Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis{5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-1*H*-pyrazol-4-yl} disulfide acetonitrile disolvate

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Received 18 April 2005
Accepted 25 April 2005
Online 7 May 2005

Key indicators

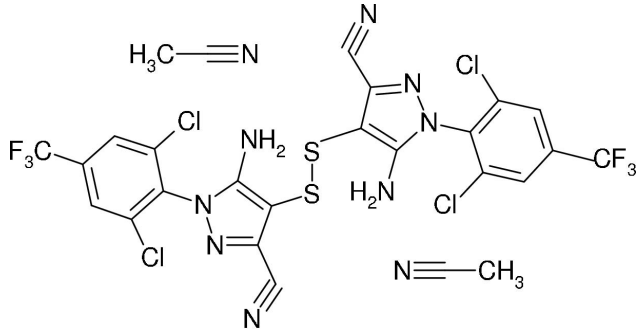
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.005 Å
R factor = 0.060
wR factor = 0.171
Data-to-parameter ratio = 13.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The disulfide moiety in the title compound, $C_{22}H_8Cl_4F_6N_8S_2\cdot 2C_2H_3N$, has an overall Z shape. The molecule possesses a crystallographically imposed twofold rotation axis. The pyrazole and adjacent benzene ring make a dihedral angle of 88.16 (12)°. Intermolecular N—H···N hydrogen bonds link the amine groups with the acetonitrile solvent molecules.

Comment

The title compound, (I) (Fig. 1), is an important starting material for the synthesis of a number of insecticides (Clavel *et al.*, 2003; Hatton *et al.*, 1993). The molecule of (I) has a central S—S fragment which links two 5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]pyrazol-4-yl groups and occupies a special position on a twofold rotation axis, which is normal to the S—S bond.. The pyrazole and adjacent benzene ring make a dihedral angle of 88.16 (12)°. One of the two amine group H atoms forms a hydrogen bond with the cyano N atom of an acetonitrile solvent molecule (Table 1).



(I)

Experimental

According to the method of Hatton *et al.* (1993), the reaction of 2,6-dichloro-4-(trifluoromethyl)aniline with a suspension of nitrosylsulfuric acid, followed by reaction with a solution of ethyl 2,3-dicyanopropionate in acetic acid, was used to obtain 5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-1*H*-pyrazole. According to the method of Clavel *et al.* (2003), to a solution of chlorobenzene (12.56 g) containing 5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-1*H*-pyrazole (7.33 g, 22.8 mmol), acetonitrile (16.74 g) was added, followed by the injection of sulfur monochloride (1.54 g 11.4 mmol). The title compound was obtained in 87.2% yield. Single crystals suitable for X-ray analysis were obtained by slow evaporation of an acetonitrile solution (m.p.575–577 K). IR (KBr, ν cm^{-1}): 3442, 3316, 2249, 1702, 1632, 1557, 1507, 1142, 881, 816; ^{1}H NMR ($CDCl_3$): δ 8.07 (*s*, 4H), 6.36 (*s*, 4H); ^{13}C NMR (C_3D_6O): δ 152.7 (2C), 137.5 (2C), 136.9 (2C), 134.7 (2C), 132.3 (2C), 127.3 (2C), 127.2 (4C), 127.1 (2C), 123.3 (2C), 113.2 (2C).

Crystal data

$C_{22}H_8Cl_4F_6N_8S_2\cdot 2C_2H_3N$
M_r = 786.39
Monoclinic, $C2/c$
a = 12.267 (3) Å
b = 13.083 (3) Å
c = 20.919 (6) Å
β = 92.423 (5)°
V = 3354.5 (15) Å^3
Z = 4
D_x = 1.557 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3364 reflections
θ = 2.3–25.0°
μ = 0.55 mm^{-1}
T = 298 (2) K
Block, yellow
0.45 × 0.34 × 0.27 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.791, T_{max} = 0.866
8406 measured reflections
2961 independent reflections
2520 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 25.2°
$h = -14 \rightarrow 8$
$k = -15 \rightarrow 15$
$l = -25 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.171
S = 1.04
2961 reflections
224 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0937P)^2 + 6.8928P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.95 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C10	1.729 (3)	N1—N2	1.374 (4)
S1—S1^{i}	2.0948 (19)	N1—C5	1.422 (4)
Cl1—C6	1.731 (3)	N2—C9	1.319 (4)
Cl2—C4	1.722 (3)	N3—C8	1.143 (5)
F1—C1	1.245 (6)	N4—C11	1.345 (4)
F2—C1	1.311 (7)	C8—C9	1.436 (5)
F3—C1	1.228 (6)	C9—C10	1.418 (5)
N1—C11	1.356 (4)	C10—C11	1.388 (4)
C10—S1—S1^{i}	104.82 (12)	N2—C9—C10	113.3 (3)
C11—N1—N2	113.3 (3)	N2—C9—C8	120.4 (3)
N2—N1—C5	120.5 (3)	C11—C10—C9	104.1 (3)
C9—N2—N1	103.2 (3)	C11—C10—S1	126.4 (3)
F3—C1—F1	112.1 (5)	C9—C10—S1	129.5 (2)
F3—C1—F2	100.8 (5)	N4—C11—N1	122.7 (3)
F1—C1—F2	100.3 (5)	N1—C11—C10	106.2 (3)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4B···N5^{ii}	0.82	2.26	3.060 (5)	164

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

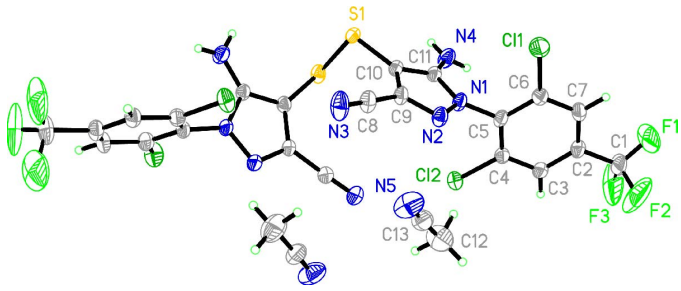


Figure 1
View of (I), showing the atom numbering scheme and displacement ellipsoids drawn at the 50% probability level. Unlabelled atoms are related to labelled atoms by $2-x, y, \frac{1}{2}-z$.

All H atoms were initially located in a difference Fourier map and then placed in geometrically idealized positions and included in the refinement in a riding-model approximation, with N—H = 0.82–0.83 Å, C—H = 0.93–0.96 Å and U_{iso}(H) = 1.2–1.5U_{eq} of the carrier atom. High displacement parameters for atoms F1, F2 and F3 indicated either large thermal motion or rotational disorder of the trifluoromethyl group. However, attempts to represent the CF_3 group using a model of disorder were unsuccessful. The inability to take properly into account the electron-density distribution in the vicinity of the CF_3 group is the most probable reason for the rather limited overall precision of the structure.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

This work was supported by the National Natural Science Foundation of China (grant No.20272043) and the Natural Science Foundation of Zhejiang Province (grant No. M203001).

References

Bruker (2002). *SMART*, *SAINT*, *SADABS* and *XP*. Bruker AXS Inc., Madison, Wisconsin, USA.
Clavel, J. L., Pelta, I., Bars, L. & Charreau, P. (2003). US Patent No. 6 620 943.
Hatton, L. R., Buntain, I. G., Hawkins, D. W., Parnell, E. W., Pearson C. J. & Roberts, D. A. (1993). US Patent No. 5 232 940.
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.