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(*E*)-2-(1,3-Benzothiazol-2-yl)-3-(4-fluorophenyl)acrylonitrile: a chain of π-stacked hydrogen-bonded rings

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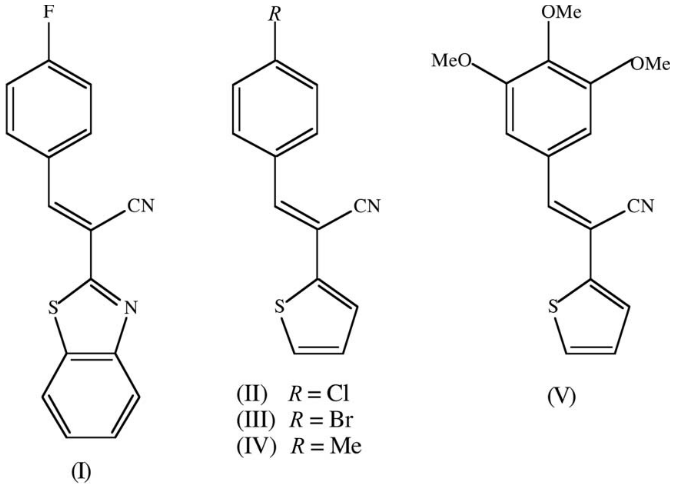
The title compound, $C_{16}H_9FN_2S$, crystallizes as a nonmerohedral twin with twin rotation about the reciprocal-lattice vector $[10\bar{1}]^*$. The molecules are nearly planar and the dihedral angle between the planes of the two aryl rings is only 4.4 (2)°. The molecules are linked by pairs of C—H$\cdots$N hydrogen bonds to form cyclic centrosymmetric $R_2^2(18)$ dimers, which are linked into chains by an aromatic π–π stacking interaction. Comparisons are made with some related 3-aryl-2-thienylacrylonitriles.

Comment

Acetonitrile derivatives are useful and versatile precursors for the synthesis of heterocyclic molecules having potential biological activity; in particular they provide a useful route to acrylonitrile derivatives. Although such derivatives are, in general, easy to synthesize, a wide diversity of methods is available, utilizing both conventional thermal reactions and those mediated by microwave irradiation (Quiroga *et al.*, 2000, 2001; Dawood *et al.*, 2010). While Knoevenagel-type products can be obtained under conventional thermal conditions in the presence of catalytic quantities of base, giving yields in the good to very low range, the corresponding condensation reactions conducted in solvent-free systems under microwave irradiation generally give better yields in much reduced reaction times (Lenardão *et al.*, 2007). We have now prepared the title compound, (*E*)-2-(1,3-benzothiazol-2-yl)-3-(4-fluorophenyl)acrylonitrile, (I), using the microwave induced condensation reaction between 2-(1,3-benzothiazol-2-yl)acetonitrile and 4-fluorobenzaldehyde under solvent-free conditions, which provided a satisfactory yield in a very short reaction time under environmentally friendly conditions, and we report here the molecular and supramolecular structure of compound (I) (Fig. 1), which we compare with the analogues (II)–(V) (Cobo *et al.*, 2005, 2006, 2009) (see Scheme).

Compound (I) crystallizes as a nonmerohedral twin. The molecule is nearly planar, as shown by the key torsion angles (Table 1), while the dihedral angle between the mean planes of the two aryl rings is only 4.4 (2)°. By contrast, in compounds (II) (Cobo *et al.*, 2005) and (III) (Cobo *et al.*, 2006), which are isomorphous and isostructural, the aryl ring is twisted out of the plane of the rest of the molecule by *ca* 38° in each case. On the other hand, in compound (IV) (Cobo *et al.*, 2009), which contains both fully ordered molecules and fourfold disordered molecules resulting in a Z' value of 0.75 in the space group $C2/m$, the non-H atoms of the ordered molecules all lie on mirror planes, while those of the disordered molecule are coplanar within experimental uncertainty, although not constrained to be so by symmetry. Similarly, the non-H atoms of compound (V) (Cobo *et al.*, 2006) are, apart from the methyl C atom of the 4-methoxy substituent, very nearly coplanar. No obvious simple explanation presents itself for



