

Three substituted (*E*)-3-aryl-2-(thienyl)-acrylonitriles: isolated molecules, simple hydrogen-bonded chains and hydrogen-bonded sheets

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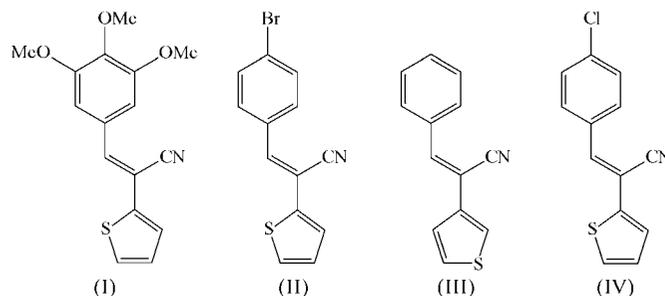
The structure of (*E*)-2-(2-thienyl)-3-(3,4,5-trimethoxyphenyl)-acrylonitrile, C₁₆H₁₅NO₃S, contains no direction-specific intermolecular interactions. The molecules of (*E*)-3-(4-bromophenyl)-2-(2-thienyl)acrylonitrile, C₁₃H₈BrNS, exhibit orientational disorder of the thienyl fragment, and the molecules are linked into simple *C*(5) chains by a single C—H···N hydrogen bond. In (*E*)-3-phenyl-2-(3-thienyl)acrylonitrile, C₁₃H₉NS, the molecules are linked into sheets by a combination of one C—H···N hydrogen bond and one C—H··· π (arene) hydrogen bond.

Comment

We report here the structures of three substituted (*E*)-3-aryl-2-(thienyl)acrylonitriles, namely (*E*)-2-(2-thienyl)-3-(3,4,5-trimethoxyphenyl)acrylonitrile, (I) (Fig. 1), (*E*)-3-(4-bromophenyl)-2-(2-thienyl)acrylonitrile, (II) (Fig. 2), and (*E*)-3-phenyl-2-(3-thienyl)acrylonitrile, (III) (Fig. 3), which have been synthesized for use as potential intermediates in the synthesis of new fused heterocyclic systems. The structure of the analogous (*E*)-3-(4-chlorophenyl)-2-(2-thienyl)acrylonitrile, (IV), was reported recently (Cobo *et al.*, 2005).

For compound (I), the key torsion angles (Table 1) show that the non-H atoms are very nearly coplanar, with the sole exception of atom C141 of the 4-methoxy group. The exocyclic angles at the methoxy substituents in (I) show the usual patterns of behaviour, with markedly different C—C—O angles for the 3- and 5-methoxy substituents, which are effectively coplanar with the aryl ring, and rather similar angles for the 4-methoxy substituent, where the methyl C atom is displaced from the plane of the aryl ring by 1.261 (2) Å.

Compound (II) is isomorphous and isostructural with the chloro analogue, *viz.* (IV) (Cobo *et al.*, 2005). In (II), there is a significant rotation of the aryl group around the



C11—C17 bond, so that this fragment is not coplanar with the rest of the molecule (Table 2). There is no obvious reason for this conformational difference between compounds (I) and (II), as the aryl ring in (II) is not involved in any hydrogen bonding. In the isostructural pair (II) and (IV), although not in compound (I), the 2-thienyl group exhibits orientational disorder over two sets of sites corresponding to a 180° rotation about the C2—C27 bond. The populations of the major and minor conformers in compounds (II) and (IV) are experimentally indistinguishable: 0.798 (3) and 0.202 (3) in (II), and 0.802 (3) and 0.198 (3) in (IV).

The molecules of compound (III) are almost planar, as shown by the key torsion angles (Table 4). In (I)–(III), the nitrile components exhibit quite long C—C bonds and very short C—N bonds. The remaining bond distances in (I)–(III) show no unusual features.

There are no direction-specific intermolecular interactions in the structure of compound (I). In particular, C—H···N, C—H···O and C—H··· π (arene) hydrogen bonds and aromatic π – π stacking interactions are all absent, so that the structure consists of effectively isolated molecules.

