organic compounds

A third polymorph of 4-(2,6-difluorophenyl)-1,2,3,5-dithiadiazolyl

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The crystal structure of a third polymorphic form of the known 4-(2,6-difluorophenyl)-1,2,3,5-dithiadiazolyl radical, $C_7H_3F_2N_2S_2$, is reported. This new polymorph represents a unique crystal-packing motif never before observed for 1,2,3,5-dithiadiazolyl (DTDA) radicals. In the two known polymorphic forms of the title compound, all of the molecules form *cis*-cofacial dimers, such that two molecules are π-stacked with like atoms one on top of the other, a common arrangement for DTDA species. By contrast, the third polymorph, reported herein, contains two crystallographically unique molecules organized such that only 50% are dimerized, while the other 50% remain monomeric radicals. The dimerized molecules are arranged in the *trans*-antarafacial mode. This less common dimer motif for DTDA species is characterized by π–π interactions between the S atoms [S···S = 3.208 (1) Å at 110 K], such that the two molecules of the dimer are related by a centre of inversion. The most remarkable aspect of this third polymorph is that the DTDA dimers are co-packed with monomers. The monomeric radicals are arranged in one-dimensional chains directed by close lateral intermolecular contacts between the two S atoms of one DTDA heterocycle and an N atom of a neighbouring coplanar DTDA heterocycle [S···N = 2.857 (2) and 3.147 (2) Å at 110 K].

Comment

Stable thiazyl radicals continue to be studied, due to interest in their conductivity (Leitch *et al.*, 2009), bistability (Brusso *et al.*, 2004) and magnetic properties (Robertson *et al.*, 2007) in the solid state. These properties are all a function of intermolecular interactions, and so crystal packing remains at the forefront of research in this field. Fluorinated aryl substituents of 1,2,3,5-dithiadiazolyl (DTDA) radicals have been of particular interest since the discovery of spin-canted antiferromagnetism below *ca* 36 K in the β-phase of 4-(4-cyanotetrafluorophenyl)-DTDA (Banister *et al.*, 1996). A series of difluorophenyl-DTDA radicals was reported by the same

group, including the title compound, (I), 4-(2,6-difluorophenyl)-DTDA (Banister *et al.*, 1997). That preliminary report documented the formation of *cis*-cofacial dimers of (I) in the solid state in the monoclinic α form, (I*a*). This is the same dimerization mode that is observed for the parent 4-phenyl-1,2,3,5-dithiadiazolyl radical [Vegas *et al.*, 1980; Cambridge Structural Database (Allen, 2002) refcode PHTHAZ]. The crystallographic data for (I*a*) were published very recently, along with data for a second polymorph, the tetragonal β form, (I*b*) (Clarke *et al.*, 2010). The *cis*-cofacial dimers of (I) persist in (I*b*). We have now reinvestigated (I) and discovered a third polymorphic form, the monoclinic γ form, (I*c*), which is unique among known DTDA species, and we report its crystal structure here.

(I)
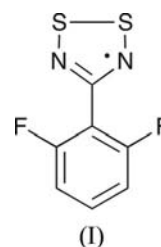
The two crystallographically unique molecules of (I*c*) (molecules 1 and 2) are shown in Fig. 1. Polymorph (I*c*) crystallizes as dark-purple blocks under static vacuum sublimation at 354 K and *ca* 10^{-3} Torr (1 Torr = 133.322 Pa). It is worth noting that (I*c*) has a similar habit to that of (I*a*), and that we have recovered crystals of both (I*a*) and (I*b*) under similar sublimation conditions used to grow crystals of (I*c*). Given that both (I*a*) and (I*c*) are monoclinic, and that our data for (I*c*) were collected at a lower temperature than those reported in the literature for (I*a*), we have collected unit-cell data for (I*a*) at both 150 and 110 K, verifying that it is not a high-temperature phase of (I*c*).