(I)

(II) $R = \text{Cl}$
(III) $R = \text{Br}$
(IV) $R = \text{Me}$

(V)

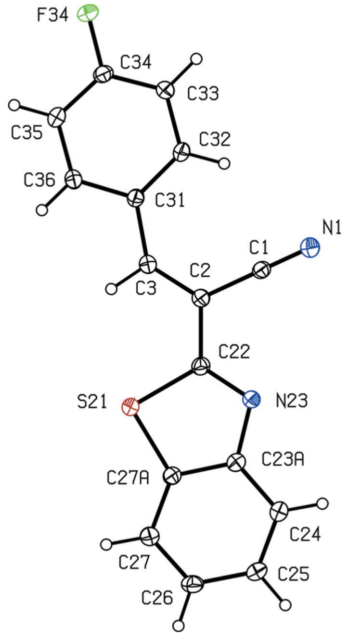


Figure 1
The molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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the nonplanarity in compounds (II) and (III), as opposed to the exact or near skeletal planarity in compounds (I), IV) and (V). However, it may also be noted here that the 2-thienyl units in the nonplanar molecules of compounds (II) and (III) are disordered over two sets of sites, corresponding to two different orientations about the exocyclic C—C bond and differing by 180°, with site occupancies of 0.802 (3) and 0.198 (3) in (II), and 0.798 (3) and 0.202 (3) in (III), while no such disorder is apparent in the planar molecules of compounds (I), (IV) and (V).

In the molecule of compound (I), the nitrile unit exhibits a long C—C bond and a short C—N bond (Table 1), in common with the nitrile units of compounds (II)–(V). There is evidence for some slight bond fixation in the fused aryl ring of compound (I), with the C24—C25 and C26—C27 bonds somewhat shorter than the remaining bonds in this ring. The other bonded distances in (I) show no unusual features. As expected, the geometry at atom C2 is strictly planar, but all of the interbond angles at C2 differ from the ideal value of 120°; the C—C—C angle at atom C3 is markedly larger than the ideal value (Table 1).

The molecules of compound (I) are linked by inversion-related pairs of C—H···N hydrogen bonds (Table 2) to form a cyclic centrosymmetric dimer (Fig. 2) characterized by an $R_2^2(18)$ motif (Bernstein *et al.*, 1995). Dimers of this type are weakly linked into a chain by an aromatic π–π stacking interaction. The fluorinated aryl ring of the molecule at (x, y, z) and the fused aryl ring of the molecule at ($x + 1$, y, z) make a dihedral angle of 4.4 (2)°; the shortest perpendicular distance from the centroid of one ring to the plane of the other ring is *ca* 3.41 Å and the ring-centroid separation is 3.883 (2) Å, corresponding to a ring-centroid offset of *ca* 1.86 Å. The hydrogen-bonded dimers are thus linked into a chain running parallel to the [100] direction, in which the $R_2^2(18)$ dimers are centred at (n, $\frac{1}{2}$, $\frac{1}{2}$), where n represents an integer (Fig. 3).

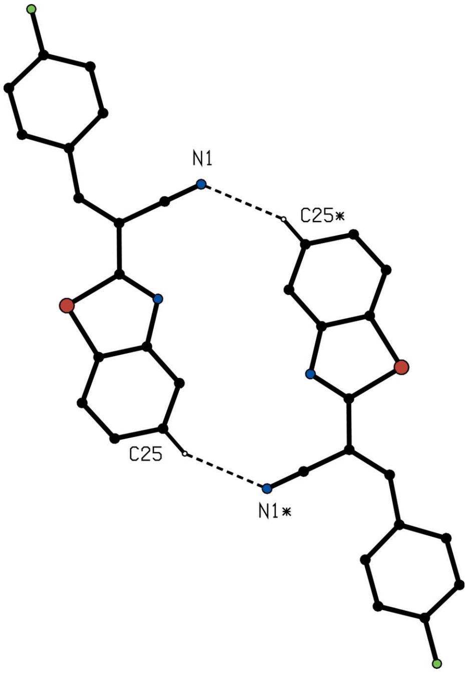

Figure 2
Part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded $R_2^2(18)$ dimer. For the sake of clarity, the unit-cell outline and H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position ($-x$, $-y + 1$, $-z + 1$).

