Synthesis, spectroscopic and crystal structure studies of N-[3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(ethylsulfanyl)-1H-pyrazol-5-yl]-2,2,2-trifluoroacetamide

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The structure of the title compound, C15H8N4Cl2F6OS, a phenylpyrazole-based insecticide related to ethiprole, fipronil, and derivatives thereof is presented. The pyrazole ring has four chemically diverse substituents, namely a nitrogen-bound 2,6-dichloro-4-trifluoromethylphenyl and carbon-bound cyano, ethylsulfanyl, and 2,2,2-trifluoroacetamide groups. The pyrazole and phenyl rings are perpendicular, subtending a dihedral angle of 89.80 (5)°. In the crystal, strong N—H···O hydrogen bonds link the molecules into chains that extend parallel to the a-axis.

1. Chemical context

The title compound is a phenylpyrazole-based insecticide. It is related to ethiprole, an insecticide used to kill or remove insects from crops and grains during storage (Arthur, 2002). Phenylpyrazole insecticides render an insect’s central nervous system toxic by blocking the body’s glutamate-gated chloride channel. Ethiprole itself is a non-systemic insecticide that is effective against a wide range of chewing and sucking insects (Wu, 1998) and is an active ingredient used in many insecticides for crop-protection products. Fipronil (see, for example, Park et al., 2017) and fipronil sulfone belong to the same class of compounds. The design, synthesis, and insecticidal activity of novel phenylpyrazoles containing a 2,2,2-trichloro-1-alkoxyethyl moiety have been published by Zhao et al. (2010).
The starting material for the title compound, 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-ethylsulfanyl-1H-pyrazole-3-carbonitrile, is also an important intermediate in the preparation of ethiprole. In view of the importance of phenylpyrazoles, especially in the context of their use in insecticides, this paper reports the synthesis, crystal structure, and spectroscopic studies of the phenylpyrazole derivative, C₁₅H₈N₄Cl₂F₆OS (I).

2. Structural commentary

The molecular structure of I (Fig. 1), consists of a pyrazole ring with four chemically diverse substituents. A 2,6-dichloro-4-trifluoromethylphenyl group is attached to atom N1 of the pyrazole ring. A 2,2,2-trifluoroacetamide group is attached to the adjacent carbon of the pyrazole, with ethylsulfanyl and cyano substituents attached sequentially at the next two carbon atoms of the pyrazole. The pyrazole and phenyl rings are essentially perpendicular, forming a dihedral angle of 89.80(5)°. The mean plane of the amide group (r.m.s. deviation = 0.0079 Å) forms a dihedral angle of 74.33(6)° with the pyrazole ring, while the dihedral angle between the plane of the ethylsulfanyl substituent and the pyrazole is 81.31(8)°. There are no unusual bond lengths, bond angles, or torsion angles in the structure, and no noteworthy intramolecular interactions.

3. Supramolecular features

There is only one strong intermolecular hydrogen bond in I, namely N3—H3N···O1 (symmetry codes as per Table 1), between c-glide related acetamide groups (Table 1), which propagates to form chains that extend parallel to the a-axis (Fig. 2). The default HTAB command in SHELXL (Sheldrick, 2015b) also flags three C—H···F close contacts (Table 1). Two of these, C11—H11···F5 and C13—H13···F6, are oriented so as to associate 2,1-screw-related molecules into chains.

Table 1
Hydrogen bonds and other short contacts (Å, °) in I.

| Atoms | D—H | H···A | D···A | D—H···A |
|-------|------|------|------|---------|
| N3—H3N···O1 | 0.855 (16) | 2.034 (16) | 2.8172 (13) | 151.9 (14) |
| C5—H5B···F2 | 0.99 | 2.58 | 3.5641 (16) | 173.9 |
| C11—H11···F5 | 0.95 | 2.62 | 3.4873 (15) | 151.8 |
| C13—H13···F6 | 0.95 | 2.39 | 3.2071 (15) | 143.8 |

Symmetry codes: (i) x + 1/2, y, z; (ii) x + 1, y + 1/2, z + 1/2; (iii) x, y + 1, z + 1; (iv) x − 1/2, −y + 1/2, −z ± 1; (v) x − 1, −y + 1, −z ± 1.

The packing plot of I showing strong hydrogen-bonded chains (thick dashed lines) along the a-axis direction.

Figure 1
An ellipsoid plot (50% probability) of I.