Polymorph (I*c*) shows a unique molecular arrangement for DTDA compounds. Only 50% of the molecules are dimerized
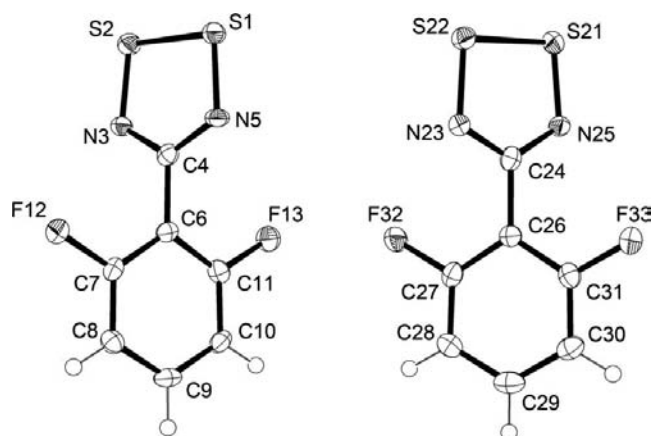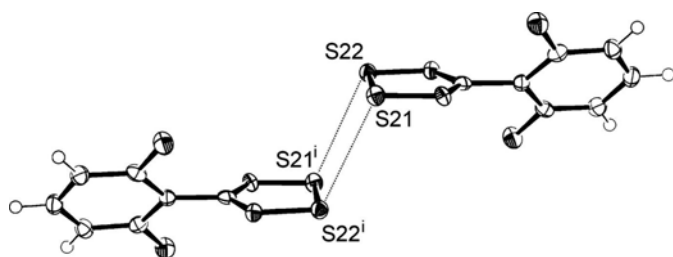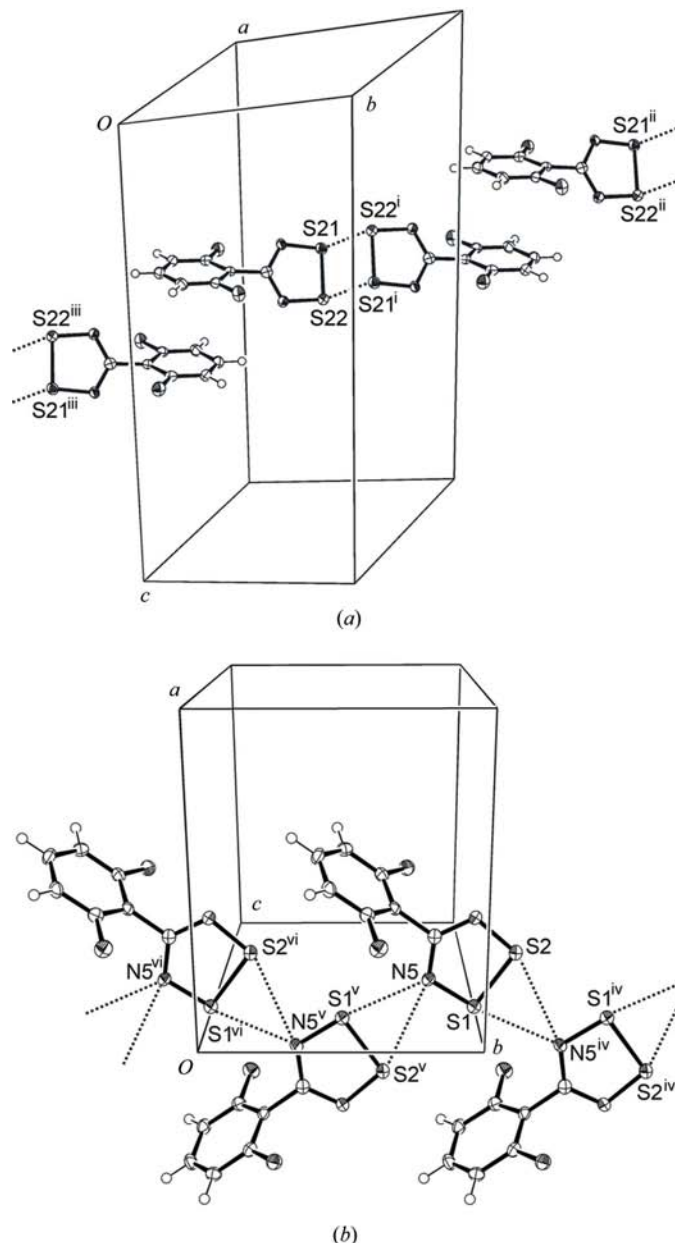

