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(*E*)-3-(4-Methylphenyl)-2-(2-thienyl)-acrylonitrile has *Z*′ = 0.75 in the space group *C*2/*m*: fourfold disordered molecules lie in channels enclosed by fully ordered molecules

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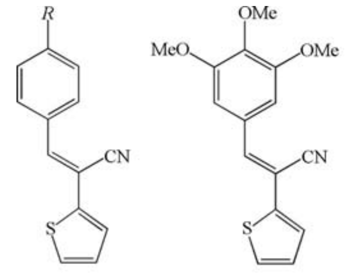
The title compound, $C_{14}H_{11}NS$, crystallizes with $Z' = 0.75$ in the space group *C*2/*m*. Two independent molecules are present, one of which lies with all the non-H atoms on a mirror plane, while the other is fourfold disordered across a site of 2/*m* symmetry. The ordered molecules are stacked such that they enclose continuous channels running along twofold rotation axes, and the disordered molecules are positioned within these channels.

Comment

We report here the structure of the title compound, (I) (Fig. 1). Although related pairs of compounds containing, respectively, Me and Cl substituents, such as (I) and (II), are not infrequently isomorphous, the crystal structure of (I) shows some significant differences from the pair of analogues (II) (Cobo *et al.*, 2005) and (III) (Cobo, Quiroga *et al.*, 2006), which are isomorphous and isostructural with one another.



(I) *R* = Me
(II) *R* = Cl
(III) *R* = Br
(IV)
(V) *R* = Me
(VI) *R* = H

While the isomorphous pair of compounds (II) and (III) both crystallize with $Z' = 1$ in the common space group $P2_1/n$, compound (I) crystallizes in the rather uncommon space group *C*2/*m* with $Z' = 0.75$. There are two independent molecules of (I) in the unit cell. For molecule 1 containing atom S1 (Fig. 1*a*), all of the non-H atoms lie on a mirror plane, selected

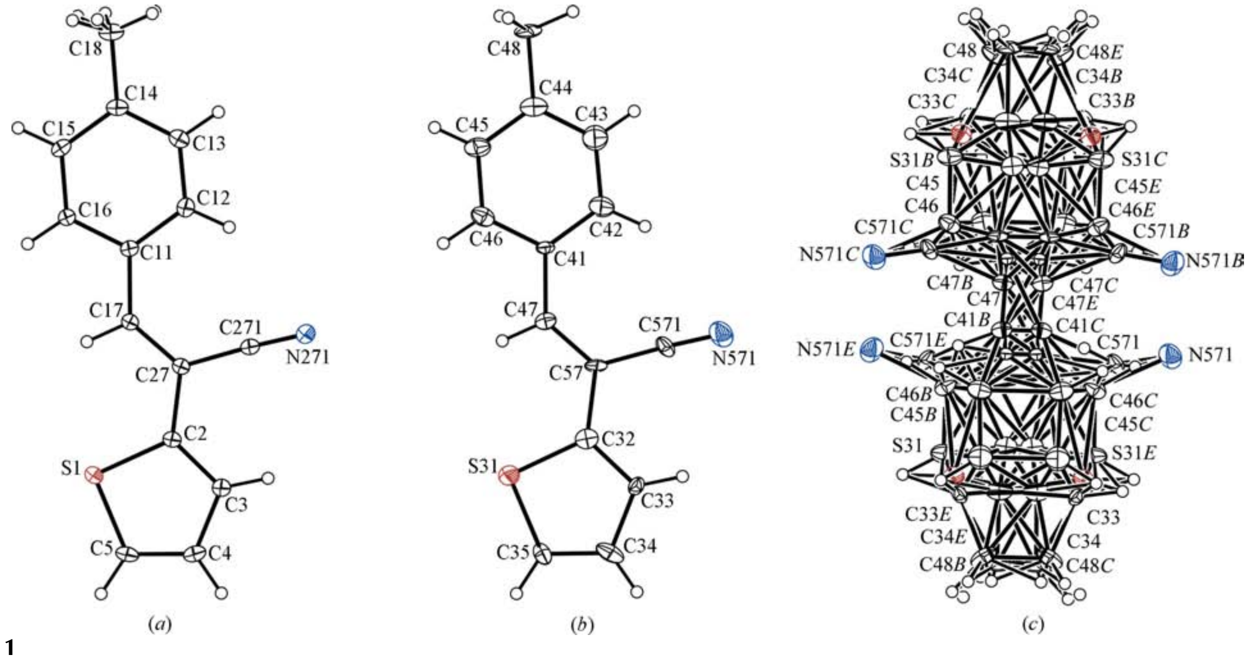


Figure 1
The independent molecular components of (I), with the atom-labelling schemes, showing (*a*) molecule 1, (*b*) a single orientation of molecule 2, and (*c*) the four orientations of molecule 2 across a site of 2/*m* symmetry at $(0, 0, \frac{1}{2})$, where the symmetry positions denoted by the suffixes *B*, *C* and *E* are $(-x, y, -z + 1)$, $(-x, -y, -z + 1)$ and $(x, -y, z)$, respectively. In (*c*), the orientation of the molecule at (x, y, z) and the viewpoint are the same as in (*b*). Displacement ellipsoids are drawn at the 30% probability level.

