

Synthesis and X-Ray Crystal Structure of a Novel Tetrathiafulvalene Dimethyl[2,4-dioxo(1*H*,3*H*)pyrimido]tetrathiafulvalene, able to form Intermolecular Hydrogen Bonds of Nucleic Acid Base-pair Type

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The efficient synthesis, molecular and crystal structure, chemical, spectroscopical and electrochemical properties and charge-transfer salts of dimethyl[2,4-dioxo(1*H*,3*H*)pyrimido]tetrathiafulvalene, a novel π -electron donor able to form intermolecular hydrogen bonds of nucleic acid base-pair type, are described.

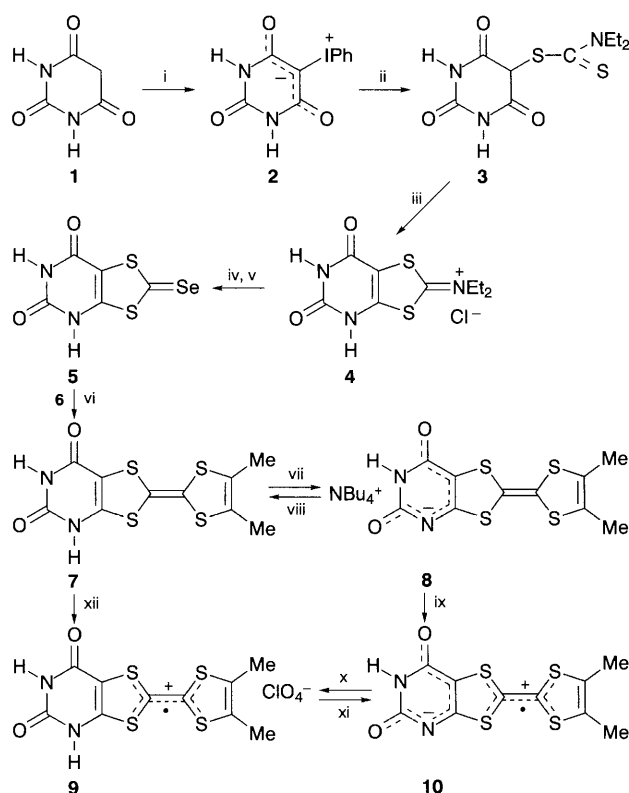
Tetrathiafulvalene (TTF) derivatives have played an important role in the development of organic conductors and semi-conductors.¹ Very few examples of TTF derivatives able to form intermolecular hydrogen bonds are known, however.² The ability to form hydrogen bonds could be of crucial importance for an efficient intermolecular interaction and for increasing the conductivity of cation radical salts. We aim to synthesize TTF derivatives which are able to form two or three strong hydrogen bonds, and we wish to study derivatives containing nucleic acid base moieties, *i.e.* uracil, guanine, cytosine and adenine. The formation of hydrogen-bonded complementary pairs has been used recently for the design of photosynthetic model systems³ and self-assembled polymeric supramolecular systems.⁴ There are no reports on the synthesis of any TTF derivatives containing oxo- or amino-pyrimidine substituents except for our recent research.⁵ In this contribution we report the efficient synthesis of the new TTF containing uracil moiety—dimethyl[2,4-dioxo(1*H*,3*H*)pyrimido]tetrathiafulvalene (DMDOP-TTF) and its molecular and crystal structure and properties.

The key molecule for synthesis of DMDOP-TTF is barbituric acid **1** as shown in Scheme 1. Treatment of **1** with diacetoxyiodobenzene gives 5-phenyliodoniumbarbituric acid betaine **2** in 95% yield. Nucleophilic attack of **2** by sodium diethyl dithiocarbamate affords the sodium salt of **3**, which on acidification gives the 5-diethylaminothiocarbonylthiobarbituric acid **3** in 40–50% yield. Cyclisation of **3** in sulfuric acid gives the 5,7-dioxo(4*H*,6*H*)-1,3-dithiolo[4.5-*d*]pyrimidine-2-diethylimmonium cation which can be isolated as a chloride (**4**) or perchlorate salt in 80% yield. Reaction of **4** with Na₂Se gives the selone **5** in a two-stage reaction⁶ in 80% yield. The poorly soluble selone **5** upon reaction with bis(trimethylsilyl)acetamide (BTSA) in benzene gives a highly soluble bistrimethylsilyl product. Since this was sensitive to hydrolysis it was not isolated but was used immediately in a coupling reaction with 4,5-dimethyl-1,3-dithiole-2-selone **6** in the presence of triphenylphosphine.⁷ The yield of the product DMDOP-TTF **7** was 54% based on **5** after purification *via* its tetrabutylammonium salt **8**. The DMDOP-TTF precipitates from solutions as a yellow–orange fine powder, its solubility being very low in water, alcohols, MeCN or halogenohydrocarbons. At room temperature it is scarcely soluble in formic acid (0.05%), acetic acid (0.01%), and only slightly more so in DMF (0.4%). Crystallisation from DMF–H₂O (96 : 4) led to the formation of orange crystals of **7**·DMF suitable for X-ray analysis.

