

2,2'-[2,3-Dihydro-2-(prop-2-enyl)-1*H*-isoindole-1,3-diylidene]bis(propanedinitrile)–tetrathiafulvalene (1/1), TCPI–TTF<sup>1</sup>

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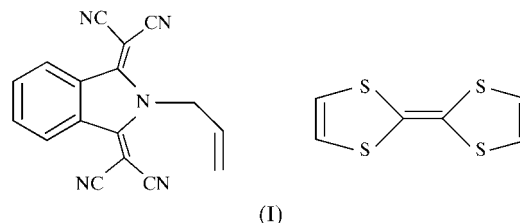
The title complex,  $C_{17}H_9N_5 \cdot C_6H_4S_4$ , contains  $\pi$ -deficient bis(dinitrile) and TTF molecules stacked alternately in columns along the *a*-axis direction; the interplanar angle between the TTF molecule and the isoindolyl  $C_4N[C(CN)_2]_2$  moiety is  $1.21(4)^\circ$ . The *N*-allyl moiety in the TCPI molecule is oriented at an angle of  $87.10(10)^\circ$  with respect to the five-membered  $C_4N$  ring, and the four  $C\equiv N$  bond lengths range from  $1.134(3)$  to  $1.142(3)$  Å, with  $C-C\equiv N$  angles in the range  $174.3(3)$ – $176.9(2)^\circ$ . In the TTF system, the  $S-C$  bond lengths are  $1.726(3)$ – $1.740(3)$  and  $1.751(2)$ – $1.763(2)$  Å for the external  $S-C(H)$  and internal  $S-C(S)$  bonds, respectively.

## Comment

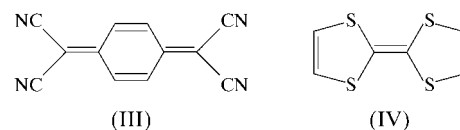
Organic conductors are currently an important research area in materials science (Martin *et al.*, 1997; Yamashita & Tomura, 1998; Bryce, 2000), of which the organic metal system TTF–TCNQ is exemplary (TCNQ is tetracyanoquinodimethane). Such complexes can be divided into (i) donor–acceptor (*D–A*) systems derived from closed-shell electron donor and acceptor organic molecules and (ii) radical salts comprising a radical ion of an organic donor or acceptor molecule and a closed-shell counter-ion. Our interest is in the former type of *D–A* complexes and in the interaction of  $\pi$ -deficient and  $\pi$ -excessive materials in 1:1 complexes, *e.g.* TCNQ–TTF, with the purpose of studying weak interactions. We report herein the crystal structure of 2,2'-[2,3-dihydro-2-(prop-2-enyl)-1*H*-isoindole-1,3-diylidene]bis(propanedinitrile)–tetrathiafulvalene (1/1), TCPI–TTF, (I) (Fig. 1).

The bond lengths and angles in the heterocyclic ring of TCPI are similar to those reported in the molecular structure of 2,2'-(cinnamylisoindoline-1,3-diylidene)bis(propanedinitrile), (II) (Crean *et al.*, 2001). As TCPI analogues are rare, an

analysis of TCNQ molecules, (III), for comparison purposes was undertaken using the April 2001 ConQuest 1.2 version of the Cambridge Structural Database (CSD; Allen & Kennard, 1993). In TCNQ systems (280 examples, 401 hits), the mean exocyclic  $Csp^2=Csp^2$  and  $Csp^2-Csp$  bond lengths are  $1.394$  (range  $1.33$ – $1.45$  Å) and  $1.425$  Å (range  $1.36$ – $1.55$  Å), respectively (full details deposited). In (I), the exocyclic indolyl ring  $C=C$  bond lengths  $C4=C6A$  and  $C5=C6B$



