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4,4′,5,5′-Tetramethyltetrathiafulvalene–1,4-dinitrobenzene (1/1)

Andrei S. Batsanov* and Svetlana B. Lyubchik†

Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England

† Present address: L. M. Litvinenko Institute of Physical Organic and Coal Chemistry, National Academy of Sciences of Ukraine, Donetsk 83114, Ukraine

Correspondence e-mail:
a.s.batsanov@durham.ac.uk

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.028
wR factor = 0.079
Data-to-parameter ratio = 14.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Tetramethyltetrathiafulvalene and 1,4-dinitrobenzene co-crystallize in a mixed-stack 1:1 complex, $C_{10}H_{12}S_4\cdot C_6H_4N_2O_4$, without appreciable charge transfer. Both molecules lie on the same crystallographic twofold axis.

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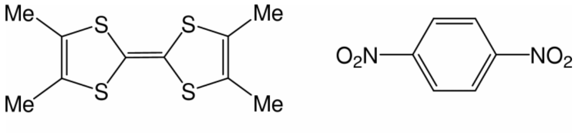
Comment

The title complex, (I), was prepared in the course of our studies of tetrathiafulvalene (TTF)-based charge-transfer (CT) systems (John *et al.*, 2000; Moore *et al.*, 2001; Batsanov *et al.*, 2001 and references therein). Whilst many hundreds of TTF derivatives have been studied structurally, a survey of the Cambridge Structural Database (Allen, 2002) found only seven complexes containing the 1,4-dinitrobenzene (DNB) moiety.



(I)

The structure contains mixed stacks of alternating molecules of the donor tetramethyltetrathiafulvalene (TMTTF) and acceptor DNB. Both molecules lie on (and perpendicular to) the same crystallographic twofold axis, resulting in maximum overlap between these molecules (Fig. 1). In this respect, (I) differs from the 1:1 complex (II) between unsubstituted TTF and DNB (Bryce *et al.*, 1982), where mixed stacks also exist, but the overlap between adjacent molecules is only partial. Alternatively, the motif of (I) can be described as layers, parallel to the (010) plane. Molecules in a layer are arranged in a checker-board pattern, each donor molecule surrounded by four acceptor ones, and *vice versa*.

The average interplanar separation in the stack of (I) is shorter than in (II), 3.44 Å *versus*. 3.64 Å, even making allowance for the different temperatures of these studies, 120 *versus* 295 K. Thus, linear expansion of pure DNB (di Rienzo *et al.*, 1980; Tonogaki *et al.*, 1993) in the same temperature range does not exceed 1%. However, the geometrical parameters in (I) give no indication of CT. Comparison of the TMTTF molecules in (I) and in the crystal of pure TMTTF (Batsanov *et al.*, 2001) shows marginal (4 e.s.d.) differences in the C1=C1′ bond lengths [1.344 (3) *versus* 1.358 (2) Å], while the C—S bond lengths, which give the most reliable measure of the positive charge on a TTF moiety (Clemente & Marzotto, 1996), are identical. Likewise, bond distances in the DNB moiety are essentially the same as in the structure of DNB itself (Tonogaki *et al.*, 1993). Thus (I) can be best described as a molecular complex.

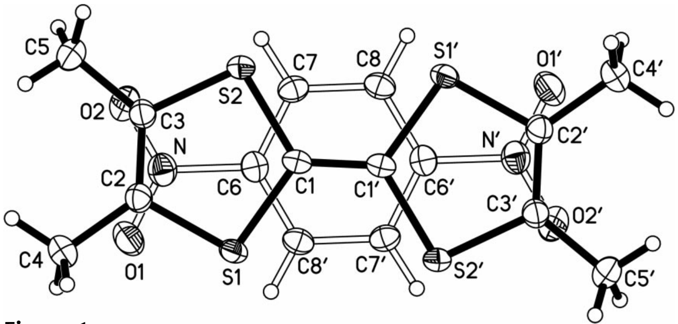


Figure 1
Tetramethyltetrathiafulvalene and 1,4-dinitrobenzene molecules in (I), viewed in a projection on the (010) plane. Displacement ellipsoids are drawn at the 50% probability level. Atoms which are symmetry-related *via* the twofold axis are primed.