Figure 2
A packing plot of I showing strong hydrogen-bonded chains (thick dashed lines) along the a-axis direction.
which again extend parallel to the \(a\)-axis (Fig. 3). There are no \(\pi-\pi\) stacking interactions, but inversion-related molecules have their Cl1 atoms mutually located directly over the benzene rings of their inversion-related counterparts [Cl1 \(\cdots\) Cg(C9–C14) = 3.4967 (6) \(\text{Å}\), where Cg represents the ring centroid], as shown in Table 1 and Fig. 4. These combine to produce pleated sheets that extend in the \(ac\) plane (Fig. 5), which then stack along the \(b\)-axis direction. Atom–atom contact coverages derived from a Hirshfeld-surface analysis using CrystalExplorer (Spackman et al., 2021) are given in Table 2.

### Table 2

| Atom contacts | % | Atom contacts | % |
|---------------|---|---------------|---|
| H \(\cdots\) F/F \(\cdots\) H | 23.0 | F \(\cdots\) Cl/Cl \(\cdots\) F | 8.3 |
| N \(\cdots\) F/F \(\cdots\) N | 7.3 | C \(\cdots\) H/H \(\cdots\) C | 7.1 |
| H \(\cdots\) Cl/Cl \(\cdots\) H | 7.1 | H \(\cdots\) N/N \(\cdots\) H | 6.9 |
| H \(\cdots\) O/O \(\cdots\) H | 5.9 | H \(\cdots\) H | 4.8 |
| C \(\cdots\) F/F \(\cdots\) C | 3.8 | C \(\cdots\) Cl/Cl \(\cdots\) C | 3.8 |
| C \(\cdots\) N/N \(\cdots\) C | 3.4 | F \(\cdots\) S/S \(\cdots\) F | 3.0 |
| S \(\cdots\) Cl/Cl \(\cdots\) S | 1.9 | Cl \(\cdots\) Cl | 1.3 |
| H \(\cdots\) S/S \(\cdots\) H | 1.3 | O \(\cdots\) Cl/Cl \(\cdots\) O | 1.2 |
| C \(\cdots\) C | 0.9 | O \(\cdots\) N/N \(\cdots\) O | 0.8 |
| N \(\cdots\) Cl/Cl \(\cdots\) N | 0.7 | N \(\cdots\) N | 0.3 |
| O \(\cdots\) F/F \(\cdots\) O | 0.2 | C \(\cdots\) S/S \(\cdots\) C | 0.2 |
| C \(\cdots\) O/O \(\cdots\) C | 0.1 | | |

All other atom–atom contact coverages are \(\approx 0.0\%\).
search on this fragment with any nitrogen-bound substituent at the equivalent of C1 (i.e., the carbon adjacent to the substituted nitrogen) gave 76 hits, and a subsequent search with 2,6-dichloro-4-(trifluoromethyl)phenyl attached at N1 of the pyrazole ring gave 60 hits. Further addition of any sulfur-bound substituent at the equivalent of C2 gave nine hits, only eight of which are unique. Two of these structures, FOCCUW (Tang, Zhong, Li et al., 2005) and TOLFUY (Du et al., 2019) are dimers. The remaining six, along with three other similar structures, are listed in Table 3.

5. Synthesis, crystallization and spectroscopic details

Trifluoroacetic anhydride (550 µL, 3.8 mmol) was added dropwise to a stirred solution of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(ethylsulfanyl)-1H-pyrazol-5-yl]-2,2,2-trifluoroacetamide (C_{15}H_{8}Cl_{2}F_{6}N_{4}OS, I, yield = 600 mg, 85%).

The product was dissolved in ethanol at 333 K and stirred for 30 min. The resulting solution was allowed to cool slowly to room temperature with slow evaporation. X-ray-quality crystals appeared in two days (m.p. 366–367 K).

The title compound was characterized by IR and 1H NMR spectroscopies, as follows: FT–IR (ν in cm⁻¹): 3227 (N–H stretching), 2250 (C=O stretching), 1737 (C=O stretching), 1694–1652 (C=C stretching), 1313, 1222 (C–F stretching), 881, 818 (s, Ar–C–H bending), 711, 628 (C–Cl). 1H NMR: DMSO–d₆ (400 MHz, δ ppm): 12.42 (b, 1H, NH), 8.36 (s, 2H, Ar–H), 2.90–2.85 (t, 3H, CH₂, J = 7.6 Hz), 1.19–1.15 (t, 3H, CH₃, J = 7.6 Hz).

6. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 4. All H atoms were found in difference-Fourier maps. Carbon-bound hydrogens were subsequently included in the refinement using riding models, with constrained distances set to 0.98 Å (CH₃), 0.99 Å (R₂CH₂) and 0.95 Å (R₂CH). The nitrogen-bound hydrogen-atom coordinates were refined freely. U(eq)(H) parameters were set to values of either 1.2Ueq or 1.5Ueq (RCH₃) only of the attached atom.

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Synthesis, spectroscopic and crystal structure studies of \(N\)-{3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(ethylsulfanyl)-1H-pyrazol-5-yl}-2,2,2-trifluoroacetamide

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Computing details

Data collection: APEX3 (Bruker, 2016); cell refinement: APEX3 (Bruker, 2016); data reduction: APEX3 (Bruker, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2019/2 (Sheldrick, 2015b); molecular graphics: XP in SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELX (Sheldrick, 2008) and publCIF (Westrip, 2010).

\(N\)-{3-Cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(ethylsulfanyl)-1H-pyrazol-5-yl}-2,2,2-trifluoroacetamide

Crystal data

\[
\begin{align*}
C_{15}H_{8}Cl_{2}F_{6}N_{4}OS & \quad D_{c} = 1.697 \text{ Mg m}^{-3} \\
M_r = 477.21 & \quad \text{Mo Kα radiation, } \lambda = 0.71073 \text{ Å} \\
\text{Orthorhombic, } Pbc & \quad \text{Cell parameters from 9972 reflections} \\
\alpha = 9.9350 (3) \text{ Å} & \quad \theta = 2.5–27.5^\circ \\
\beta = 17.5133 (7) \text{ Å} & \quad \mu = 0.53 \text{ mm}^{-1} \\
\gamma = 21.4662 (8) \text{ Å} & \quad T = 90 \text{ K} \\
V = 3735.0 (2) \text{ Å}^3 & \quad \text{Cut block, colourless} \\
Z = 8 & \quad 0.30 \times 0.23 \times 0.19 \text{ mm} \\
F(000) = 1904 & \\
\end{align*}
\]

Data collection

Bruker D8 Venture dual source diffractometer

27352 measured reflections

2471 independent reflections

3893 reflections with \(I > 2\sigma(I)\)

\(\theta_{\text{min}} = 0.036\)

\(\theta_{\text{max}} = 27.5^\circ, \theta_{\text{min}} = 2.3^\circ\)

\(h = -12 \rightarrow 10\)

\(k = -22 \rightarrow 22\)

\(l = -27 \rightarrow 27\)

Refinement

Refinement on \(F^2\)

4271 reflections

267 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

\[
\begin{align*}
\text{Least-squares matrix: full} & \\
R(F^2 > 2\sigma(F^2)) = 0.026 & \\
wR(F^2) = 0.064 & \\
S = 1.04 & \\
\end{align*}
\]
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
\( w = \frac{1}{\sigma^2(\text{Fo}^2) + (0.0273P)^2 + 2.0142P} \)
where \( P = (\text{Fo}^2 + 2\text{Fc}^2)/3 \)

(\(\Delta/\sigma\))\(_{\text{max}}\) = 0.001
\(\Delta\rho_{\text{max}}\) = 0.42 e Å\(^{-3}\)
\(\Delta\rho_{\text{min}}\) = −0.25 e Å\(^{-3}\)

Extinction correction: SHELXL-2019/2 (Sheldrick 2015b),
\(\text{Fc}^* = k\text{Fc}[1 + 0.001x\text{Fc}^2/\sin(2\theta)]^{1/4}\)
Extinction coefficient: 0.0017 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