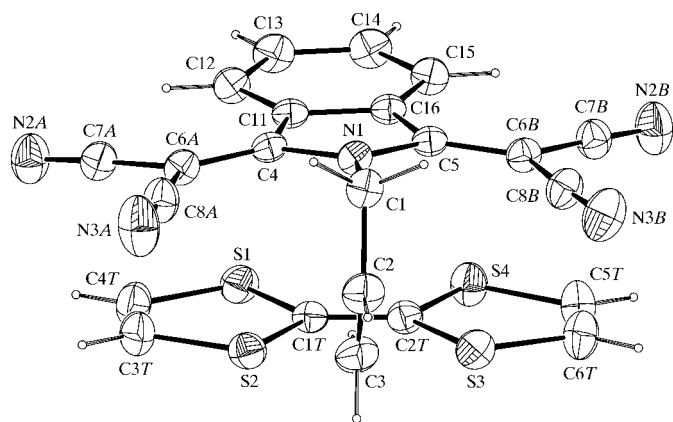
are  $1.372(3)$  and  $1.374(3)$  Å, respectively, and longer than typical double bonds; the  $C6A-C7A/C6A-C8A$  and  $C6B-C7B/C6B-C8B$  bond lengths are in the range  $1.430(3)$ – $1.440(3)$  Å and similar to those reported for (II) (Crean *et al.*, 2001) and found in the CSD (Allen & Kennard, 1993). The four nitrile  $C\equiv N$  values range from  $1.134(3)$  to  $1.142(3)$  Å and are comparable with the average literature  $C\equiv N$  length of  $1.144(8)$  Å (Orpen *et al.*, 1994). The angles which the  $C(C\equiv N)_2$  groups make with the  $C_4N$  ring are  $7.56(10)$  ( $C6A$ ) and  $6.57(10)^\circ$  ( $C6B$ ), demonstrating a small twist from coplanarity about the  $C4-C6A/C5-C6B$  bonds, and are similar to the values of  $7.01(10)$  and  $2.33(10)^\circ$  in (II). The *N*-allyl moiety is oriented at an angle of  $87.10(10)^\circ$  to the  $C_4N$  heterocyclic ring, with bond lengths along the  $N1-C1-C2=C3$  group of  $1.471(2)$ ,  $1.496(3)$  and  $1.296(3)$  Å, which are analogous to the values of  $1.469(2)$ ,  $1.495(2)$  and  $1.319(2)$  Å in (II) (Crean *et al.*, 2001); the  $C=C$  bond length is shorter in (I). A search for  $N-CH_2-CH=CH_2$  systems in the CSD (Allen & Kennard, 1993) with the terminal  $C=C$  atoms limited to three-coordination, yielded 109 examples (151 hits) and gave mean bond lengths of  $1.476$ ,  $1.480$  and  $1.275$  Å, and angles of  $112.9$  and  $126.6^\circ$  along the chain.



The  $S-C$  bond lengths in the TTF molecule of (I) are in the range  $1.726(3)$ – $1.740(3)$  Å for the external  $S-C(H)$  and  $1.751(2)$ – $1.763(2)$  Å for the internal  $S-C(S)$  bonds. The mean CSD value is  $1.735$  Å for TTF systems, (IV) (91 entries, 164 examples), for all of the *exo/endo-C–S* bond lengths. The  $C=C$  bond lengths of  $1.344(3)$  and  $1.314(4)/1.325(4)$  Å (*exo*) are shorter than the CSD values of  $1.37$  and  $1.34$  Å. This suggests that the TTF and TCPI molecules experience little perturbation on forming the TCPI–TTF 1:1 complex.

The hydrogen-bonding in (I) is dominated by intramolecular  $C-H \cdots N$  interactions and close contacts (details are given in Table 2). This results in angles at  $C6A$  and  $C6B$  of  $121.10(17)/127.01(18)$  and  $120.75(18)/127.29(19)^\circ$ , respectively; the smaller angle reflects the favourable effect of the

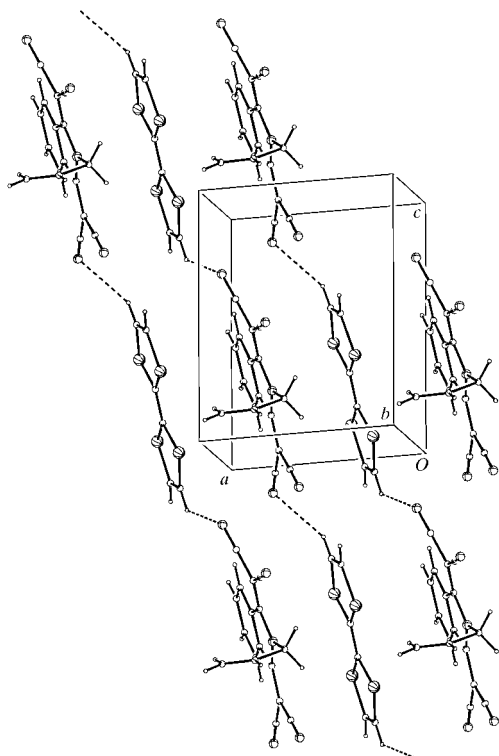
<sup>1</sup> TCPI and TTF are abbreviations for 2,2'-(allylisoindolin-1,3-diylidene)bis(propanedinitrile) and tetrathiafulvalene, respectively.



