Stacked Supramolecular Structures involving Hydrogen-bonded Networks in Highly Functionalised Tetrathiafulvalene Derivatives

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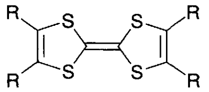
The solid-state structures of tetrathiafulvalene derivatives **1**·2MeOH and **2** are established by single-crystal X-ray analysis, which reveals the coexistence of uniform π–π stacking and hydrogen-bonded O···H···O networks.

The self-assembly of molecules into well-defined supramolecular structures in the solid state is an area of considerable current interest.[1] This type of crystal engineering[2] involves the subtle manipulation of non-covalent interactions, such as π–π stacking,[3] electrostatic interactions,[4] van der Waals forces[4] and hydrogen bonding.[5] The (relative) strength and selectivity of the hydrogen bond places it at the forefront of studies in this field.[5,6] There has recently been rapid progress in the exploitation of tetrathiafulvalene (TTF) derivatives as building-blocks in supramolecular chemistry,[7] and intermolecular hydrogen bonding has been observed in the crystal structures of TTF-thioamide and TTF-amide derivatives, although uniform TTF stacks are not formed in these systems.[8] In this communication we report the single-crystal X-ray structures of **1**·2MeOH and **2**, both of which form extensive hydrogen-bonded networks, and uniform TTF stacks.



1 R = $S(CH_2)_2OH$
2 R = $S(CH_2)_2O(CH_2)_2OH$
3 R = $S(CH_2)_2CN$

Compound **1** was synthesised as described recently.[9] Compound **2** was prepared in 84% yield by deprotection of compound **3**[9] using caesium hydroxide in DMF (20° C) followed by trapping of the intermediate TTF-tetrathiolate with 1-iodoethyleneglycol.‡

X-Ray single-crystal structure determinations§ of **1**·2MeOH and **2** revealed similar conformations of the molecules **1** and **2**, both situated at crystallographic inversion centres (Fig. 1). Their TTF moieties, which are folded along the S(1)···S(2) and S(1′)···S(2′) vectors by 6.0° in a chair-like fashion in **1**, and are essentially planar in **2**, form stacks parallel to the *a* axis, with close interplanar separations (3.36 Å in **1**, 3.40 Å in **2**), but with large longitudinal and lateral shifts between adjacent molecules. These short intrastack distances between the TTF moieties in **1** and **2** provide evidence for strong π–π interactions; the distances are shorter than those observed in TTF–$(SC_8H_{17})_4$ (3.43 and 3.50 Å, in two crystallographic forms)[10] and TTF–$(CH_2OC_7H_{15})_4$ (3.5 Å).[11]

The side-chains, bound to C(2) and C(3), are stretched approximately perpendicular to the TTF plane (on the same side of it) and parallel to each other and the side-chains of the neighbouring molecules. The resulting peculiar stacks of Z-shaped molecules are the backbone of similar crystal packing motifs in both structures (Fig. 2), which gives rise to similar, highly anisometric, unit cells. There is, however, sufficient conformational flexibility of the side chains to give rise to different patterns of hydrogen bonding in the two structures. In **2**, side-chain hydroxy groups are linked by an intramolecular O(4)–H···O(2) bond and an intermolecular one, O(2)–H···O(4), between glide-plane related molecules [O···O 2.652(3) and 2.673(3) Å, respectively], forming chains in the *z* direction. In

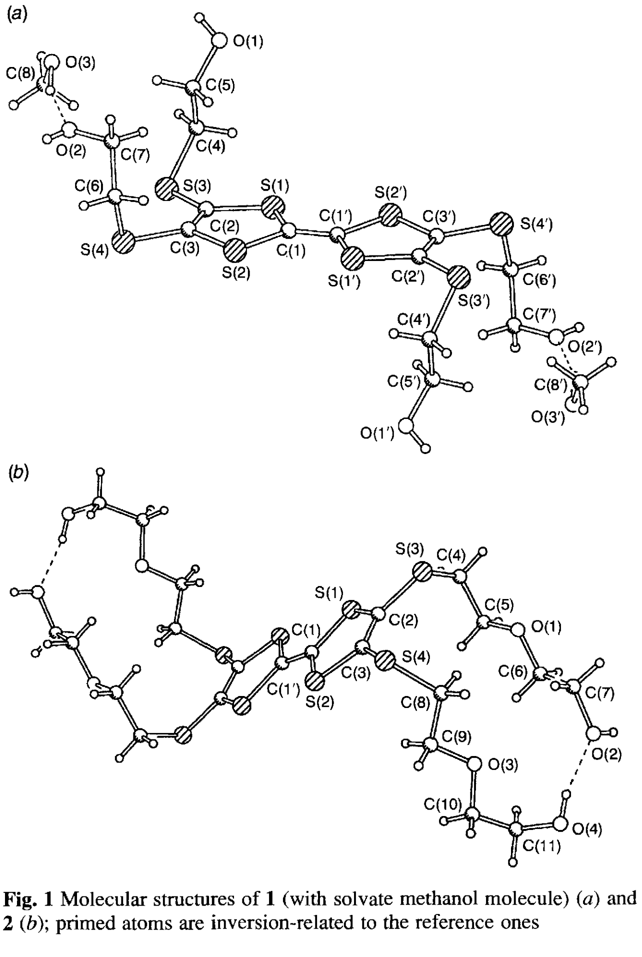


Fig. 1 Molecular structures of **1** (with solvate methanol molecule) (*a*) and **2** (*b*); primed atoms are inversion-related to the reference ones