By contrast, the molecules of compound (II) are linked by a single C—H···N hydrogen bond (Table 3), exactly as in compound (IV). Alkene atom C17 in the molecule at (*x*, *y*, *z*)

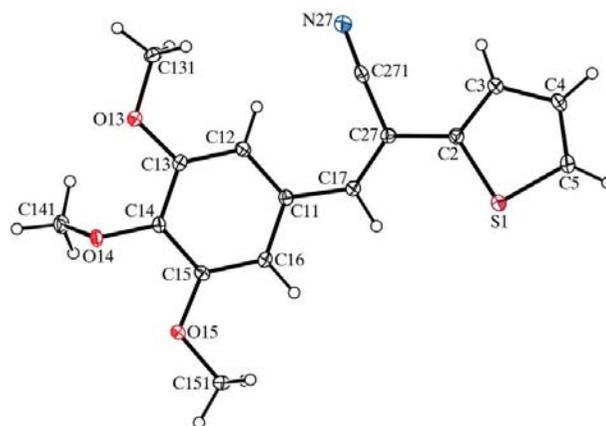


Figure 1

The molecule of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

acts as hydrogen-bond donor to atom N27 in the molecule at $(-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$, so forming a $C(5)$ chain (Bernstein *et al.*, 1995) running parallel to the $[101]$ direction and generated by

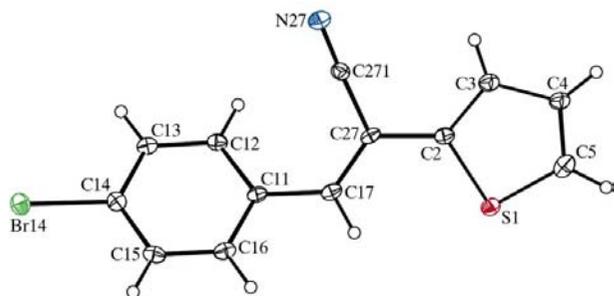


Figure 2

The molecule of compound (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

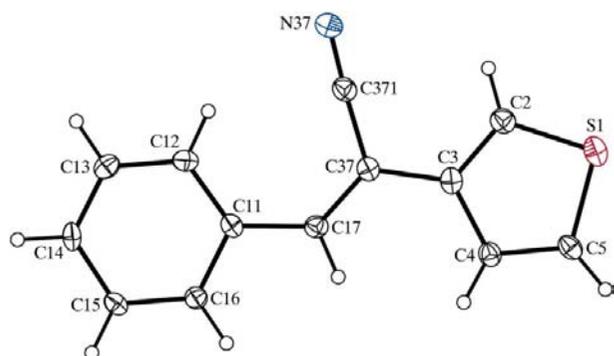


Figure 3

The molecule of compound (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. For the sake of clarity, only the major orientation of the disordered thiophyl ring is shown.

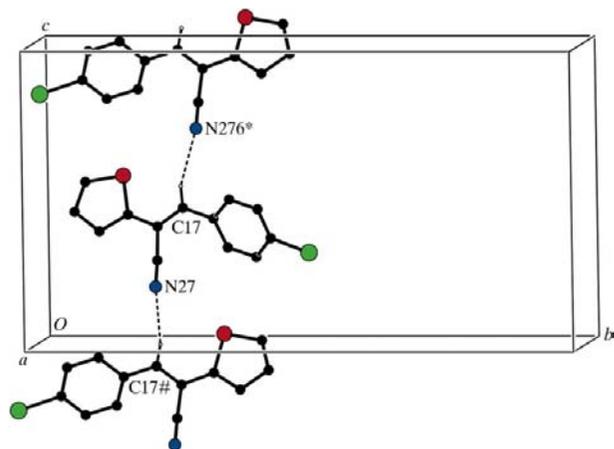


Figure 4

Part of the crystal structure of compound (II), showing the formation of a $C(5)$ chain along $[101]$. For the sake of clarity, only the major orientation of the disordered thiophyl ring is shown, and H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash symbol (#) are at the symmetry positions $(-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$ and $(\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$, respectively.

the n -glide plane at $y = \frac{1}{4}$ (Fig. 4). Two chains of this type, which are related to one another by inversion and hence are anti-parallel, and generated by the n -glide planes at $y = \frac{1}{4}$ and $y = \frac{3}{4}$, pass through each unit cell, but there are no direction-specific interactions between adjacent chains.