|     | x       | y       | z       | Uiso* / Ueq         |
|-----|---------|---------|---------|---------------------|
| Cl1 | 0.63935 | 0.51208 | 0.40861 | 0.01864 (8)         |
| Cl2 | 0.09945 | 0.53537 | 0.40975 | 0.02419 (9)         |
| S1  | 0.32287 | 0.38515 | 0.20184 | 0.01658 (8)         |
| F1  | 0.35596 | 0.62440 | 0.15112 | 0.02447 (19)        |
| F2  | 0.38608 | 0.69639 | 0.23078 | 0.02336 (18)        |
| F3  | 0.18898 | 0.68747 | 0.18872 | 0.02659 (19)        |
| F4  | 0.36645 | 0.70022 | 0.59601 | 0.02648 (19)        |
| F5  | 0.30334 | 0.77508 | 0.52258 | 0.0323 (2)          |
| F6  | 0.51380 | 0.75448 | 0.53817 | 0.02669 (19)        |
| O1  | 0.15013 | 0.55566 | 0.24758 | 0.01724 (19)        |
| N1  | 0.36297 | 0.47239 | 0.36809 | 0.0145 (2)          |
| N2  | 0.35250 | 0.39898 | 0.38684 | 0.0168 (2)          |
| N3  | 0.37119 | 0.55065 | 0.27566 | 0.0130 (2)          |
| H3N | 0.4502  | 0.5686  | 0.2699  | 0.016*              |
| N4  | 0.30803 | 0.21428 | 0.33539 | 0.0255 (3)          |
| C1  | 0.36015 | 0.47954 | 0.30511 | 0.0131 (2)          |
| C2  | 0.34539 | 0.40781 | 0.28031 | 0.0141 (2)          |
| C3  | 0.34127 | 0.36032 | 0.33357 | 0.0155 (2)          |
| C4  | 0.32423 | 0.27879 | 0.33502 | 0.0185 (3)          |
| C5  | 0.49124 | 0.35383 | 0.18065 | 0.0234 (3)          |
| H5A | 0.55653 | 0.395746| 0.187298| 0.028*              |
| H5B | 0.51838 | 0.309910| 0.206827| 0.028*              |
| C6  | 0.48964 | 0.33069 | 0.11230 | 0.0275 (3)          |
| H6A | 0.460330| 0.374098| 0.086883| 0.041*              |
| H6B | 0.427263| 0.287945| 0.106458| 0.041*              |
| H6C | 0.580318| 0.315148| 0.099566| 0.041*              |
| C7  | 0.26356 | 0.58029 | 0.24545 | 0.0131 (2)          |
| C8  | 0.29906 | 0.64906 | 0.20371 | 0.0166 (3)          |
| C9  | 0.37120 | 0.53275 | 0.41254 | 0.0141 (2)          |
| C10 | 0.49581 | 0.55813 | 0.43330 | 0.0140 (2)          |
| C11 | 0.50542 | 0.61972 | 0.47388 | 0.0145 (2)          |
| H11 | 0.590543| 0.637395| 0.487965| 0.017*              |
Atomic displacement parameters (Å²)