The molecular and crystal structures are shown in Figs. 1–3. Both **7** and DMF molecules in the crystal possess nearly planar structures. The N–H...O hydrogen bonds between molecules of **7** as well as with DMF contribute to the stability of the structure. Two molecules of **7** form dimers by means of two identical hydrogen bonds with N–H 0.92 Å, and N–H...O 2.85 Å. There are strong stacking interactions between molecules of **7** in the crystal (see Fig. 3). The distances between the covering molecules are 3.035 and 3.53 Å.

Compound **7** is an NH-acid and readily forms salts in a similar manner to selone **5**.⁸ Yellow **8** crystallises well and is useful for further reactions such as alkylation or oxidation.

Upon reaction with an iodine solution a deep green extremely insoluble fine powder is obtained, the intramolecular cation radical salt (betaine) **10** containing both radical cations and anions. Betaine **10** reacts with strong acids to give cation radical



Scheme 1 Reagents and conditions: i, PhI(OAc)₂, DMF–H₂O (1 : 1), room temp.; ii, Et₂NCS₂Na·3H₂O, DMF, room temp., 6 days, then Et₂O, H₂O, HCl; iii, conc. H₂SO₄, 55–60 °C, 1 h, then H₂O–conc. HCl–acetone (2 : 2 : 5 v/v/v); iv, H₂O, Na₂Se, HCl; v, AcOH, conc. HCl, 60 °C; vi, PhH, BTSA, 60 °C, **6**, room temp., then Ph₃P, 24 h, EtOH; vii, DMF, 10% NBu₄OH, 60 °C, H₂O; viii, EtOH, AcOH; ix, MeCN, I₂; x, MeCN, 60% HClO₄, Ac₂O, 80 °C, cooling; xi, wet MeCN; xii, MeCN, 60% HClO₄, Ac₂O, PhI(OAc)₂, 80 °C, cooling

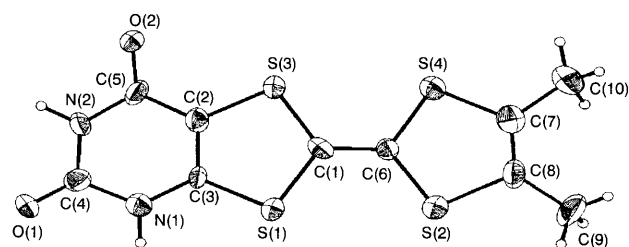


Fig. 1 Perspective view of **7**. Important bond lengths (Å): C(1)–C(6) 1.35, C(7)–C(8) 1.346, C(2)–C(3) 1.403, C(2)–S(3) 1.748, C(3)–S(1) 1.705, C(2)–C(5) 1.39, C(5)–O(2) 1.269, C(4)–O(1) 1.205.