In the structure of compound (III), the molecules are linked into sheets by a combination of $C-H \cdots N$ and $C-H \cdots \pi(\text{arene})$ hydrogen bonds (Table 5). Atom C2 in the molecule at (x, y, z) acts as hydrogen-bond donor to atom N37 in the molecule at $(1 - x, -y, 1 - z)$, so generating by inversion an $R_2^2(12)$ dimer centred at $(\frac{1}{2}, 0, \frac{1}{2})$ (Fig. 5). In addition, atoms C13 in the molecules at (x, y, z) and $(1 - x, -y, 1 - z)$, which form a dimer centred at $(\frac{1}{2}, 0, \frac{1}{2})$, act as hydrogen-bond donors to the aryl rings of the molecules at $(2 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$ and $(-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z)$, respectively, which themselves are components of dimers centred at $(\frac{3}{2}, -\frac{1}{2}, 1)$ and $(-\frac{1}{2}, \frac{1}{2}, 0)$, respectively. Similarly, the aryl rings at (x, y, z) and $(1 - x, -y, 1 - z)$ accept hydrogen bonds from atom C13 in the molecules at $(2 - x, \frac{1}{2} + y, \frac{3}{2} - z)$ and $(-1 + x, -\frac{1}{2} - y, -\frac{1}{2} + z)$, themselves parts of dimers centred at $(\frac{3}{2}, \frac{1}{2}, 1)$

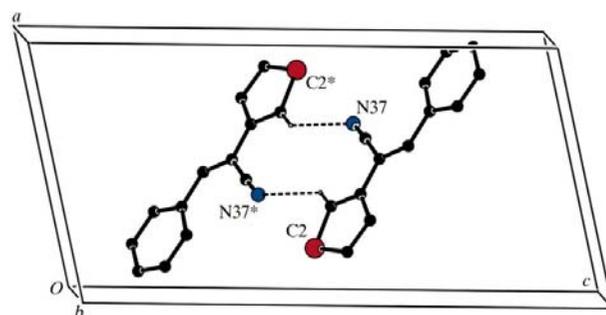


Figure 5

Part of the crystal structure of compound (III), showing the formation of an $R_2^2(12)$ dimer. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, -y, 1 - z)$.

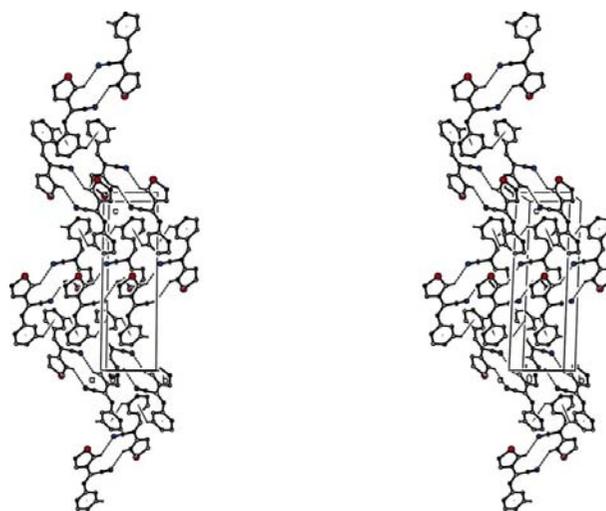


Figure 6

A stereoview of part of the crystal structure of compound (III), showing the formation of a hydrogen-bonded sheet parallel to $(10\bar{2})$. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

and $(-\frac{1}{2}, -\frac{1}{2}, 0)$, respectively. Propagation of this interaction then links the $R_2^2(12)$ dimers into a sheet parallel to $(10\bar{2})$ (Fig. 6).

