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5-Amino-1-[2-(4-chlorophenyl)-3-methylbutanoyl]-3-(methylsulfanyl)-1*H*-pyrazole-4-carbonitrile

Bao-Han Zhou

Chemical and Environmental Engineering Department, Hu Bei University of Technology, Wuhan 430068, People's Republic of China
Correspondence e-mail: zhoubaohan@mails.ccnu.edu.cn

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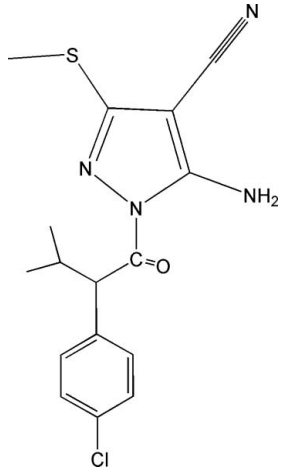
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.004 Å; R factor = 0.059; wR factor = 0.159; data-to-parameter ratio = 16.3.

The title compound, $C_{16}H_{17}ClN_4OS$, belongs to a class of pyrazole derivatives containing the pyrethroid unit. In the molecule, the mean planes of the pyrazole and benzene rings make a dihedral angle of 86.52 (16)°. In the crystal structure, molecules are linked into centrosymmetric dimers by weak intermolecular N—H···N hydrogen bonds.

Related literature

For preparation of the title compound, see: Kashima & Harada (1994). For details of the synthesis of heterocyclic compounds containing the pyrethroid unit attached to the N1 site, see Zhou *et al.* (2005). The biological activities of pyrazole derivatives have been discussed by Pande & Saxena (1987); Patel *et al.* (1990); Morimoto *et al.* (1990); Huang *et al.* (1996); Zhao *et al.* (2001).



Experimental

Crystal data

$C_{16}H_{17}ClN_4OS$
M_r = 348.85
Triclinic, $P\overline{1}$
a = 5.9962 (6) Å
b = 11.2616 (11) Å
c = 14.0125 (11) Å
α = 71.243 (2)°
β = 84.181 (2)°
γ = 83.948 (2)°
V = 888.68 (14) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.34 mm^{-1}
T = 294 (2) K
0.10 × 0.10 × 0.10 mm

Data collection

Bruker SMART 4 K CCD area-detector diffractometer
Absorption correction: none
6363 measured reflections
3440 independent reflections
2200 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.159
S = 1.00
3440 reflections
211 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···N4^{i}	0.86	2.15	3.007 (4)	175

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2274).

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supplementary materials

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5-Amino-1-[2-(4-chlorophenyl)-3-methylbutanoyl]-3-(methylsulfanyl)-1*H*-pyrazole-4-carbonitrile

B.-H. Zhou

Comment

Pyrazole and its derivatives represent one of the most active classes of compounds possessing a wide spectrum of biological activities. During the past years considerable evidence has been accumulated to demonstrate the efficacy of pyrazole derivatives including antibacterial (Patel *et al.*, 1990), anti-fungal (Zhao *et al.*, 2001), herbicidal (Morimoto *et al.*, 1990), insecticidal (Huang *et al.*, 1996) and other biological activities (Pande *et al.*, 1987). Up to now, a great variety of these kinds of compounds have been synthesized. Particularly, the synthesis of heterocyclic compounds containing pyrethroid moiety attached to the N1 site has attracted our attention (Zhou *et al.*, 2005). Here we report the structure of the title compound (I) (Fig. 1).

The molecular structure of (I) is shown in Fig. 1. In the crystal, the molecules are linked into centrosymmetric dimers by weak intermolecular N—H···N hydrogen bonds (Table 1).

Experimental

The title compound was synthesized according to the procedure of Kashima & Harada (1994) in 40% isolated yield. Crystals of (I) suitable for X-ray data collection were obtained by slow evaporation of acetone solution at 293 K.

Refinement

C-bound H atoms were positioned geometrically (C—H = 0.93–0.98 Å) and refined using a riding model, with U_{iso}(H) = 1.2–1.5U_{eq}(C). Atoms H3A and H3B were located in a difference map, placed in idealized positions (N—H = 0.86 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(N).

Figures

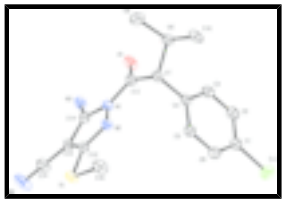


Fig. 1. The molecular structure of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms omitted for clarity.