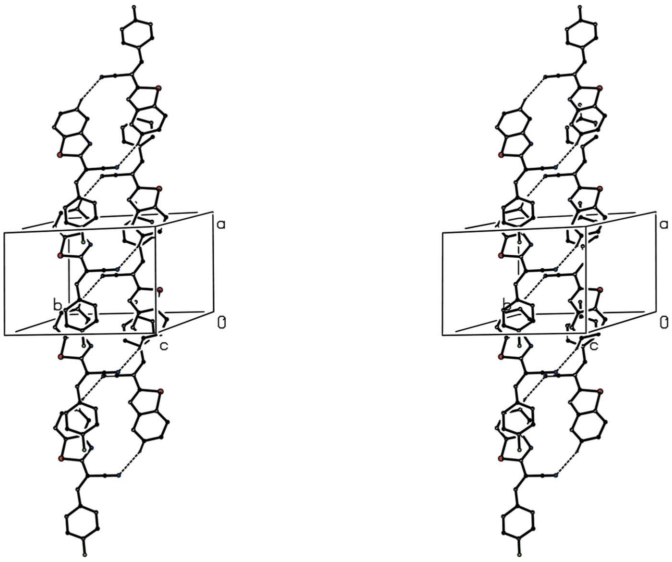

Figure 3
A stereoview of part of the crystal structure of compound (I), showing the formation of a π-stacked chain of hydrogen-bonded dimers along [100]. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

It is of interest briefly to compare the supramolecular assembly in compound (I) with the corresponding behaviour in compounds (II)–(V). There are C—H···N hydrogen bonds present in the crystal structures of isostructural compounds (II) and (III); as in compound (I), the nitrile N atom in (II) and (III) acts as the hydrogen-bond acceptor, but here the donor is the C—H bond of the central spacer unit, as opposed to a ring C atom in compound (I). In this way, molecules of (II) and (III) which are related by an n-glide plane are linked into $C(5)$ chains running parallel to [$\bar{1}$01]. There are no direction-specific intermolecular interactions in the structure of compound (IV), but the ordered molecules are nonetheless arranged such that they enclose continuous rectangular channels along the twofold rotation axes in the space group $C2/m$, within which the fourfold disordered molecules are located across sites of $2/m$ symmetry. There are no direction-specific intermolecular interactions in the structure of compound (V), which simply consists of effectively isolated molecules.

Experimental

An intimate mixture of 2-(1,3-benzothiazol-2-yl)acetonitrile and 4-fluorobenzaldehyde (1 mmol of each component) was subjected to microwave irradiation (maximum power 150 W) for 10 min under solvent-free conditions at a controlled temperature and pressure of 473 K and 250 psi (1 psi = 6894.76 Pa), respectively, using a focused microwave reaction (CEM Discover). After cooling the reaction mixture to ambient temperature, product (I) was isolated by crys-

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.152 (3)	C25—C26	1.409 (4)
C1—C2	1.441 (3)	C26—C27	1.381 (3)
C23*A*—C24	1.403 (3)	C27—C27*A*	1.390 (3)
C24—C25	1.377 (4)	C27*A*—C23*A*	1.408 (3)
N1—C1—C2	179.3 (3)	C3—C2—C22	122.3 (2)
C1—C2—C3	122.7 (2)	C2—C3—C31	132.8 (2)
C1—C2—C22	115.0 (2)		
C1—C2—C3—C31	0.6 (5)	C3—C2—C22—N23	176.3 (2)
C22—C2—C3—C31	−179.1 (2)	C3—C2—C22—S21	−4.0 (3)
C1—C2—C22—N23	−3.5 (4)	C2—C3—C31—C32	7.9 (5)
C1—C2—C22—S21	176.24 (18)	C2—C3—C31—C36	−174.4 (3)

tallization of the reaction mixture, at ambient temperature and in air, from ethanol to give brown crystals suitable for single-crystal X-ray diffraction (yield 50%; m.p. 423–425 K). MS (EI, 70 eV) *m*/*z* (%): 281 $[(M+1)^+$, 10], 280 (M^+, 39), 279 (100), 254 (22).