Experimental

Compounds (I)–(III) were prepared using procedures similar to that employed for the synthesis of compound (IV) (Cobo *et al.*, 2005). A solution of 2-thiopheneacetonitrile [for (I) and (II)] or 3-thiopheneacetonitrile [for (III)] (1 mmol) and potassium *tert*-butoxide (1 mmol) in anhydrous ethanol (3 ml) was stirred at room temperature for 15 min. A solution of the appropriate benzaldehyde (1 mmol) in anhydrous ethanol (3 ml) was then added, and the overall mixtures were then heated under reflux for 2–3 h. The resulting solid products were collected by filtration, washed with ethanol, dried, and finally crystallized from dimethylformamide to give yellow crystals suitable for single-crystal X-ray diffraction. Compound (I): m.p. 391–392 K, yield 70%; MS EI (30 eV) m/z (%): 302 (21), 301 (100, M^+), 286 (39 $M^+ - CH_3$), 226 (16). Compound (II): m.p. 368–370 K, yield 68%; MS EI (30 eV) m/z (%): 292 (17), 291/289 (100/98, M^+), 290 (22), 211 (16), 210 (81), 209 (89), 208 (91), 183 (16), 177 (35), 166 (19), 139 (16), 154 (17), 127 (10), 45 (14). Compound (III): m.p. 348–349 K [literature m.p. 348 K (Stuart *et al.*, 1986)], yield 60%.

Compound (I)

Crystal data

$C_{16}H_{15}NO_3S$ $Z = 4$
 $M_r = 301.36$ $D_x = 1.413 \text{ Mg m}^{-3}$
 Monoclinic, $P2_1/c$ Mo $K\alpha$ radiation
 $a = 22.5423$ (6) Å $\mu = 0.24 \text{ mm}^{-1}$
 $b = 8.4647$ (3) Å $T = 120$ (2) K
 $c = 7.4243$ (2) Å Block, colourless
 $\beta = 91.510$ (2)° $0.30 \times 0.20 \times 0.10 \text{ mm}$
 $V = 1416.17$ (7) Å³

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer 17457 measured reflections
 φ and ω scans 3228 independent reflections
 Absorption correction: multi-scan 2538 reflections with $I > 2\sigma(I)$
 (SADABS; Sheldrick, 2003) $R_{\text{int}} = 0.041$
 $T_{\text{min}} = 0.920$, $T_{\text{max}} = 0.977$ $\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0648P)^2 + 0.0444P]$
 $R[F^2 > 2\sigma(F^2)] = 0.038$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.113$ $(\Delta/\sigma)_{\text{max}} = 0.001$
 $S = 1.12$ $\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$
 3228 reflections $\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$
 193 parameters
 H-atom parameters constrained

Table 1

Selected geometric parameters (Å, °) for (I).

C27–C271	1.443 (2)	C271–N27	1.145 (2)
O13–C13–C12	124.05 (14)	O14–C14–C15	119.86 (13)
O13–C13–C14	115.33 (13)	O15–C15–C14	115.80 (12)
O14–C14–C13	120.47 (14)	O15–C15–C16	124.47 (14)
S1–C2–C27–C17	–9.0 (2)	C12–C13–O13–C131	7.9 (2)
C2–C27–C17–C11	174.72 (15)	C13–C14–O14–C141	75.54 (17)
C27–C17–C11–C12	–5.5 (3)	C16–C15–O15–C151	2.2 (2)

Compound (II)

Crystal data

$C_{13}H_8BrNS$ $Z = 4$
 $M_r = 290.17$ $D_x = 1.669 \text{ Mg m}^{-3}$
 Monoclinic, $P2_1/n$ Mo $K\alpha$ radiation
 $a = 3.8557$ (2) Å $\mu = 3.71 \text{ mm}^{-1}$
 $b = 24.0484$ (7) Å $T = 120$ (2) K
 $c = 12.5466$ (4) Å Needle, colourless
 $\beta = 96.877$ (2)° $0.38 \times 0.04 \times 0.03 \text{ mm}$
 $V = 1154.99$ (8) Å³

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer 12766 measured reflections
 φ and ω scans 2598 independent reflections
 Absorption correction: multi-scan 1983 reflections with $I > 2\sigma(I)$
 (SADABS; Sheldrick, 2003) $R_{\text{int}} = 0.059$
 $T_{\text{min}} = 0.333$, $T_{\text{max}} = 0.897$ $\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.032P)^2 + 0.6935P]$
 $R[F^2 > 2\sigma(F^2)] = 0.040$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.081$ $(\Delta/\sigma)_{\text{max}} = 0.001$
 $S = 1.09$ $\Delta\rho_{\text{max}} = 0.54 \text{ e \AA}^{-3}$
 2598 reflections $\Delta\rho_{\text{min}} = -0.76 \text{ e \AA}^{-3}$
 147 parameters Extinction correction: SHELXL97
 H-atom parameters constrained (Sheldrick, 1997)
 Extinction coefficient: 0.0211 (12)

Table 2

Selected geometric parameters (Å, °) for (II).