**Figure 1**

A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

intramolecular  $C12-H12 \cdots C7A \equiv N2A$  and  $C15-H15 \cdots C7B \equiv N2A$  interactions in the TCPI system. This difference is also present in (II), with an average difference of  $7^\circ$  between the two  $Csp^2=Csp^2-Csp$  angles. TTF and the TCPI isoindolinyl moiety  $C_4N[C(CN)_2]_2$  are essentially coplanar [ $1.21(4)^\circ$ ] and stack in an alternate fashion along the  $a$ -axis direction, with a mean interplanar spacing between the ligands of  $ca$  3.5 Å. Columns of  $[TCPI-TTF]_n$  molecules are linked by two weak (TTF) $C-H \cdots N$  interactions (Table 2). A close  $N3A \cdots S2^{iii}$  contact is also present [symmetry code: (iii)  $-x, 1-y, 1-z$ ].



**Figure 2**

A view of the interactions and packing in the crystal structure of (I).

A CSD search using ConQuest (Version 1.2; Allen & Kennard, 1993) for molecular systems containing the TTF group and bis(propanedinitrile) ligands revealed several related structures, including 2,5-bis(dicyanomethylene)-thieno[3,4-*b*]pyrazine-TTF (1/1) (CSD refcode PUMVOI; Suzuki *et al.*, 1998), bis(tetracyano-3,5-diimino-3,5-dihydropyrrolizinide-*N,N'*)nickel(II)-TTF-THF (1/1/2) (SOLGUV; Bonamico *et al.*, 1991) and pentakis[bis(ethylenedioxy)TTF]-tris(dicyanomethylene)cyclopropanoide acetonitrile solvate (TOKXUM; Horiuchi *et al.*, 1996).

## Experimental

For the synthesis of TCPI, diisopropylazodicarboxylate (0.37 g, 1.9 mmol) and triphenylphosphine (0.49 g, 1.9 mmol) were shaken together in tetrahydrofuran (40 ml) for 30 s. Allyl alcohol (0.2 g, 3.4 mmol) was added and the mixture was allowed to stand for 2 min, then 2-(3-dicyanomethylene-2,3-dihydroisoindol-1-ylidene)malononitrile (0.50 g, 2.1 mmol) was added. The reaction mixture was sealed under argon and allowed to stand at ambient temperature for one week. The solvent was removed and the residue subjected to chromatography. TCPI was isolated as a green solid (m.p. 240–242 K). Analysis for  $C_{17}H_9N_5$ , calculated: C 72.08, H 3.20, N 24.72%; found: C 71.83, H 3.28, N 24.60%. IR (KBr,  $cm^{-1}$ ): 3106, 2222, 1560, 1459, 1332, 1222, 1162, 1111, 783. UV-vis [ $CH_3CN$ ,  $\lambda_{max}$  nm ( $\epsilon$ ): 414 (35589), 391 (35522), 291 (9394), 279 (10303), 269 (10202), 243 (19966)].  $^1H$  NMR (400 MHz,  $\delta$ ,  $CDCl_3$ ), 8.74 (*m*, 2H, aromatic), 7.85 (*m*, 2H, aromatic), 6.05 (*m*, 1H), 5.50 (*d*,  $J = 10.4$  Hz, 1H), 5.35 (*s*, 2H), 5.05 (*d*,  $J = 17.2$  Hz, 1H).  $^{13}C$  NMR ( $\delta$ , DMSO): 157.81 [ $C=C(CN)_2$ ], 135.04, 132.60, 125.30 (aromatic C), 114.52, 113.27 (CN), 60.60 [ $C=C(CN)_2$ ], 131.30, 116.69, 48.78 (*N*-allyl).