Crystal data

$C_{16}H_9FN_2S$
$M_r = 280.32$
Monoclinic, $P2_1/n$
$a = 8.2432$ (12) Å
$b = 13.327$ (3) Å
$c = 11.6819$ (19) Å
$\beta = 99.743$ (11)°
$V = 1264.8$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.26$ mm^{-1}
$T = 120$ K
0.39 × 0.35 × 0.20 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.906$, $T_{\max} = 0.950$
2899 measured reflections
2899 independent reflections
1997 reflections with $I > 2\sigma(I)$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.130$
$S = 1.09$
2899 reflections
182 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.37$ e Å^{-3}

All H atoms were located in difference maps and were then treated as riding atoms in geometrically idealized positions, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. Conventional refinement converged to $R = 0.069$ and analysis of the observed and calculated structure factor data at this stage indicated nonmerohedral twinning, with a twinning matrix of (0.399, 0, −0.601/ 0, −1, 0/ −1.399, 0, −0.399). Using the original input reflection file (16480 measured reflections, of which 2900 were unique with a merging index of 0.0696), a modified file was prepared by use of the TwinRotMat option in *PLATON* (Spek, 2009); this was used in the subsequent refinement, giving twin fractions of 0.819 (3) and 0.181 (3). In the final cycles of refinement, the bad outlier reflection $\overline{1}01$, partially attenuated by the beamstop, was omitted.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C25—H25···N1^{i}	0.95	2.57	3.440 (4)	152

Symmetry code: (i) $-x, -y+1, -z+1$.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DIRAX*/*LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); 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: SK3489). Services for accessing these data are described at the back of the journal.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
Cobo, D., Quiroga, J., Cobo, J. & Glidewell, C. (2009). *Acta Cryst.* C**65**, o444–o446.
Cobo, D., Quiroga, J., Cobo, J., Low, J. N. & Glidewell, C. (2005). *Acta Cryst.* E**61**, o3639–o3641.
Cobo, D., Quiroga, J., de la Torre, J. M., Cobo, J., Low, J. N. & Glidewell, C. (2006). *Acta Cryst.* C**62**, o550–o553.
Dawood, K. M., Elwan, N. M., Farahat, A. A. & Abdel-Wahab, B. F. (2010). *J. Heterocycl. Chem.* **47**, 243–267.
Duisenberg, A. J. M., Hooft, R. W. W., Schreurs, A. M. M. & Kroon, J. (2000). *J. Appl. Cryst.* **33**, 893–898.
Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
Hooft, R. W. W. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Lenardão, E. J., Silva, M. S., Mendes, S. R., de Azambuja, F., Jacob, R. G., Silva dos Santos, P. C. & Perin, G. (2007). *J. Braz. Chem. Soc.* **18**, 943–950.
Quiroga, J., Cruz, S., Insuasty, B. & Abonía, R. (2000). *Heterocycl. Commun.* **6**, 275–282.
Quiroga, J., Cruz, S., Insuasty, B., Abonía, R., Nogueras, M., Sánchez, A., Cobo, J. & Low, J. N. (2001). *J. Heterocycl. Chem.* **38**, 53–60.
Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

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(*E*)-2-(1,3-Benzothiazol-2-yl)-3-(4-fluorophenyl)acrylonitrile: a chain of *π*-stacked hydrogen-bonded rings

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(*E*)-2-(1,3-Benzothiazol-2-yl)-3-(4-fluorophenyl)acrylonitrile