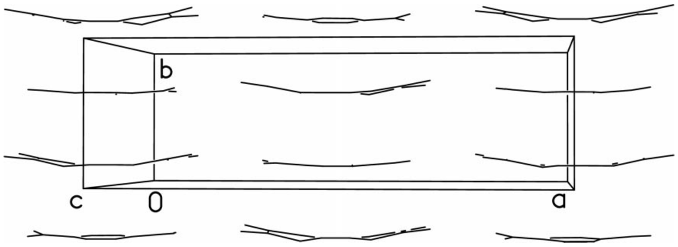


Figure 2
The stacking motif in (I).

Both the TMTTF and DNB molecules in (I) are not strictly planar, but show a boat-like distortion (note that within a stack, all molecules are concave in the same direction). The TMTTF molecule is folded along the S1···S2 and S1′···S2′ vectors by 11.63 (4)°. It is also twisted by 2.78 (1)° around the central C1═C1′ bond. In the DNB molecule, the benzene ring is folded along the C7···C8′ and C7′···C8 vectors by 1.64 (1)°, while the nitro-group plane C6/N/O1/O2 is inclined to the C7/C6/C8′ plane by 4.22 (4)°. In the structures of pure components (see above), the DNB molecule is practically planar, and the TMTTF molecule is folded (by 6.5°) along the S···S vectors in a chair-like fashion.

Experimental

Tetramethyltetrathiafulvalene TMTTF (3.5 mg, 0.013 mmol) was dissolved in hot chloroform (2 ml) and DNB (2.3 mg, 0.013 mmol) was added. The mixture was stirred until fully dissolved and the solution was left to stand in a jar at room temperature, allowing very slow evaporation of the solvent for several days, resulting in dark green crystals of (I). The same complex was obtained when benzene was used as solvent, whereas from acetonitrile or dioxane the crystals of the original TMTTF appeared first from the solution, perhaps due to a solubility effect.

Crystal data

$C_{10}H_{12}S_4 \cdot C_6H_4N_2O_4$
$M_r = 428.55$
Monoclinic, $C2/c$
$a = 22.184\ (3)$ Å
$b = 6.871\ (1)$ Å
$c = 12.063\ (1)$ Å
$\beta = 94.39\ (1)°$
$V = 1833.3\ (4)$ Å^3
$Z = 4$

$D_x = 1.553$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 969 reflections
$\theta = 12.0$–$28.4°$
$\mu = 0.54$ mm^{-1}
$T = 120\ (2)$ K
Trapezoid, black
$0.55 \times 0.31 \times 0.16$ mm

Data collection

SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: by integration [*SHELXTL* (*XPREP*); Bruker, 1998]
$T_{\min} = 0.755$, $T_{\max} = 0.919$
6260 measured reflections

2096 independent reflections
1904 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\max} = 27.5°$
$h = -26 \rightarrow 28$
$k = -5 \rightarrow 8$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.079$
$S = 1.15$
2096 reflections
150 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0316P)^2 + 2.5429P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.7579 (15)	C1—C1$^{\rm i}$	1.344 (3)
S1—C2	1.7638 (17)	C2—C3	1.348 (2)
S2—C1	1.7560 (16)	C2—C4	1.496 (2)
S2—C3	1.7632 (16)	C3—C5	1.498 (2)
O1—N	1.229 (2)	C6—C8$^{\rm i}$	1.384 (2)
O2—N	1.225 (2)	C6—C7	1.388 (2)
N—C6	1.478 (2)	C7—C8	1.385 (2)
C1—S1—C2	95.59 (7)	C4—C2—S1	115.83 (12)
C1—S2—C3	95.40 (7)	C2—C3—C5	127.03 (15)
O2—N—O1	124.15 (15)	C2—C3—S2	117.20 (13)
O2—N—C6	117.96 (14)	C5—C3—S2	115.74 (12)
O1—N—C6	117.87 (14)	C8$^{\rm i}$—C6—C7	123.33 (15)
C1$^{\rm i}$—C1—S2	123.33 (16)	C8$^{\rm i}$—C6—N	118.42 (14)
C1$^{\rm i}$—C1—S1	122.70 (16)	C7—C6—N	118.18 (15)
S2—C1—S1	113.96 (9)	C8—C7—C6	118.46 (15)
C3—C2—C4	127.42 (16)	C6$^{\rm i}$—C8—C7	118.18 (15)
C3—C2—S1	116.70 (12)		

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

All H atoms were refined in isotropic approximation; bond lengths C—H 0.92 (2)–0.98 (3) Å.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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