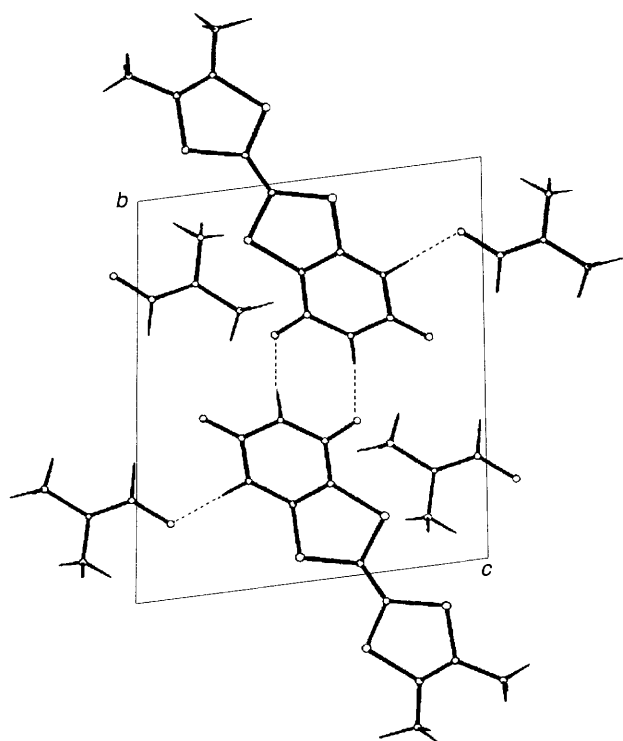


Fig. 2 Crystal structure of 7-DMF viewed along the *x*-axis

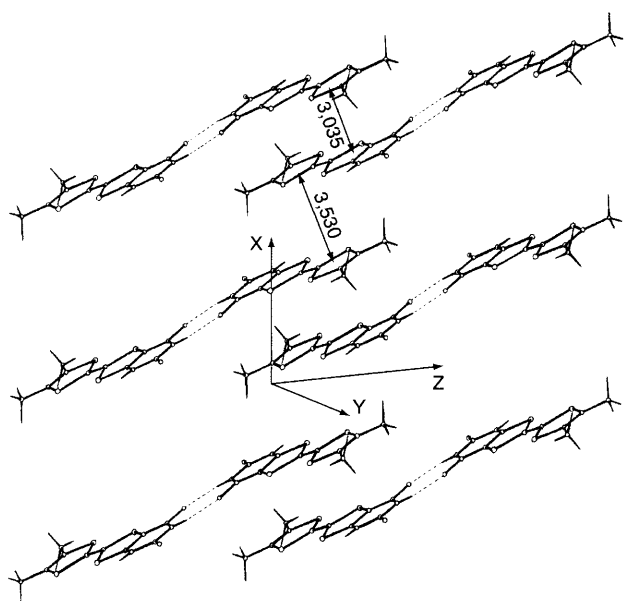


Fig. 3 Stacking of molecules of 7 in the crystal

salts of 7, for example, the deep green perchlorate **9**, which crystallises from MeCN in the presence of HClO₄. Cyclic voltammetry of **9** (10⁻⁴ mol dm⁻³) in MeCN containing HClO₄ with NBu₄ClO₄ as supporting electrolyte and using a glassy carbon working electrode, showed two pairs of reversible redox waves; $E_1^{\text{red}} = 0.57$, $E_1^{\text{ox}} = 0.72$ and $E_2^{\text{red}} = 0.84$, $E_2^{\text{ox}} = 0.94$ V (vs. Ag/AgCl) at 200 mV s⁻¹. Thus, the first oxidation potential of 7 (0.72 V) is higher than that of bis(ethylenedithio)-TTF by

0.16 V, therefore charge-transfer complexes of 7 are formed with greater difficulty than those for bis(ethylenedithio)-TTF. The iodine complex of 7 crystallises from a hot solution of the components in sulfolane–acetonitrile (2:1) as black fine needles and has a composition 7·I₃ upon crystallisation. The perchlorate **9** can also be obtained directly from 7 by oxidation with diacetoxyiodobenzene as two-electron oxidant in equimolar quantity in MeCN containing HClO₄.

Due to low solubility we were not able to perform an electrocrystallisation process of 7 on an anode. We are currently investigating the preparation of radical cation salts of the type [DMDOP-TTF]₂X in other ways.

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Footnotes

† **7**: mp > 250 °C (decomp.), IR (v/cm⁻¹): 1578, 1646, 1715, 2815, 2985, 3135, 3450. **8**: mp 197–198 °C, IR (v/cm⁻¹): 1620, 2800, 2915, 2935, 3010, 3100. **9**: mp 250 °C (decomp.), IR (v/cm⁻¹): 1560, 1676, 1722, 1750, 2840, 3050, 3170, 3270; UV (MeCN–HClO₄), $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 260 (10300), 463 (16000), 702 (4000). **10** mp > 250 °C (decomp.), IR (v/cm⁻¹): 1620, 1650, 2785, 2955, 3090, 3390. **7**·I₃: mp > 300 °C (decomp.), IR (v/cm⁻¹): 1556, 1624, 1670, 1714, 2920, 3150. Satisfactory elemental analyses were obtained.

‡ *Crystal data for 7-DMF*: C₁₀H₈N₂O₂S₄·C₃H₇NO, triclinic, space group *P* $\bar{1}$, $a = 7.862(2)$, $b = 9.096(2)$, $c = 12.167(2)$ Å, $\alpha = 82.06(1)$, $\beta = 88.22(1)$, $\gamma = 89.81(1)^\circ$; $V = 861.3(6)$ Å³, $Z = 2$, $D_c = 1.502(1)$ g cm⁻³, Mo-K α radiation, $\lambda = 0.71069$ Å, $\mu_{\text{Mo}} = 2.9$ cm⁻¹, $F(000) = 404$. A single crystal of dimensions 0.3 × 0.3 × 0.5 mm was used for X-ray measurements at room temperature on a Syntex *P2a* diffractometer with graphite-monochromated Mo-K α radiation. Cell constants were determined from 20 reflections with $14 < \theta < 17^\circ$. The intensity data were collected to a maximum 2θ of 45° by ω -scans. The total number of independent reflections measured was 1830, of which 1272 reflections were considered as observed by the criterion $|F| \geq 4.0 \delta(F)$. No absorption correction was applied. The structure was solved by direct methods and refined by block-diagonal least squares with anisotropic temperature factors to $R = 0.0662$, $R_w = 0.0795$. The hydrogen atoms were located by difference Fourier synthesis. The coordinates and isotropic thermal parameters of the H atoms were not refined. All crystallographic calculations were made with the help of the AREN program.⁹ Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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