|   | U¹¹  | U¹²  | U¹³  | U¹²  | U¹³  | U¹³  |
|---|------|------|------|------|------|------|
| C11 | 0.01593 (15) | 0.01905 (15) | 0.02095 (16) | 0.00316 (11) | 0.00334 (11) | 0.00045 (11) |
| C12 | 0.01509 (16) | 0.02479 (17) | 0.03269 (19) | −0.00092 (12) | −0.00540 (13) | −0.00730 (13) |
| S1  | 0.01774 (16) | 0.01755 (15) | 0.01445 (15) | 0.00235 (11) | −0.00419 (12) | −0.00360 (11) |
| F1  | 0.0328 (5) | 0.0231 (4) | 0.0175 (4) | −0.0014 (3) | 0.0079 (3) | −0.0003 (3) |
| F2  | 0.0286 (4) | 0.0160 (4) | 0.0255 (4) | −0.0086 (3) | −0.0006 (3) | −0.0001 (3) |
| F3  | 0.0246 (4) | 0.0215 (4) | 0.0336 (5) | 0.0074 (3) | −0.0018 (4) | 0.0101 (3) |
| F4  | 0.0389 (5) | 0.0253 (4) | 0.0152 (4) | −0.0056 (4) | 0.0072 (3) | −0.0047 (3) |
| F5  | 0.0409 (5) | 0.0182 (4) | 0.0378 (5) | 0.0121 (4) | −0.0129 (4) | −0.0102 (4) |
| F6  | 0.0286 (4) | 0.0231 (4) | 0.0285 (4) | −0.0110 (3) | 0.0052 (4) | −0.0093 (3) |
| O1  | 0.0122 (4) | 0.0175 (4) | 0.0220 (5) | −0.0002 (3) | −0.0008 (4) | 0.0010 (4) |
| N1  | 0.0183 (5) | 0.0108 (5) | 0.0143 (5) | 0.0006 (4) | −0.0015 (4) | −0.0007 (4) |
| N2  | 0.0213 (5) | 0.0118 (5) | 0.0172 (5) | 0.0005 (4) | −0.0025 (4) | 0.0006 (4) |
| N3  | 0.0104 (5) | 0.0123 (5) | 0.0162 (5) | −0.0111 (4) | −0.0003 (4) | 0.0007 (4) |
| N4  | 0.0355 (7) | 0.0170 (5) | 0.0239 (6) | −0.0005 (5) | −0.0053 (5) | 0.0002 (4) |
| C1  | 0.0109 (5) | 0.0138 (5) | 0.0146 (6) | 0.0012 (4) | −0.0017 (4) | −0.0001 (4) |
| C2  | 0.0131 (5) | 0.0145 (6) | 0.0147 (6) | 0.0012 (4) | −0.0017 (5) | −0.0018 (4) |
| C3  | 0.0164 (6) | 0.0132 (5) | 0.0168 (6) | 0.0008 (5) | −0.0026 (5) | −0.0006 (4) |
| C4  | 0.0230 (7) | 0.0172 (6) | 0.0153 (6) | 0.0009 (5) | −0.0040 (5) | −0.0005 (5) |
| C5  | 0.0188 (6) | 0.0332 (7) | 0.0181 (6) | 0.0040 (6) | 0.0001 (5) | −0.0035 (5) |
| C6  | 0.0248 (7) | 0.0388 (8) | 0.0190 (7) | −0.0018 (6) | 0.0022 (6) | −0.0067 (6) |
| C7  | 0.0145 (5) | 0.0116 (5) | 0.0132 (5) | 0.0018 (4) | 0.0006 (5) | −0.0026 (4) |
| C8  | 0.0180 (6) | 0.0142 (6) | 0.0177 (6) | 0.0007 (5) | −0.0001 (5) | −0.0002 (5) |
| C9  | 0.0200 (6) | 0.0110 (5) | 0.0115 (6) | −0.0001 (4) | −0.0017 (5) | 0.0004 (4) |
| C10 | 0.0150 (6) | 0.0139 (5) | 0.0131 (6) | 0.0013 (4) | 0.0014 (5) | 0.0024 (4) |
| C11 | 0.0161 (6) | 0.0144 (5) | 0.0132 (6) | −0.0024 (5) | −0.0015 (4) | 0.0016 (4) |
| C12 | 0.0195 (6) | 0.0114 (5) | 0.0120 (5) | 0.0000 (4) | −0.0002 (5) | 0.0013 (4) |
| C13 | 0.0169 (6) | 0.0144 (5) | 0.0166 (6) | 0.0029 (5) | 0.0003 (5) | 0.0003 (4) |
| C14 | 0.0151 (6) | 0.0150 (5) | 0.0166 (6) | −0.0003 (5) | −0.0027 (5) | 0.0014 (5) |
| C15 | 0.0209 (6) | 0.0146 (6) | 0.0173 (6) | −0.0005 (5) | 0.0000 (5) | −0.0012 (5) |

Geometric parameters (Å, °)

|   |        |   |        |   |        |   |
|---|--------|---|--------|---|--------|---|
| C1—C10 | 1.7219 (12) | C1—C2 | 1.3722 (16) | C2—C3 | 1.4143 (17) | C3—C4 | 1.4381 (17) |
| S1—C2 | 1.7450 (13) | C3—C4 | 1.5222 (19) | C5—C6 | 0.9900 | C5—H5A | 0.9900 | C6—H6A | 0.9800 |
| Bond                  | Distance (Å) | Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|----------------------|--------------|----------------------|--------------|----------------------|--------------|
| F4—C15               | 1.3333 (15)  | C6—H6B               | 0.9800       |                     |              |
| F5—C15               | 1.3381 (15)  | C6—H6C               | 0.9800       |                     |              |
| F6—C15               | 1.3327 (15)  | C7—C8                | 1.5421 (16)  |                     |              |
| O1—C7                | 1.2075 (15)  | C9—C10               | 1.3888 (17)  |                     |              |
| N1—N2                | 1.3511 (14)  | C9—C14               | 1.3898 (17)  |                     |              |
| N1—C1                | 1.3581 (16)  | C10—C11              | 1.3898 (17)  |                     |              |
| N1—C9                | 1.4264 (15)  | C11—C12              | 1.3865 (17)  |                     |              |
| N2—C3                | 1.3337 (16)  | C11—H11              | 0.9500       |                     |              |
| N3—C7                | 1.3540 (16)  | C12—C13              | 1.3877 (18)  |                     |              |
| N3—C1                | 1.4010 (15)  | C12—C15              | 1.5059 (17)  |                     |              |
| N3—H3N               | 0.855 (16)   | C13—C14              | 1.3843 (17)  |                     |              |
| N4—C4                | 1.1412 (17)  | C13—H13              | 0.9500       |                     |              |