C27–C271	1.446 (4)	C271–N27	1.143 (4)
S1–C2–C27–C17	5.2 (4)	C27–C17–C11–C12	38.7 (4)
C2–C27–C17–C11	–178.1 (3)		

Table 3

Hydrogen-bond geometry (Å, °) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C17–H17 \cdots N27 ⁱ	0.95	2.55	3.450 (4)	159

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

Compound (III)

Crystal data

$C_{13}H_9NS$ $Z = 4$
 $M_r = 211.27$ $D_x = 1.360 \text{ Mg m}^{-3}$
 Monoclinic, $P2_1/c$ Mo $K\alpha$ radiation
 $a = 9.6280$ (11) Å $\mu = 0.27 \text{ mm}^{-1}$
 $b = 5.7190$ (3) Å $T = 120$ (2) K
 $c = 19.247$ (2) Å Block, yellow
 $\beta = 103.129$ (7)° $0.49 \times 0.31 \times 0.20 \text{ mm}$
 $V = 1032.09$ (17) Å³

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer 24963 measured reflections
 φ and ω scans 2368 independent reflections
 Absorption correction: multi-scan 1788 reflections with $I > 2\sigma(I)$
 [SADABS (Sheldrick, 2003) and EVALCCD (Duisenberg *et al.*, 2003)] $R_{\text{int}} = 0.036$
 $T_{\text{min}} = 0.878$, $T_{\text{max}} = 0.947$ $\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1146P)^2 + 1.443P]$
$R[F^2 > 2\sigma(F^2)] = 0.067$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.206$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.07$	$\Delta\rho_{\max} = 0.57 \text{ e } \text{\AA}^{-3}$
2368 reflections	$\Delta\rho_{\min} = -0.67 \text{ e } \text{\AA}^{-3}$
136 parameters	
H-atom parameters constrained	

Table 4

Selected geometric parameters (\AA , $^\circ$) for (III).

C37—C371	1.444 (4)	C371—N37	1.146 (4)
C2—C3—C37—C17	179.0 (3)	C37—C17—C11—C12	-1.7 (5)
C3—C37—C17—C11	-178.1 (2)		

Table 5

Hydrogen-bond geometry (\AA , $^\circ$) for (III).

Cg is the centroid of the C11—C16 ring.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C2—H2 \cdots N37 ⁱ	0.95	2.59	3.324 (5)	135
C13—H13 \cdots Cg ⁱⁱ	0.95	2.86	3.566 (4)	132

Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$.

The space groups $P2_1/c$, $P2_1/n$ and $P2_1/c$ for compounds (I), (II) and (III), respectively, were uniquely assigned from the systematic absences. All H atoms were located in difference maps and then treated as riding atoms, with C—H distances of 0.95 \AA and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, or C—H = 0.98 \AA and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for the methyl groups. In compound (II), the disorder of the thienyl group was modelled using a common set of sites for atoms C2, C4 and C5 in the two orientations and individual sites for the remaining atoms of this unit, denoted S1 and C3 for the major orientation, and S3 and C1 for the minor orientation. The refined site occupancies for the two orientations were 0.798 (3) and 0.202 (3).

For all compounds, data collection: *COLLECT* (Nonius, 1999). Cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* for (I) and (II); *DIRAX/LSQ* (Duisenberg *et al.*, 2000) for (III). Data reduction: *DENZO* and *COLLECT* for (I) and (II); *EVALCCD* (Duisenberg *et al.*, 2003) for (III). For all compounds,

program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3037). Services for accessing these data are described at the back of the journal.

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