-Kα) = 3.850 mm^{-1}, 25 427 reflections measured, 8168 unique (R_{int} = 0.084), $R1[I > 2\sigma(I)]$ = 0.050, w$R2$(all data) = 0.114. **4b**: $C_{38}H_{50}I_4N_2S_{12}$, M = 1427.12, triclinic, a = 11.6853(3), b = 14.9902(4), c = 16.1737(4) Å, α = 112.847(1), β = 90.668(1), γ = 105.679(1)°, U = 2491.85(11) Å^3, T = 180(2) K, space group $P\bar{1}$, Z = 2, μ(Mo-Kα) = 3.035 mm^{-1}, 20 960 reflections measured, 12 179 unique (R_{int} = 0.034), $R1[I > 2\sigma(I)]$ = 0.038, w$R2$(all data) = 0.080. CCDC 649631–649634. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b708191j

|| The catalytic amount of Br$_2$ required for the dimerisation process is most likely formed by elimination from the dibromo-MPTTF derivative **3a**. The process of generation of Br$_2$ from **3a** has not yet been established definitively, but it could be because of radical formation.

** An alternative mechanism involving oxidation of **3** by bromine to form radical cations of **3** cannot be ruled out.†

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