Figure 1
The crystal structures of the two molecules in the asymmetric unit of (I*c*), showing the atom-numbering scheme; the molecules are not shown in their relative positions in the structure. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Monomeric molecule 1 (left) is labelled S1, S2, N3, *etc.*, and dimerized molecule 2 (right) is labelled S21, S22, N23, *etc.*

Figure 2
The *trans*-antarafacial mode of dimerization observed for molecule 2, *i.e.*
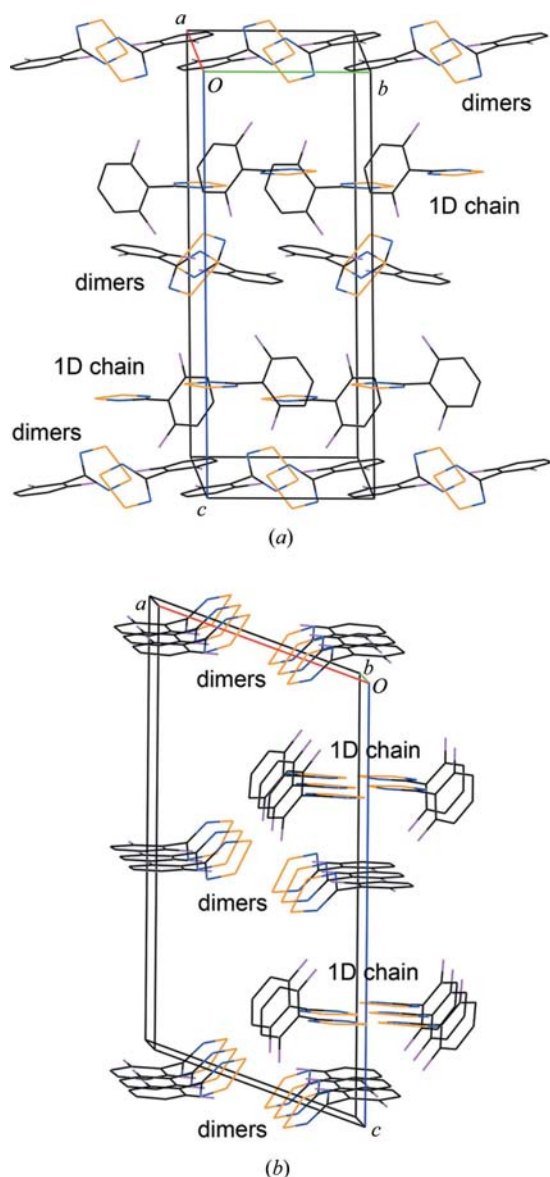50% of the molecules in (I*c*). [Symmetry code: (i) $1 - x, 2 - y, 1 - z$.]

Figure 3
In polymorph (I*c*), (*a*) the molecule 2 dimers pack along [110], with π–π
stacking of aryl moieties, and (*b*) the molecule 1 monomers pack in one-
dimensional chains along [010], with coplanar DTDA rings, directed by
intermolecular S···N contacts. [Symmetry codes: (i) $1 - x, 2 - y, 1 - z$;
(ii) $1 + x, 1 + y, z$; (iii) $-x, 1 - y, 1 - z$; (iv) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (v) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (vi) $x, y - 1, z$.]