5-Amino-1-[2-(4-chlorophenyl)-3-methylbutanoyl]-3-(methylsulfanyl)- 1*H*-pyrazole-4-carbonitrile

Crystal data

$C_{16}H_{17}ClN_4OS$	$Z = 2$
$M_r = 348.85$	$F_{000} = 364$

Triclinic, $P\bar{1}$	D_x = 1.304 Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 5.9962 (6) Å	Cell parameters from 1166 reflections
b = 11.2616 (11) Å	θ = 2.8–22.1º
c = 14.0125 (11) Å	μ = 0.34 mm^{-1}
α = 71.243 (2)º	T = 294 (2) K
β = 84.181 (2)º	Block, colourless
γ = 83.948 (2)º	0.10 × 0.10 × 0.10 mm
V = 888.68 (14) Å^3	

Data collection

Bruker SMART 4K CCD area-detector diffractometer	2200 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.033
Monochromator: graphite	θ_{max} = 26.0º
T = 294(2) K	θ_{min} = 1.5º
φ and ω scans	h = −7→7
Absorption correction: none	k = −12→13
6363 measured reflections	l = −17→17
3440 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.059	H-atom parameters constrained
$wR(F^2)$ = 0.159	$w = 1/[\sigma^2(F_o^2) + (0.0807P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.00	$(\Delta/\sigma)_{max} < 0.001$
3440 reflections	$\Delta\rho_{max}$ = 0.27 e Å^{-3}
211 parameters	$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.9577 (6)	0.7887 (3)	0.5095 (2)	0.0514 (8)
C2	1.0442 (5)	0.8888 (3)	0.4347 (2)	0.0516 (8)
H2	1.1774	0.9189	0.4426	0.062*
C3	0.9334 (5)	0.9439 (3)	0.3487 (2)	0.0485 (8)
H3	0.9936	1.0109	0.2980	0.058*
C4	0.7328 (5)	0.9017 (3)	0.3357 (2)	0.0375 (7)
C5	0.6489 (5)	0.8013 (3)	0.4125 (2)	0.0458 (7)
H5	0.5154	0.7710	0.4053	0.055*
C6	0.7586 (5)	0.7456 (3)	0.4993 (2)	0.0527 (8)
H6	0.6983	0.6794	0.5507	0.063*
C7	0.6143 (5)	0.9593 (2)	0.23917 (19)	0.0398 (7)
H7	0.4643	0.9281	0.2500	0.048*
C8	0.5883 (5)	1.1035 (3)	0.2017 (2)	0.0507 (8)
H8	0.7385	1.1348	0.1859	0.061*
C9	0.4625 (7)	1.1493 (4)	0.1053 (3)	0.0814 (12)
H9A	0.3171	1.1165	0.1189	0.122*
H9B	0.5464	1.1205	0.0538	0.122*
H9C	0.4450	1.2395	0.0828	0.122*
C10	0.4658 (6)	1.1546 (3)	0.2824 (3)	0.0644 (10)
H10A	0.3155	1.1282	0.2961	0.097*
H10B	0.4604	1.2448	0.2590	0.097*
H10C	0.5441	1.1229	0.3431	0.097*
C11	0.7512 (5)	0.9082 (3)	0.1613 (2)	0.0463 (7)
C12	0.5097 (5)	0.6291 (3)	0.19760 (19)	0.0421 (7)
C13	0.6965 (5)	0.6104 (3)	0.1310 (2)	0.0439 (7)
C14	0.8102 (5)	0.7179 (3)	0.1051 (2)	0.0439 (7)
C15	0.7501 (6)	0.5041 (3)	0.0980 (2)	0.0592 (9)
C16	0.1331 (6)	0.6033 (3)	0.3248 (3)	0.0696 (10)
H16A	0.2130	0.6039	0.3806	0.104*
H16B	−0.0020	0.5610	0.3499	0.104*
H16C	0.0950	0.6882	0.2841	0.104*
Cl1	1.10155 (17)	0.71653 (9)	0.61768 (7)	0.0799 (4)
N1	0.6925 (4)	0.7937 (2)	0.15689 (16)	0.0420 (6)
N2	0.5051 (4)	0.7364 (2)	0.21506 (16)	0.0437 (6)
N4	0.7914 (6)	0.4176 (3)	0.0726 (3)	0.0933 (12)
O1	0.9083 (4)	0.9579 (2)	0.10827 (16)	0.0684 (7)
N3	0.9937 (4)	0.7514 (2)	0.04463 (17)	0.0566 (8)
H3A	1.0618	0.7014	0.0139	0.068*
H3B	1.0444	0.8230	0.0362	0.068*
S1	0.30682 (15)	0.52251 (7)	0.24978 (6)	0.0559 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}