| Bond                  | Distance (Å) | Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|----------------------|--------------|----------------------|--------------|----------------------|--------------|
| C2—S1—C5             | 101.08 (6)   | N3—C7—C8             | 113.4 (1)    |                     |              |
| N2—N1—C1             | 112.5 (1)    | F3—C8—F2             | 109.04 (10)  |                     |              |
| N2—N1—C9             | 120.69 (10)  | F3—C8—F1             | 108.0 (1)    |                     |              |
| C1—N1—C9             | 126.78 (10)  | F2—C8—F1             | 107.2 (1)    |                     |              |
| C3—N2—N1             | 103.54 (10)  | F3—C8—C7             | 110.44 (10)  |                     |              |
| C7—N3—C1             | 119.68 (10)  | F2—C8—C7             | 112.41 (10)  |                     |              |
| C7—N3—H3N            | 121 (1)      | F1—C8—C7             | 109.61 (10)  |                     |              |
| C1—N3—H3N            | 117.7 (10)   | C10—C9—C14           | 119.89 (11)  |                     |              |
| N1—C1—C2             | 107.7 (1)    | C10—C9—N1            | 120.19 (11)  |                     |              |
| N1—C1—N3             | 121.98 (10)  | C14—C9—N1            | 119.90 (11)  |                     |              |
| C2—C1—N3             | 130.32 (12)  | C9—C10—C11           | 120.71 (11)  |                     |              |
| C1—C2—C3             | 103.17 (11)  | C9—C10—C11           | 119.31 (9)   |                     |              |
| C1—C2—S1             | 126.61 (10)  | C11—C10—C11          | 119.97 (10)  |                     |              |
| C3—C2—S1             | 130.01 (9)   | C12—C11—C10          | 118.20 (11)  |                     |              |
| N2—C3—C2             | 113.09 (11)  | C12—C11—H11          | 120.9        |                     |              |
| N2—C3—C4             | 119.69 (11)  | C10—C11—H11          | 120.9        |                     |              |
| C2—C3—C4             | 127.21 (11)  | C11—C12—C13          | 122.05 (11)  |                     |              |
| N4—C4—C3             | 178.42 (15)  | C11—C12—C15          | 119.94 (11)  |                     |              |
| C6—C5—S1             | 108.17 (10)  | C13—C12—C15          | 118.00 (11)  |                     |              |
| C6—C5—H5A            | 110.1        | C14—C13—C12          | 118.84 (12)  |                     |              |
| S1—C5—H5A            | 110.1        | C14—C13—H13          | 120.6        |                     |              |
| C6—C5—H5B            | 110.1        | C12—C13—H13          | 120.6        |                     |              |
| S1—C5—H5B            | 110.1        | C13—C14—C9           | 120.27 (12)  |                     |              |
| H5A—C5—H5B           | 108.4        | C13—C14—C12          | 119.47 (10)  |                     |              |
| C5—C6—H6A            | 109.5        | C9—C14—C12           | 120.26 (9)   |                     |              |