(molecule 2). The *trans*-antarafacial π–π dimers present in
(I*c*), shown in Fig. 2, exhibit intermolecular S···S contacts
(Table 1) that are slightly longer than the typical range of 2.9–
3.1 Å for this dimerization mode (Cordes *et al.*, 1992). The two
molecules of a dimer are related by a centre of inversion, so
the mean angle between the planes of the DTDA rings is
necessarily zero. The mean distance between planes is
2.918 (2) Å, which is significantly less than the distance
between planes in graphite (Nelson & Riley, 1945) and is in
keeping with the prevailing consensus that these dimers
provide an example of four-centred two-electron bonding
(Harcourt, 1991).

Interestingly, an intermolecular antara-cofacial π–π
stacking of the aryl rings assists in the co-packing of the dimers
in (I*c*) along [110], shown in Fig. 3(*a*); the distance between the
mean planes of the aryl rings is 3.392 (4) Å. The formation of
π–π dimers *via* close intermolecular S···S contacts is a
common feature in crystal structures of DTDA radicals and is
known to occur in a variety of geometries (Rawson *et al.*,
1995), including those observed in all three polymorphs of (I).

The remaining molecules (50%) in polymorph (I*c*) remain
as monomeric radicals (molecule 1) and are organized in
linear arrays, or one-dimensional chains propagating along
[010], such that the DTDA rings of neighbouring molecules
are roughly coplanar [angle of 1.21 (14)° between the mean
planes of neighbouring DTDA rings], as shown in Fig. 3(*b*).
Intermolecular electrostatic $S^{\delta+}···N^{\delta-}$ interactions create
close lateral contacts that direct this packing arrangement
(Table 1). This also results in relatively close lateral S···S
contacts (Table 1). These one-dimensional chains of neutral
radicals are isolated from one another by linear arrays of the
dimers. A segment of the crystal structure illustrating this
relationship is shown from two different perspectives in Fig. 4.
The most significant contact directing the co-packing of the
dimers with the one-dimensional chains of monomers appears
to be the close intermolecular $S^{\delta+}···F^{\delta-}$ distances between an
F atom of molecule 1 and the two S atoms of a neighbouring
molecule 2 (Table 1). This interaction is expanded and
presented in Fig. 5. The influence of electrostatic interactions
in the crystal-packing arrangements of DTDA species has
been noted elsewhere (Rawson & Palacio, 2001). These typi-
cally occur between the partially positively charged S atoms
and atoms with partial negative charge, including the ring N
atoms and pendant atoms on the aryl ring or other groups.

The co-packing of monomers and dimers in (I*c*) gives a rare
opportunity to compare the molecular structures of dimerized
and monomeric DTDA species that are chemically identical
and that are under identical externally applied conditions. In
particular, the mean S—S bond length in the DTDA ring has
been a measure of interest (Banister *et al.*, 1990). The singly
occupied molecular orbital (SOMO) of the neutral DTDA
radical is a π* orbital delocalized over the S and N atoms of
the heterocycle. Therefore, lengthening of the S—S bond can
be used as an indication of increased occupation of this mol-
ecular orbital. In (I*c*), the S—S bond of molecule 1 is slightly
shorter than that of molecule 2 (Table 1). However, assump-
tions regarding the electronic implications of this small

Figure 4
In order to illustrate the packing of the dimers, together with the one-dimensional chains of monomers, a section of (I*c*) is shown from two different perspectives, *viz.* (*a*) down the *a* axis and (*b*) down the *b* axis.

difficult to predict, although the norm is the formation of π–π dimers. For (I), the intermolecular interactions appear to include weak electrostatic forces competing with the four-centred two-electron S—S bonding interactions that generate *trans*-antarafacial and *cis*-cofacial π–π dimers. Other factors also contribute, such as the large twist angle between the aryl and DTDA ring planes, which likely results from repulsion between the exocyclic N-atom lone pairs and the F atoms at the *ortho* positions of the phenyl ring. This twisting allows for packing of the monomers into one-dimensional chains. The low melting point of (I) (<313 K under an inert atmosphere) hints at relatively small lattice energies and is reminiscent of perfluoroalkyl-substituted DTDA radicals that are liquids at temperatures below 333 K (Shuvaev *et al.*, 2008).