C1	0.057 (2)	0.0470 (19)	0.0510 (18)	−0.0014 (16)	−0.0035 (15)	−0.0177 (15)
C2	0.0394 (18)	0.053 (2)	0.066 (2)	−0.0092 (15)	−0.0043 (16)	−0.0226 (17)
C3	0.0473 (19)	0.0413 (18)	0.0557 (19)	−0.0088 (15)	0.0063 (15)	−0.0147 (15)
C4	0.0375 (16)	0.0342 (16)	0.0431 (15)	−0.0027 (13)	0.0072 (13)	−0.0184 (13)
C5	0.0440 (18)	0.0456 (18)	0.0482 (17)	−0.0112 (14)	0.0025 (14)	−0.0145 (15)
C6	0.060 (2)	0.0492 (19)	0.0464 (17)	−0.0135 (16)	0.0008 (16)	−0.0102 (15)
C7	0.0454 (17)	0.0336 (16)	0.0436 (15)	−0.0099 (13)	0.0041 (13)	−0.0165 (13)
C8	0.055 (2)	0.0357 (17)	0.0589 (19)	−0.0100 (15)	−0.0080 (16)	−0.0082 (15)
C9	0.104 (3)	0.059 (2)	0.074 (2)	−0.009 (2)	−0.031 (2)	−0.003 (2)
C10	0.066 (2)	0.0399 (19)	0.094 (3)	0.0003 (17)	−0.003 (2)	−0.0337 (19)
C11	0.055 (2)	0.0429 (18)	0.0425 (16)	−0.0123 (15)	0.0035 (15)	−0.0143 (14)
C12	0.0556 (19)	0.0329 (16)	0.0376 (15)	−0.0038 (14)	−0.0028 (14)	−0.0107 (13)
C13	0.061 (2)	0.0331 (16)	0.0396 (15)	−0.0056 (14)	0.0014 (14)	−0.0145 (13)
C14	0.0522 (19)	0.0432 (18)	0.0363 (15)	−0.0032 (15)	0.0010 (14)	−0.0139 (14)
C15	0.067 (2)	0.048 (2)	0.065 (2)	−0.0162 (17)	0.0192 (17)	−0.0243 (17)
C16	0.065 (2)	0.060 (2)	0.086 (3)	−0.0131 (19)	0.021 (2)	−0.032 (2)
Cl1	0.0835 (7)	0.0783 (7)	0.0732 (6)	−0.0088 (6)	−0.0319 (5)	−0.0085 (5)
N1	0.0510 (16)	0.0354 (14)	0.0412 (12)	−0.0087 (12)	0.0034 (11)	−0.0146 (11)
N2	0.0505 (16)	0.0378 (14)	0.0443 (13)	−0.0117 (12)	0.0051 (12)	−0.0151 (11)
N4	0.109 (3)	0.062 (2)	0.123 (3)	−0.031 (2)	0.052 (2)	−0.059 (2)
O1	0.0868 (18)	0.0602 (15)	0.0659 (14)	−0.0362 (14)	0.0334 (13)	−0.0329 (12)
N3	0.071 (2)	0.0521 (17)	0.0539 (16)	−0.0154 (15)	0.0173 (14)	−0.0291 (13)
S1	0.0664 (6)	0.0361 (5)	0.0661 (6)	−0.0130 (4)	0.0110 (4)	−0.0192 (4)

Geometric parameters (Å, °)