Crystal data

$C_{16}H_9FN_2S$	$F(000) = 576$
$M_r = 280.32$	$D_x = 1.472$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 2900 reflections
$a = 8.2432$ (12) Å	$\theta = 2.8$–27.5°
$b = 13.327$ (3) Å	$\mu = 0.26$ mm^{-1}
$c = 11.6819$ (19) Å	$T = 120$ K
$\beta = 99.743$ (11)°	Block, brown
$V = 1264.8$ (4) Å^3	0.39 × 0.35 × 0.20 mm
$Z = 4$	

Data collection

Bruker–Nonius KappaCCD diffractometer	$T_{min} = 0.906$, $T_{max} = 0.950$
Radiation source: Bruker–Nonius FR591 rotating anode	2899 measured reflections
Graphite monochromator	2899 independent reflections
Detector resolution: 9.091 pixels mm^{-1}	1997 reflections with $I > 2\sigma(I)$
φ & ω scans	$R_{int} = 0.0000$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	$\theta_{max} = 27.5°$, $\theta_{min} = 2.9°$
	$h = -10\rightarrow10$
	$k = -17\rightarrow17$
	$l = -14\rightarrow15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.049$	H-atom parameters constrained
$wR(F^2) = 0.130$	$w = 1/[\sigma^2(F_o^2) + (0.0548P)^2 + 0.6112P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{max} = 0.001$
2899 reflections	$\Delta\rho_{max} = 0.34$ e Å^{-3}
182 parameters	$\Delta\rho_{min} = -0.37$ e Å^{-3}
0 restraints	
Primary atom site location: structure-invariant direct methods	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
N1	0.4507 (3)	0.60285 (16)	0.3715 (2)	0.0338 (5)