| C5—C6—H6B            | 109.5        | F6—C15—F4            | 106.92 (11)  |                     |              |
| H6A—C6—H6B           | 109.5        | F6—C15—F5            | 107.08 (10)  |                     |              |
| C5—C6—H6C            | 109.5        | F4—C15—F5            | 106.75 (11)  |                     |              |
| H6A—C6—H6C           | 109.5        | F6—C15—C12           | 112.23 (11)  |                     |              |
| H6B—C6—H6C           | 109.5        | F4—C15—C12           | 111.94 (10)  |                     |              |
| O1—C7—N3             | 125.59 (11)  | F5—C15—C12           | 111.58 (11)  |                     |              |
| O1—C7—C8             | 120.96 (11)  | N3—C7—C8—F1          | 77.52 (13)   |                     |              |
| C1—N1—N2—C3          | −0.77 (14)   | N3—C7—C8—F1          | 77.52 (13)   |                     |              |
| C9—N1—N2—C3          | 177.32 (11)  | N2—N1—C9—C10         | 91.61 (15)   |                     |              |
N2—N1—C1—C2 0.79 (14)  C1—N1—C9—C10  −90.59 (15)
C9—N1—C1—C2 −177.16 (11)  N2—N1—C9—C14  −90.12 (14)
N2—N1—C1—N3 −179.23 (11)  C1—N1—C9—C14  87.67 (16)
C9—N1—C1—N3  2.82 (19)  C14—C9—C10—C11 −1.93 (18)
C7—N3—C1—N1 −111.17 (13)  N1—C9—C10—C11  176.34 (11)
C7—N3—C1—C2  68.80 (18)  C14—C9—C10—C11  177.67 (9)
N1—C1—C2—C3 −0.45 (13)  N1—C9—C10—C11 −4.06 (16)
N3—C1—C2—C3  179.58 (12)  C9—C10—C11—C12  0.37 (18)
N1—C1—C2—S1  174.65 (9)  C11—C10—C11—C12 −179.23 (9)
N3—C1—C2—S1 −5.30 (2)  C10—C11—C12—C13  1.06 (18)
C5—S1—C2—C1  101.74 (12)  C10—C11—C12—C13 −179.53 (11)
C5—S1—C2—C3 −84.50 (13)  C11—C12—C13—C14  0.90 (18)
N1—N2—C3—C2 −0.45 (14)  N1—C9—C10—C11 −176.18 (11)
N1—N2—C3—C4  179.48 (10)  C11—C9—C10—Cl2  3.11 (16)
C1—C2—C3—N2  10.00 (18)  C10—C9—C14—C13  2.09 (18)
C1—C2—C3—C4 −178.34 (12)  C10—C9—C14—C13 −176.18 (11)
N3—C1—C2—S1  0.47 (14)  C10—C9—C14—C13 −178.62 (9)
N1—N2—C3—C6 −173.93 (11)  C15—C12—C13—C14  3.11 (16)
N1—N2—C3—C4 −173.93 (11)  C10—C9—C14—C13 −178.62 (9)
C1—C2—C3—C6 −173.93 (11)  C10—C9—C14—C13  3.11 (16)
C1—C2—C3—N2 −173.93 (11)  C10—C9—C14—Cl2  3.11 (16)
C1—C2—C3—C4  173.93 (11)  C10—C9—C14—Cl2  3.11 (16)
N3—C1—C2—S1  173.93 (11)  C10—C9—C14—Cl2  3.11 (16)
C2—S1—C5—C6  3.8 (2)  C10—C9—C14—Cl2 −178.62 (9)
C2—S1—C5—C6  3.8 (2)  C10—C9—C14—Cl2 −178.62 (9)
C1—N3—C7—O1  10.00 (18)  C11—C12—C15—F6  20.04 (16)
C1—N3—C7—C8 −167.28 (10)  C13—C12—C15—F6 −161.43 (11)
O1—C7—C8—F3  18.96 (16)  C11—C12—C15—F6  −100.19 (13)
N3—C7—C8—F3 −163.61 (10)  C13—C12—C15—F6  78.33 (14)
O1—C7—C8—F2 −140.97 (12)  C11—C12—C15—F5  140.24 (12)
N3—C7—C8—F2 −140.97 (12)  C13—C12—C15—F5  −41.23 (16)
O1—C7—C8—F1 −99.91 (13)  C13—C12—C15—F5  −41.23 (16)

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| N3—H3V···O1i | 0.855 (16) | 2.034 (16) | 2.8172 (13) | 151.9 (14) |
| C5—H5B···F2ii | 0.99 | 2.58 | 3.5641 (16) | 174 |
| C11—H11···F5iii | 0.95 | 2.62 | 3.4873 (15) | 152 |
| C13—H13···F6iv | 0.95 | 2.39 | 3.2071 (15) | 144 |

Symmetry codes: (i) x+1/2, y, −z+1/2; (ii) −x+1, y−1/2, −z+1/2; (iii) x+1/2, −y+3/2, −z+1; (iv) x−1/2, −y+3/2, −z+1.