C1—C6	1.371 (4)	C10—H10A	0.9600
C1—C2	1.375 (4)	C10—H10B	0.9600
C1—Cl1	1.740 (3)	C10—H10C	0.9600
C2—C3	1.369 (4)	C11—O1	1.206 (3)
C2—H2	0.9300	C11—N1	1.394 (3)
C3—C4	1.388 (4)	C12—N2	1.305 (3)
C3—H3	0.9300	C12—C13	1.426 (4)
C4—C5	1.384 (4)	C12—S1	1.737 (3)
C4—C7	1.513 (4)	C13—C14	1.380 (4)
C5—C6	1.375 (4)	C13—C15	1.412 (4)
C5—H5	0.9300	C14—N3	1.327 (3)
C6—H6	0.9300	C14—N1	1.386 (3)
C7—C11	1.522 (4)	C15—N4	1.137 (4)
C7—C8	1.534 (4)	C16—S1	1.792 (3)
C7—H7	0.9800	C16—H16A	0.9600
C8—C10	1.520 (4)	C16—H16B	0.9600
C8—C9	1.527 (4)	C16—H16C	0.9600
C8—H8	0.9800	N1—N2	1.404 (3)
C9—H9A	0.9600	N3—H3A	0.8600
C9—H9B	0.9600	N3—H3B	0.8600
C9—H9C	0.9600		
C6—C1—C2	120.4 (3)	H9B—C9—H9C	109.5
C6—C1—Cl1	119.9 (2)	C8—C10—H10A	109.5

C2—C1—Cl1	119.7 (3)	C8—C10—H10B	109.5
C3—C2—C1	119.7 (3)	H10A—C10—H10B	109.5
C3—C2—H2	120.1	C8—C10—H10C	109.5
C1—C2—H2	120.1	H10A—C10—H10C	109.5
C2—C3—C4	121.2 (3)	H10B—C10—H10C	109.5
C2—C3—H3	119.4	O1—C11—N1	119.9 (3)
C4—C3—H3	119.4	O1—C11—C7	124.0 (3)
C5—C4—C3	117.7 (3)	N1—C11—C7	116.0 (2)
C5—C4—C7	120.9 (3)	N2—C12—C13	112.7 (2)
C3—C4—C7	121.3 (3)	N2—C12—S1	122.9 (2)
C6—C5—C4	121.4 (3)	C13—C12—S1	124.4 (2)
C6—C5—H5	119.3	C14—C13—C15	127.7 (3)
C4—C5—H5	119.3	C14—C13—C12	105.7 (2)
C1—C6—C5	119.4 (3)	C15—C13—C12	126.6 (3)
C1—C6—H6	120.3	N3—C14—C13	131.3 (3)
C5—C6—H6	120.3	N3—C14—N1	123.0 (3)
C4—C7—C11	105.3 (2)	C13—C14—N1	105.7 (2)
C4—C7—C8	115.2 (2)	N4—C15—C13	179.1 (4)
C11—C7—C8	111.0 (2)	S1—C16—H16A	109.5
C4—C7—H7	108.4	S1—C16—H16B	109.5
C11—C7—H7	108.4	H16A—C16—H16B	109.5
C8—C7—H7	108.4	S1—C16—H16C	109.5
C10—C8—C9	110.4 (3)	H16A—C16—H16C	109.5
C10—C8—C7	110.9 (2)	H16B—C16—H16C	109.5
C9—C8—C7	109.9 (2)	C14—N1—C11	127.3 (2)
C10—C8—H8	108.5	C14—N1—N2	111.5 (2)
C9—C8—H8	108.5	C11—N1—N2	120.9 (2)
C7—C8—H8	108.5	C12—N2—N1	104.3 (2)
C8—C9—H9A	109.5	C14—N3—H3A	120.0
C8—C9—H9B	109.5	C14—N3—H3B	120.0
H9A—C9—H9B	109.5	H3A—N3—H3B	120.0
C8—C9—H9C	109.5	C12—S1—C16	100.40 (14)
H9A—C9—H9C	109.5		
C6—C1—C2—C3	−1.5 (5)	S1—C12—C13—C14	178.1 (2)
Cl1—C1—C2—C3	178.7 (2)	N2—C12—C13—C15	179.5 (3)
C1—C2—C3—C4	0.8 (5)	S1—C12—C13—C15	−1.1 (4)
C2—C3—C4—C5	−0.3 (4)	C15—C13—C14—N3	0.0 (6)
C2—C3—C4—C7	−177.8 (3)	C12—C13—C14—N3	−179.2 (3)
C3—C4—C5—C6	0.5 (4)	C15—C13—C14—N1	−179.9 (3)
C7—C4—C5—C6	178.0 (3)	C12—C13—C14—N1	0.9 (3)
C2—C1—C6—C5	1.7 (5)	C14—C13—C15—N4	161 (28)
Cl1—C1—C6—C5	−178.5 (2)	C12—C13—C15—N4	−20 (29)
C4—C5—C6—C1	−1.2 (4)	N3—C14—N1—C11	−5.3 (5)
C5—C4—C7—C11	−102.5 (3)	C13—C14—N1—C11	174.7 (3)
C3—C4—C7—C11	74.9 (3)	N3—C14—N1—N2	179.8 (3)
C5—C4—C7—C8	134.9 (3)	C13—C14—N1—N2	−0.3 (3)
C3—C4—C7—C8	−47.8 (4)	O1—C11—N1—C14	8.0 (5)
C4—C7—C8—C10	−56.5 (3)	C7—C11—N1—C14	−169.1 (3)
C11—C7—C8—C10	−176.0 (2)	O1—C11—N1—N2	−177.5 (3)