Dimers of DTDA radicals are generally considered to be diamagnetic and of little interest in terms of material properties. The monomers in (I*c*), however, can be expected to remain paramagnetic. The close lateral contacts between these monomeric radicals, the one-dimensional orientation of the resulting chains, and the isolation of these chains from one another by arrays of dimers, are all features unique to (I*c*). Furthermore, the sum of these features is a molecular material for which the structure suggests the possibility of strong intermolecular magnetic exchange coupling, probably antiferromagnetic in nature. We are currently attempting to isolate a pure sample of (I*c*) large enough to perform magnetic measurements and conductivity tests. This is challenging, owing in part to co-sublimation of crystals with different habits and in part to the low melting point of all three polymorphs of (I), which impedes extensive handling of the samples.
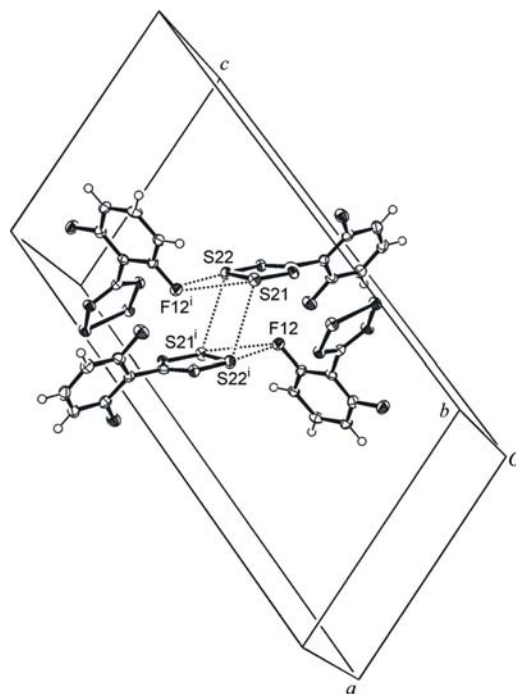
difference should be made with caution, since the S—S bonds in (I*a*) are shorter than those of molecule 1 in (I*c*), and the S—S bonds in (I*b*) are roughly the same length as those of molecule 2 in (I*c*) (Table 1).

Comparing other geometric features of the molecules in (I*a*) and (I*b*) with those in (I*c*), we find that the twist angles between the DTDA and aryl rings (Table 1) for both molecules in the asymmetric unit of (I*c*) are larger than for either molecule in the asymmetric unit of (I*a*) and for either molecule in the asymmetric unit of (I*b*). In (I*c*), the twist angle is largest in molecule 1, permitting close lateral interactions between neighbouring DTDA rings in the one-dimensional chains of monomers.

It is, perhaps, unsurprising that more than one polymorphic form of (I) can be isolated under a given set of conditions. The crystal packing of DTDA radicals in general is notoriously

Figure 5
In (I*c*), short lateral contacts between atom F12 of a monomeric molecule and atoms S21^i and S22^i of a neighbouring dimerized molecule direct the co-packing of the dimers with the one-dimensional chains of monomers. [Symmetry code: (i) $1 - x, 2 - y, 1 - z$.]

Table 1
Selected structural parameters (Å, °) for polymorphs (I*a*), (I*b*) and (I*c*).

Molecules 1 and 2 in the asymmetric unit are labelled S1, S2, N3, *etc.*, and S21, S22, N23, *etc.*, respectively. In (I*c*), molecule 1 is the monomer and molecule 2 is dimerized.