For the synthesis of the TCPI-TTF complex, TCPI (0.05 g, 0.2 mmol) and TTF were added to acetonitrile (15.0 ml). The mixture was heated under reflux until all the solid material had dissolved. The resulting green solution was allowed to cool to ambient temperature and the TCPI-TTF (1/1) complex crystallized from solution as dark-green needles. The needles were isolated by filtration and recrystallized from acetonitrile to give black-green needles (0.04 g, 41.0%; m.p. 169–172 K). Analysis for  $C_{17}H_9N_5 \cdot C_6H_4S_4$ , calculated: C 56.65, H 2.69, N 14.36, S 26.30%; found: C 56.61, H 2.62, N 14.24, S 25.11%. IR (KBr,  $cm^{-1}$ ): 2218, 1551, 1472, 1327, 1145, 975, 651.

## Crystal data

$C_{17}H_9N_5 \cdot C_6H_4S_4$   
 $M_r = 487.62$   
 Monoclinic,  $P2_1/c$   
 $a = 7.3982(11)$  Å  
 $b = 31.854(5)$  Å  
 $c = 9.516(2)$  Å  
 $\beta = 94.608(17)^\circ$   
 $V = 2235.3(7)$  Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.449$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 5.5$ – $19.9^\circ$   
 $\mu = 0.45$  mm<sup>-1</sup>  
 $T = 294(1)$  K  
 Needle, black-green  
 0.50 × 0.50 × 0.35 mm

## Data collection

Bruker AXS P4 diffractometer  
 $\omega$  scans  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{min} = 0.806$ ,  $T_{max} = 0.860$   
 5764 measured reflections  
 5366 independent reflections  
 4247 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.018$   
 $\theta_{max} = 28.0^\circ$   
 $h = -1 \rightarrow 9$   
 $k = -42 \rightarrow 1$   
 $l = -12 \rightarrow 12$   
 3 standard reflections every 296 reflections  
 intensity decay: 1%

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.121$   
 $S = 1.09$   
 5366 reflections  
 289 parameters  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 0.6527P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.71 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.38 \text{ e } \text{\AA}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

S1—C1T	1.751 (2)	C1T—C2T	1.344 (3)
S1—C4T	1.740 (3)	C3T—C4T	1.314 (4)
S2—C1T	1.763 (2)	C5T—C6T	1.325 (4)
S2—C3T	1.733 (3)	N1—C1	1.471 (2)
S3—C2T	1.760 (2)	N1—C4	1.385 (2)
S3—C6T	1.731 (3)	N1—C5	1.382 (2)
S4—C2T	1.761 (2)	C1—C2	1.496 (3)
S4—C5T	1.726 (3)	C2—C3	1.296 (3)
N1—C1—C2	112.65 (17)	C1—C2—C3	126.6 (2)

**Table 2**

Hydrogen-bond parameters and contact geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C12—H12 $\cdots$ N2A	0.93	2.60	3.391 (3)	143
C12—H12 $\cdots$ C7A	0.93	2.47	3.027 (3)	118
C15—H15 $\cdots$ N2B	0.93	2.61	3.399 (3)	144
C15—H15 $\cdots$ C7B	0.93	2.47	3.020 (3)	118
C4T—H4T $\cdots$ N2B <sup>i</sup>	0.93	2.63	3.479 (3)	152
C6T—H6T $\cdots$ N2A <sup>ii</sup>	0.93	2.63	3.273 (3)	127

Symmetry codes: (i)  $1+x, y, 1+z$ ; (ii)  $x, y, z-1$ .

The title compound crystallized in the monoclinic system; space group  $P2_1/c$  was assumed from the systematic absences and confirmed by the analysis. All H atoms were allowed for as riding atoms, with C—H distances in the range 0.93–0.97  $\text{\AA}$ , using *SHELXL97* (Sheldrick, 1997) defaults.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *PLATON* (Spek, 1998); software used to prepare material for publication: *SHELXL97* and *WordPerfect* macro *PREP8* (Ferguson, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1518). Services for accessing these data are described at the back of the journal.

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