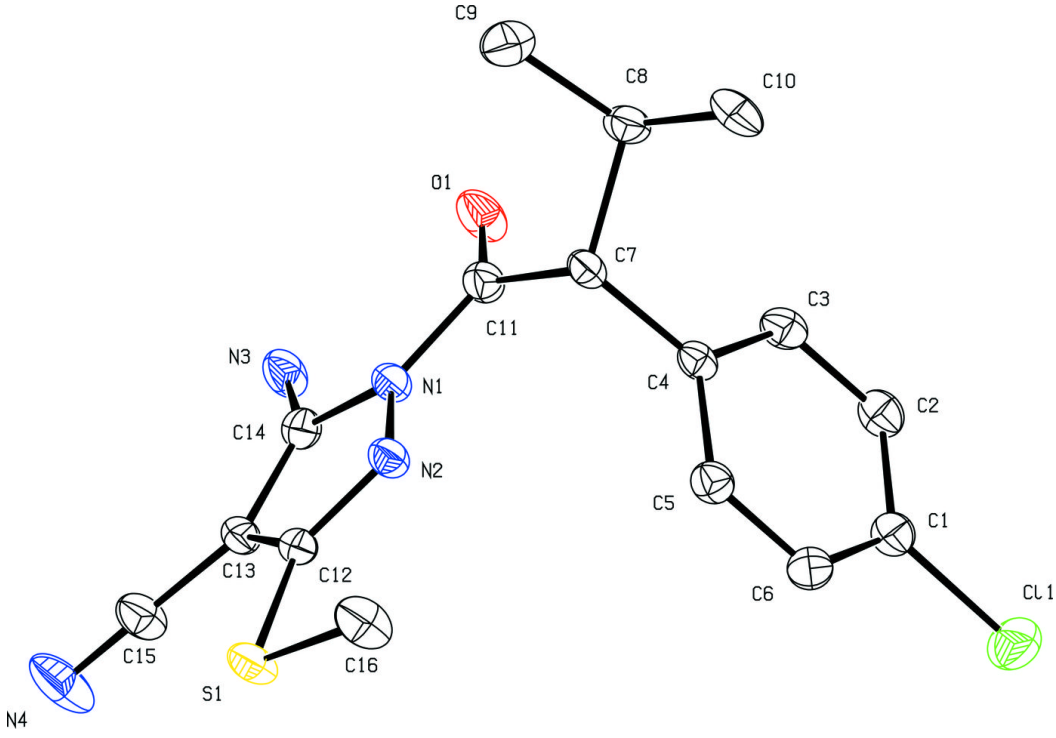
C4—C7—C8—C9	−178.9 (3)	C7—C11—N1—N2	5.4 (4)
C11—C7—C8—C9	61.6 (3)	C13—C12—N2—N1	1.1 (3)
C4—C7—C11—O1	−89.2 (3)	S1—C12—N2—N1	−178.29 (19)
C8—C7—C11—O1	36.1 (4)	C14—N1—N2—C12	−0.5 (3)
C4—C7—C11—N1	87.8 (3)	C11—N1—N2—C12	−175.8 (3)
C8—C7—C11—N1	−147.0 (3)	N2—C12—S1—C16	−1.6 (3)
N2—C12—C13—C14	−1.4 (3)	C13—C12—S1—C16	179.0 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7···N2	0.98	2.35	2.789 (3)	107
N3—H3B···O1	0.86	2.13	2.731 (3)	126
N3—H3A···N4^{i}	0.86	2.15	3.007 (4)	175

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*.

Fig. 1


C9
C8
C10
O1
C7
C11
C3
N3
N1
C4
C2
C14
N2
C5
C1
C13
C12
C6
Cl1
C15
C16
S1
N4