C1	0.4517 (3)	0.51738 (19)	0.3567 (2)	0.0261 (5)
C2	0.4514 (3)	0.41065 (18)	0.3370 (2)	0.0258 (5)
C3	0.5690 (3)	0.36372 (19)	0.2885 (2)	0.0267 (5)
H3	0.5526	0.2934	0.2800	0.032*
S21	0.29074 (8)	0.22740 (5)	0.34760 (6)	0.0305 (2)
C22	0.3145 (3)	0.35624 (19)	0.3737 (2)	0.0261 (5)
N23	0.2051 (2)	0.39923 (15)	0.42593 (18)	0.0256 (5)
C23A	0.0915 (3)	0.32781 (19)	0.4504 (2)	0.0256 (5)
C24	−0.0429 (3)	0.3473 (2)	0.5063 (2)	0.0294 (6)
H24	−0.0640	0.4133	0.5308	0.035*
C25	−0.1438 (3)	0.2687 (2)	0.5249 (2)	0.0305 (6)
H25	−0.2348	0.2810	0.5632	0.037*
C26	−0.1151 (3)	0.1705 (2)	0.4884 (2)	0.0333 (6)
H26	−0.1866	0.1178	0.5025	0.040*
C27	0.0158 (3)	0.1501 (2)	0.4323 (2)	0.0323 (6)
H27	0.0357	0.0840	0.4074	0.039*
C27A	0.1177 (3)	0.22943 (18)	0.4135 (2)	0.0262 (5)
C31	0.7152 (3)	0.39951 (18)	0.2470 (2)	0.0254 (5)
C32	0.7773 (3)	0.49749 (19)	0.2621 (2)	0.0324 (6)
H32	0.7220	0.5459	0.3012	0.039*
C33	0.9183 (3)	0.52394 (19)	0.2205 (2)	0.0336 (6)
H33	0.9602	0.5904	0.2303	0.040*
C34	0.9977 (3)	0.4528 (2)	0.1645 (2)	0.0293 (6)
F34	1.13733 (18)	0.47945 (11)	0.12503 (14)	0.0392 (4)
C35	0.9438 (3)	0.35539 (19)	0.1497 (2)	0.0295 (6)
H35	1.0017	0.3074	0.1119	0.035*
C36	0.8021 (3)	0.32955 (19)	0.1917 (2)	0.0283 (6)
H36	0.7628	0.2625	0.1827	0.034*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0341 (13)	0.0279 (13)	0.0414 (13)	0.0018 (10)	0.0117 (10)	0.0010 (10)
C1	0.0237 (12)	0.0273 (14)	0.0283 (13)	0.0018 (11)	0.0074 (10)	0.0020 (11)
C2	0.0262 (13)	0.0244 (13)	0.0273 (13)	0.0003 (10)	0.0055 (10)	0.0008 (10)
C3	0.0271 (13)	0.0239 (13)	0.0293 (13)	0.0001 (10)	0.0058 (10)	−0.0020 (10)
S21	0.0311 (4)	0.0244 (3)	0.0390 (4)	−0.0015 (3)	0.0152 (3)	−0.0035 (3)
C22	0.0246 (12)	0.0258 (13)	0.0283 (13)	0.0029 (10)	0.0058 (10)	0.0032 (10)
N23	0.0257 (11)	0.0230 (11)	0.0290 (11)	0.0005 (9)	0.0072 (9)	0.0016 (9)
C23A	0.0249 (12)	0.0285 (13)	0.0234 (12)	0.0013 (10)	0.0039 (10)	0.0012 (10)
C24	0.0290 (13)	0.0296 (14)	0.0302 (14)	0.0030 (11)	0.0067 (11)	−0.0017 (11)
C25	0.0269 (13)	0.0371 (15)	0.0294 (13)	−0.0002 (12)	0.0100 (10)	0.0006 (12)
C26	0.0330 (14)	0.0352 (15)	0.0337 (15)	−0.0059 (12)	0.0111 (12)	0.0036 (12)
C27	0.0356 (14)	0.0288 (14)	0.0349 (15)	−0.0024 (12)	0.0128 (12)	−0.0017 (12)
C27A	0.0248 (12)	0.0272 (13)	0.0271 (12)	−0.0003 (11)	0.0058 (10)	−0.0010 (11)
C31	0.0264 (12)	0.0235 (13)	0.0274 (12)	0.0023 (10)	0.0077 (10)	0.0004 (10)
C32	0.0315 (14)	0.0254 (13)	0.0438 (16)	0.0047 (11)	0.0166 (12)	−0.0007 (12)
C33	0.0335 (14)	0.0233 (13)	0.0475 (17)	−0.0012 (11)	0.0168 (12)	0.0001 (12)
C34	0.0251 (13)	0.0311 (14)	0.0334 (14)	0.0014 (11)	0.0101 (11)	0.0040 (11)
F34	0.0331 (8)	0.0364 (9)	0.0538 (10)	−0.0020 (7)	0.0237 (8)	0.0007 (8)

C35	0.0282 (13)	0.0312 (14)	0.0302 (14)	0.0042 (11)	0.0085 (11)	−0.0025 (11)
C36	0.0290 (13)	0.0238 (13)	0.0325 (14)	0.0002 (11)	0.0061 (11)	−0.0037 (11)

Geometric parameters (Å, º)

N1—C1	1.152 (3)	C26—H26	0.9500
C1—C2	1.441 (3)	C27—C27A	1.390 (3)
C2—C3	1.355 (3)	C27—H27	0.9500
C2—C22	1.465 (3)	C27A—C23A	1.408 (3)
C3—C31	1.453 (3)	C31—C36	1.399 (3)
C3—H3	0.9500	C31—C32	1.403 (3)
S21—C27A	1.732 (2)	C32—C33	1.380 (3)
S21—C22	1.749 (3)	C32—H32	0.9500
C22—N23	1.304 (3)	C33—C34	1.378 (4)
N23—C23A	1.398 (3)	C33—H33	0.9500
C23A—C24	1.403 (3)	C34—F34	1.358 (3)
C24—C25	1.377 (4)	C34—C35	1.373 (4)
C24—H24	0.9500	C35—C36	1.385 (3)
C25—C26	1.409 (4)	C35—H35	0.9500
C25—H25	0.9500	C36—H36	0.9500
C26—C27	1.381 (3)		