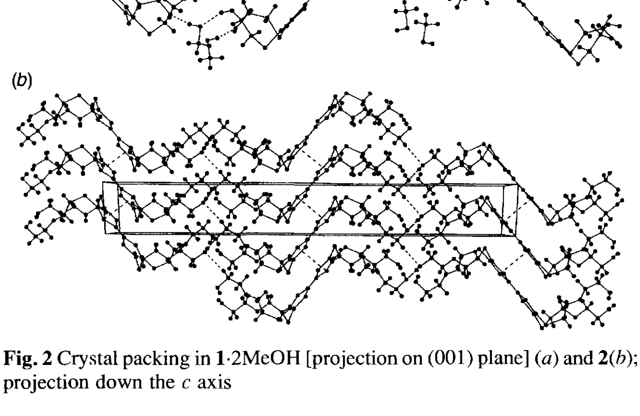


Fig. 2 Crystal packing in **1**·2MeOH [projection on (001) plane] (*a*) and **2**(*b*); projection down the *c* axis

1·2MeOH the hydroxy groups are further apart [O(1)···O(2) 5.28 Å], with a methanol molecule of crystallization accommodated between the side chains and linking molecules of **1** in the *y* direction by O(1)–H···O(3) (x, $3/2 - y$, $z - 1/2$) and O(3)–H···O(2) hydrogen bonds of 2.75(1) and 2.70(1) Å, while the O(2)–H···O(1) bonds of 2.65(1) Å link the molecules related *via* the *z* translation.

It is an important step forward to have characterised structurally the first two TTF systems which display both uniform π–π stacking and hydrogen-bonded O···H···O networks. There is clearly considerable potential for modifying the supramolecular architecture of TTF systems by hydrogen-bonding interactions involving substituent groups. This work paves the way for the study of a range of new TTF systems bearing functionalised side chains.

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Footnotes

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‡ Compound **2**, red crystals (from methanol) mp 81–83 °C. Analysis: Found C, 38.59; H, 5.36; S, 37.30. $C_{22}H_{36}O_8S_8$ requires C, 38.58; H, 5.30; S, 37.44%. δ_H [$CD_3S(O)CD_3$] 4.56 (t, 4H, J = 5.3 Hz), 3.60 (t, 8H, J = 6.5 Hz), 3.46 (m, 16H) and 3.04 (t, 8H, J = 6.3 Hz); δ_C [$CD_3S(O)CD_3$] 127.00, 109.52, 72.09, 69.01, 60.06 and 35.06; *m/z* (FAB) 683.9 (M^+); CV $E_1{}^{1/2}$ +0.47, $E_2{}^{1/2}$ +0.79 (*vs.* Ag/AgCl, Pt electrode, NBu_4PF_6, CH_2Cl_2, scan speed 100 mV s^{-1}).

§ Experiments were performed on a Rigaku AFC6S four-circle diffractometer (graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, ω scan mode, Lehmann–Larsen profile analysis). The structures were solved by direct methods (SHELXS-86 programs[12]) and refined by full-matrix least-squares methods (SHELXL-93 software[13]) against F^2 of all data with Chebyshev weighting scheme. All non-H atoms were refined anisotropically; all H atoms in **2** and hydroxy ones in **1** were refined isotropically, other H atoms in **1** were treated 'riding' (methyl groups rotating). 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.

Crystal data for $C_{14}H_{20}O_4S_8$(**1**)·$2CH_3OH$ (from methanol): M = 572.86, monoclinic, space group $P2_1/c$ (no. 14), T = 293 K, a = 5.171(2), b = 31.286(7), c = 7.946(1) Å, β = 99.98(2)°, V = 1266.1(5) Å^3 (from 20 reflections, $13 < \theta < 14°$), Z = 2, D_c = 1.50 g cm^{-3}, $F(000)$ = 600, μ = 7.35 cm^{-1}, crystal size 0.17 x 0.48 x 0.52 mm (primary pinakoid), decay during data collection (41% decline of three standard intensities), 2771 total and 1884 unique reflections ($\theta \leqslant 25°$), R_{int} = 0.017; analytical absorption correction[14] (TEXSAN software[15]), T_{max} = 0.8851, T_{min} = 0.7175; 150 variables, $R(F)$ = 0.064 for 1521 data with $F \geqslant 2\sigma(F^2)$, $wR(F^2)$ = 0.209 for all data, goodness-of-fit S = 1.18, $\Delta\rho_{max}$ = 0.44, $\Delta\rho_{min}$ = −0.48 e Å^{-3}.

For $C_{22}H_{36}O_8S_8$ **2**: M = 684.99, monoclinic, space group $P2_1/c$ (no. 14), T = 150 K (a Cryostream open-flow N_2 gas cryostat[16]), a = 5.051(2), b = 37.876(13), c = 8.319(3) Å, β = 107.63(3)°, V = 1517(1) Å^3 (from 24 reflections, $13 < \theta < 17°$), Z = 2, D_c = 1.50 g cm^{-3}, $F(000)$ = 720, μ = 6.32 cm^{-1}, crystal size 0.08 x 0.22 x 0.35 mm (primary pinakoid), 4790 total and 3502 unique reflections ($\theta \leqslant 27.5°$), R_{int} = 0.025, semiempirical absorption correction[17] (TEXSAN software, 108 ψ-scans of three reflections, $T_{min}:T_{max}$ = 0.882 : 1.000), 244 variables, $R(F)$ = 0.039 for 2578 data with $F^2 \geqslant 2\sigma(F^2)$, $wR(F^2)$ = 0.085 for all data, S = 1.005, $\Delta\rho_{max}$ = 0.37, $\Delta\rho_{min}$ = −0.30 e Å^{-3}. At 293 K, a = 5.106(1), b = 38.015(4), c = 8.369(1) Å, β = 107.73(1)°, V = 1547.2(3) Å^3.

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