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for the reference molecule 1 as that at $y = \frac{1}{2}$, so providing four molecules per unit cell. Molecule 2 containing atom S31 (Fig. 1*b*) lies across a site of $2/m$ symmetry, selected for the reference molecule 2 as that at $(0, 0, \frac{1}{2})$, so that each such molecule is disordered over four sets of atomic sites (Fig. 1*c*), and thus provides a further two molecules per unit cell. Hence, there are, overall, six molecules of (I) per unit cell, giving $Z' = 0.75$. The June 2009 release of the Cambridge Structural Database (Allen, 2002) records a total of 2477 structures in this space group, fewer than 0.8% of the total, of which only 17 have $Z' = 0.75$; of these 17 entries, coordinates have been deposited for only 14, so that a Z' value of 0.75 in the space group $C2/m$ is indeed rare for both organic and organometallic compounds.

For molecule 1 of (I), the non-H atoms are constrained to be coplanar, and the rather short intramolecular C—H⋯N contact distance (Table 2) may be a direct consequence of this. In molecule 2, the non-H atoms are planar within experimental uncertainty, although not constrained by symmetry, as shown by the key torsion angles (Table 1). There is no evidence for any orientational disorder of the 2-thienyl unit in molecule 1. By contrast, both (II) and (III) show orientational disorder of the thienyl unit, with unequal populations for the two orientations in an approximate 4:1 ratio (Cobo *et al.*, 2005; Cobo, Quiroga *et al.*, 2006). In addition, the non-H skeletons of (II) and (III) are not planar, with the aryl ring markedly displaced from the plane of the rest of the molecule in both cases; the respective C27—C17—C11—C12 torsion angles in (II) and (III) are 37.9 (3) and 38.7 (4)°. On the other hand, the molecules of (IV) (Cobo, Quiroga *et al.*, 2006) are almost planar apart from the C atom of the central methoxy group. As in compounds (II)–(IV), the nitrile units in (I) show long C—C distances and short C—N distances (Table 1), but otherwise the bond distances in (I) show no unexpected features.

The molecules in each of (II) and (III) are linked into simple *C*(5) (Bernstein *et al.*, 1995) chains by a single C—H⋯N hydrogen bond, while the structure of (IV) shows no direction-specific intermolecular interactions of any kind, but in (I) the molecular aggregation is quite complex. Type 1 molecules related by a twofold rotation axis form pairs of short C—H⋯N contacts in an $R_2^2(12)$ motif (Table 2), although these contacts are probably too long to be regarded as genuine hydrogen bonds. There are no other direction-specific interactions between the type 1 molecules, but nonetheless, these molecules are arranged such that they enclose channels running parallel to [010] (Fig. 2). The channels lie along the twofold rotation axes at $z = \frac{1}{2}$, and they are approximately rectangular with approximate dimensions 13.3 × 3.7 Å, giving a cross-sectional area of *ca* 49.2 Å^2. The disordered type 2 molecules lie within the channels generated by the ordered type 1 molecules, such that the long axes of the type 2 molecules lie approximately along the long diameter of the channels (Fig. 3).

Isomeric with (I) is the 3-thienyl analogue (V) (Cobo, Cobo *et al.*, 2006), which crystallizes with $Z' = 1$ in $P2_1/c$ with fully ordered molecules. In both (V) and the unsubstituted analogue (VI) (Cobo, Quiroga *et al.*, 2006), pairs of molecules again form short contacts involving paired C—H⋯N interactions, leading to an $R_2^2(12)$ motif similar to that in (I), except that in (V) and (VI) the participating molecules are related by inversion, whereas in (I) they are related by rotation. Compounds (I) and (V) show very similar dimensions for this contact, but only in compound (VI) are the dimensions of the C—H⋯N interaction such that it can be regarded as a genuine hydrogen bond.

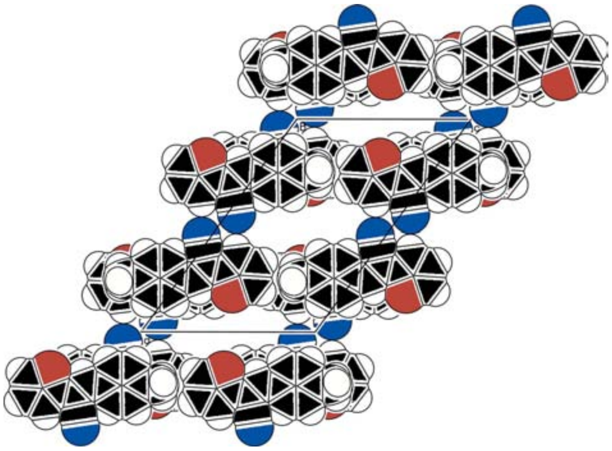

Figure 2
A space-filling projection on to (010) of part of the crystal structure of (I), showing only the ordered type 1 molecules and the channels running parallel to [010]. H atoms have been retained to emphasize the size and shape of the channels.