N1—C1—C2	179.3 (3)	C26—C27—C27A	117.7 (2)
C1—C2—C3	122.7 (2)	C26—C27—H27	121.1
C1—C2—C22	115.0 (2)	C27A—C27—H27	121.1
C3—C2—C22	122.3 (2)	C27—C27A—C23A	122.2 (2)
C2—C3—C31	132.8 (2)	C27—C27A—S21	128.5 (2)
C2—C3—H3	113.6	C23A—C27A—S21	109.31 (18)
C31—C3—H3	113.6	C36—C31—C32	118.3 (2)
C27A—S21—C22	89.05 (11)	C36—C31—C3	117.0 (2)
N23—C22—C2	123.2 (2)	C32—C31—C3	124.7 (2)
N23—C22—S21	116.56 (18)	C33—C32—C31	120.3 (2)
C2—C22—S21	120.25 (18)	C33—C32—H32	119.8
C22—N23—C23A	109.7 (2)	C31—C32—H32	119.8
N23—C23A—C24	125.3 (2)	C34—C33—C32	119.2 (2)
N23—C23A—C27A	115.4 (2)	C34—C33—H33	120.4
C24—C23A—C27A	119.3 (2)	C32—C33—H33	120.4
C25—C24—C23A	118.5 (2)	F34—C34—C35	118.6 (2)
C25—C24—H24	120.7	F34—C34—C33	118.6 (2)
C23A—C24—H24	120.7	C35—C34—C33	122.7 (2)
C24—C25—C26	121.5 (2)	C34—C35—C36	117.7 (2)
C24—C25—H25	119.3	C34—C35—H35	121.2
C26—C25—H25	119.3	C36—C35—H35	121.2
C27—C26—C25	120.8 (2)	C35—C36—C31	121.8 (2)
C27—C26—H26	119.6	C35—C36—H36	119.1
C25—C26—H26	119.6	C31—C36—H36	119.1

C1—C2—C3—C31	0.6 (5)	N23—C23A—C27A—C27	179.5 (2)
C22—C2—C3—C31	−179.1 (2)	C24—C23A—C27A—C27	−1.1 (4)
C1—C2—C22—N23	−3.5 (4)	N23—C23A—C27A—S21	0.5 (3)

C1—C2—C22—S21	176.24 (18)	C24—C23A—C27A—S21	179.90 (18)
C3—C2—C22—N23	176.3 (2)	C22—S21—C27A—C27	−179.1 (3)
C3—C2—C22—S21	−4.0 (3)	C22—S21—C27A—C23A	−0.09 (19)
C27A—S21—C22—N23	−0.4 (2)	C2—C3—C31—C32	7.9 (5)
C27A—S21—C22—C2	179.9 (2)	C2—C3—C31—C36	−174.4 (3)
C2—C22—N23—C23A	−179.6 (2)	C36—C31—C32—C33	1.6 (4)
S21—C22—N23—C23A	0.7 (3)	C3—C31—C32—C33	179.3 (3)
C22—N23—C23A—C24	179.9 (2)	C31—C32—C33—C34	−0.3 (4)
C22—N23—C23A—C27A	−0.8 (3)	C32—C33—C34—F34	−179.3 (2)
N23—C23A—C24—C25	−179.7 (2)	C32—C33—C34—C35	−1.0 (4)
C27A—C23A—C24—C25	1.0 (4)	F34—C34—C35—C36	179.4 (2)
C23A—C24—C25—C26	−0.4 (4)	C33—C34—C35—C36	1.0 (4)
C24—C25—C26—C27	−0.1 (4)	C34—C35—C36—C31	0.3 (4)
C25—C26—C27—C27A	0.1 (4)	C32—C31—C36—C35	−1.6 (4)
C26—C27—C27A—C23A	0.5 (4)	C3—C31—C36—C35	−179.5 (2)
C26—C27—C27A—S21	179.3 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C25—H25···N1^{i}	0.95	2.57	3.440 (4)	152

Symmetry code: (i) −*x*, −*y*+1, −*z*+1.