	(I*a*)		(I*b*)		(I*c*)	
Reference	Clarke *et al.* (2010)		Clarke *et al.* (2010)		This work	
Temperature	150 K		180 K		110 K	
S—S bond	Molecule 1	2.080 (3)	Molecule 1	2.0917 (7)	Molecule 1	2.0838 (10)
	Molecule 2	2.081 (3)	Molecule 2	2.0944 (7)	Molecule 2	2.0960 (11)
Twist angle between mean planes of aryl and DTDA rings	Molecule 1	48.7 (11)	Molecule 1	29.4 (3)	Molecule 1	68.5 (4)
	Molecule 2	47.7 (8)	Molecule 2	24.9 (3)	Molecule 2	52.2 (4)
Intra-dimer S···S contact distance	S11···S21	3.069 (3)	S11···S21	3.2167 (7)	S21···S22$^{\mathrm{i}}$	3.208 (1)
	S12···S22	3.129 (3)	S12···S22	3.0692 (8)		
Angle between mean planes of DTDA rings in a dimer		18.1 (8)		6.4 (6)		0.00 (0)
Lateral intermolecular contacts defining one-dimensional chains	n/a	n/a	n/a	n/a	S1···N5$^{\mathrm{iv}}$	2.857 (2)
					S2···N5$^{\mathrm{iv}}$	3.147 (2)
					S2···S1$^{\mathrm{iv}}$	3.392 (4)
Intermolecular contacts between dimers and one-dimensional chains	n/a	n/a	n/a	n/a	F12···S21$^{\mathrm{i}}$	2.973 (3)
					F12···S22$^{\mathrm{i}}$	2.948 (3)

Symmetry codes: (i) $1-x, 2-y, 1-z$; (iv) $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Experimental

The synthesis of (I) was achieved following standard procedures for the preparation of DTDA radicals (Boeré *et al.*, 1987; Del Bel Belluz *et al.*, 1989). Large purple–black block- and plate-shaped crystals of polymorph (I*a*) were grown by sublimation at 323 K under a static vacuum of 10^{-2} Torr over several days, green–bronze needles and blocks of (I*b*) were grown by sublimation at 308 K under a static vacuum of 10^{-2} Torr within 24 h, and blue–red block-shaped crystals of (I*c*) were grown by sublimation at 354 K under a static vacuum of 10^{-3} Torr over several days.

Crystal data

$C_7H_3F_2N_2S_2$	$V = 1600.32\ (12)$ Å^3
$M_r = 217.23$	$Z = 8$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.3839\ (5)$ Å	$\mu = 0.64$ mm^{-1}
$b = 7.9745\ (3)$ Å	$T = 110$ K
$c = 20.5463\ (8)$ Å	$0.40 \times 0.11 \times 0.05$ mm
$\beta = 109.846\ (2)°$	

Data collection

Nonius KappaCCD diffractometer	141999 measured reflections
Absorption correction: multi-scan	2831 independent reflections
(*DENZO-SMN*; Otwinowski &	2045 reflections with $I > 2\sigma(I)$
Minor, 1997)	$R_{\mathrm{int}} = 0.085$
$T_{\min} = 0.783, T_{\max} = 0.969$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	235 parameters
$wR(F^2) = 0.092$	H-atom parameters constrained
$S = 0.99$	$\Delta\rho_{\max} = 0.32$ e Å^{-3}
2831 reflections	$\Delta\rho_{\min} = -0.49$ e Å^{-3}

H atoms were positioned geometrically and refined using a riding model, with C—H = 0.95 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Version 2.02; Farrugia, 1997), *POV-Ray for Windows* (Cason, 2003)

and *Mercury* (Version 2.3; Macrae *et al.*, 2006); software used to prepare material for publication: *PLATON* (Spek, 2009) and *SHELXTL/PC* (Sheldrick, 2008).

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