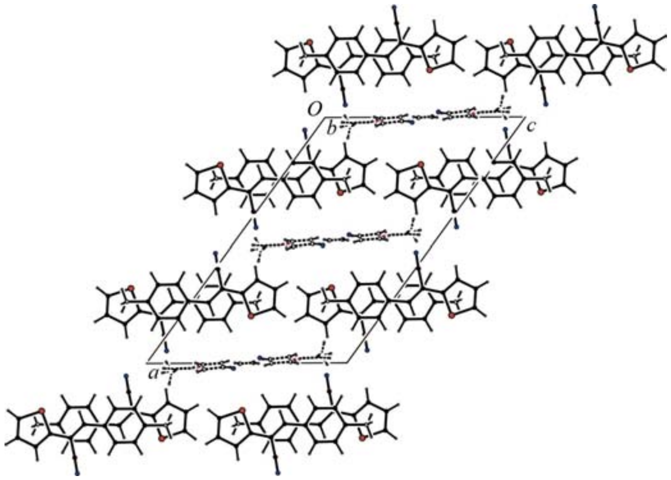

Figure 3
A projection on to (010) of part of the crystal structure of (I), showing the relative locations and orientations of the molecules of types 1 and 2. As in Fig. 2, H atoms have been retained to emphasize the spacing of the molecules.

Hence, within the closely similar series of compounds (I)–(VI), the crystallization characteristics and the supramolecular aggregation show some surprising and unexpected variations.

Experimental

A solution of 2-thiopheneacetonitrile (1 mmol) and potassium *tert*-butoxide (1 mmol) in anhydrous ethanol (3 ml) was stirred at room temperature for 15 min; a solution of 4-methylbenzaldehyde (1 mmol) in anhydrous ethanol (3 ml) was added, and the mixture was then heated under reflux for 3 h. The resulting solid product was collected by filtration, washed with ethanol, dried and finally crystallized from dimethylformamide to give yellow crystals suitable for single-crystal X-ray diffraction (yield 55%, m.p. 379–381 K). MS EI (30 eV) m/z (%): 225 (100, M^+), 210 (10), 177 (31), 176 (11), 165 (10), 152 (9), 150 (17), 105 (26) 93 (22), 89 (11), 76 (25), 65 (29), 28 (26).

Crystal data

$C_{14}H_{11}NS$
$M_r = 225.31$
Monoclinic, $C2/m$
$a = 21.4869\ (7)$ Å
$b = 7.0302\ (3)$ Å
$c = 14.1810\ (5)$ Å
$\beta = 126.173\ (2)^\circ$
$V = 1729.22\ (12)$ Å^3
$Z = 6$
Mo $K\alpha$ radiation
$\mu = 0.25$ mm^{-1}
$T = 120$ K
$0.22 \times 0.18 \times 0.16$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.943$, $T_{\max} = 0.961$
9286 measured reflections
2133 independent reflections
1956 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.132$
$S = 1.25$
2133 reflections
238 parameters
39 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C27—C271	1.436 (4)	C271—N271	1.142 (4)
S31—C32—C57—C47	4 (3)	C57—C47—C41—C42	3 (4)
C32—C57—C47—C41	−179.3 (11)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···N271$^{\rm i}$	0.95	2.75	3.689 (6)	171
C12—H12···N271	0.95	2.62	3.471 (7)	150

Symmetry code: (i) $-x, y, -z$.

It was apparent at any early stage in the structure solution that, while one of the two independent molecules (molecule 1 containing S1) is fully ordered with all of its non-H atoms lying on a mirror plane in $C2/m$, the second molecule (molecule 2, containing S31) is lying across a site of $2/m$ symmetry and is thus disordered over four sets of sites (see Fig. 1c). A structural model for molecule 2 was initially developed on geometric grounds and then refined using a substantial number of individually specified geometric restraints, with the bonded distances usually subject to s.u. values of 0.01 Å and the 1,3 nonbonded distances to s.u. values of 0.02 Å. Once this refinement model had stabilized, the individually specified restraints were all removed, and the bonded and 1,3 nonbonded distances in molecule 2 were all restrained to have the same values as the corresponding distances in molecule 1, subject in all cases to an s.u. of 0.005 Å. On this basis, satisfactory convergence was achieved, but attempts to remove these similarity restraints led to unsatisfactory behaviour of the atomic displacement parameters. The H atoms in molecule 1 were all clearly located in difference maps, but it was necessary to introduce those in molecule 2 in calculated positions; thereafter all H atoms were treated as riding atoms in geometrically idealized positions, with C—H distances of 0.98 (methyl) or 0.95 Å (all other H atoms) and $U_{\rm iso}({\rm H}) = kU_{\rm eq}({\rm C})$, where $k = 1.5$ for the methyl groups, which were permitted to rotate but not to tilt, and $k = 1.2$ for all other H atoms. Because methyl atom C18 lies on a mirror plane, the three H atoms bonded to it are disordered over two sets of sites, with each of these H-atom sites having 0.5 occupancy. The torsion angles C13—C14—C18—H18x (where x represents A, B or C) for the six sites have values of ±19, ±139 and ±101° for x = A, B and C, respectively.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3209). Services for accessing these data are described at the back of the journal.

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