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6-Dichloromethyl-3-propyl-1,2,4-triazolo[3,4-*b*][1,3,4]thiadiazole

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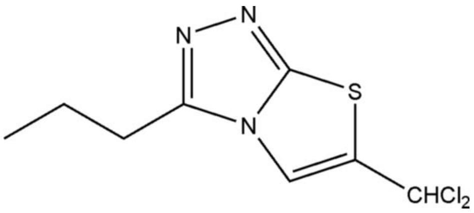
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.039; wR factor = 0.101; data-to-parameter ratio = 14.7.

In the title compound, $C_7H_8Cl_2N_4S$, the triazole ring and the thiadiazole ring are each planar and the C—N and N—N distances in the triazole ring indicate partial electron localization of the double bonds over the ring. π–π stacking interactions between the thiadiazole and triazole rings of neigboring molecules [centroid-to-centroid distance 3.8520 (15) Å] and close contacts between the N and S atoms of neighboring molecules are observed in the crystal structure.

Related literature

For related literature, see: Al-Soud *et al.* (2004); Colanceska-Ragenovic *et al.* (2001); Cozzolino *et al.* (2005); Foroumadi *et al.* (2001); Gupta *et al.* (1984); Hirpara *et al.* (2003); Jain & Mishra (2004); Labanauskas *et al.* (2004); Lei, Huang *et al.* (2006); Lei, Zhang *et al.* (2006); Swamy *et al.* (2006); Udupi *et al.* (1999); Wang *et al.* (1996); Zhang *et al.* (1996).



Experimental

Crystal data

$C_7H_8Cl_2N_4S$	V = 2105.8 (6) Å^3
M_r = 251.13	Z = 8
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
a = 21.116 (4) Å	μ = 0.78 mm^{-1}
b = 5.1836 (9) Å	T = 298 (2) K
c = 19.781 (3) Å	0.35 × 0.19 × 0.18 mm
β = 103.440 (3)°	

Data collection

Bruker APEX area-detector diffractometer	5254 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)	1880 independent reflections
T_{min} = 0.772, T_{max} = 0.872	1678 reflections with $I > 2\sigma(I)$
	R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039	128 parameters
$wR(F^2)$ = 0.101	H-atom parameters constrained
S = 1.06	$\Delta\rho_{max}$ = 0.40 e Å^{-3}
1880 reflections	$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N2—C3	1.365 (3)	N3—N4	1.409 (3)
N2—C4	1.369 (3)	N4—C4	1.307 (3)
N3—C3	1.299 (3)		
C3—N2—C4	106.2 (2)	N3—C3—N2	110.9 (2)
C3—N3—N4	105.6 (2)	N4—C4—N2	108.2 (2)
C4—N4—N3	109.1 (2)		

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: *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2015).

References

Al-Soud, Y. A., Al-Dweri, M. N. & Al-Masoudi, N. A. (2004). *Farmaco*, **59**, 775–783.
Bruker (2002). *SADABS* (Version 2.03), *SAINT* (Version 6.02), *SMART* (Version 5.62) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.
Colanceska-Ragenovic, K., Dimova, V., Kakurinov, V., Labor, D. & Molnar, A. B. (2001). *Molecules*, **6**, 815–824.
Cozzolino, A. F., Vargas-Baca, I., Mansour, S. & Mahmoudkhani, A. H. (2005). *J. Am. Chem. Soc.* **127**, 3184–3190.
Foroumadi, A., Mirzaei, M. & Shafiee, A. (2001). *Farmaco*, **56**, 621–625.
Gupta, R., Sudan, S. & Kachroo, P. L. (1984). *Indian J. Chem. Sect. B*, **23**, 793–798.
Hirpara, H. M., Sodha, V. A., Trivedi, A. M., Khatri, B. L. & Parikh, A. R. (2003). *Indian J. Chem. Sect. B*, **42**, 1756–1759.
Jain, S. K. & Mishra, P. (2004). *Indian J. Chem. Sect. B*, **43**, 184–188.
Labanauskas, L., Udrenaite, E., Gaidelis, P. & Bruktus, A. (2004). *Farmaco*, **59**, 255–259.
Lei, X.-X., Huang, X.-B., Zhang, A.-J. & Zhang, L.-X. (2006). *Acta Cryst.* E**62**, o4416–o4417.
Lei, X.-X., Zhang, A.-J., Huang, X.-B. & Zhang, L.-X. (2006). *Acta Cryst.* E**62**, o4418–o4419.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Swamy, S. N., Basappa, B. S., Prabhuswamy, P. B., Doreswamy, B. H., Prasad, J. S. & Rangappa, K. S. (2006). *Eur. J. Med. Chem.* **41**, 531–538.
Udupi, R. H., Kushnoor, A. & Bhat, A. R. (1999). *J. Indian Chem. Soc.* **76**, 461–462.
Wang, Z., You, T., Xu, Y., Haijian, S. & Haoxin, S. (1996). *Molecules*, **1**, 68–75.
Zhang, Z.-Y., Zou, N., Zhu, Y., Zhao, L. & Li, M. (1996). *Acta Cryst.* C**52**, 2787–2789.

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supplementary materials

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6-Dichloromethyl-3-propyl-1,2,4-triazolo[3,4-*b*][1,3,4]thiadiazole

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Comment

1,2,4-Triazole and 1,3,4-thiadiazoles represent one of the most biologically active classes of compounds, possessing a wide spectrum of activities (Colanceska-Ragenovic *et al.*, 2001; Labanauskas *et al.*, 2004; Al-Soud *et al.*, 2004; Foroumadi *et al.*, 2001; Jain & Mishra, 2004). Various substituted 1,2,4-triazolo[3,4-b]-1,3,4-thiadiazoles and their dihydro analogues are associated with diverse pharmacological activities such as antimicrobial (Swamy *et al.*, 2006), antibacterial (Wang *et al.*, 1996), antitubercular (Udupi *et al.*, 1999), anti-inflammatory (Gupta *et al.*, 1984), and antifungal (Hirpara *et al.*, 2003). If a dichloromethyl group is attached to the parent molecule, many new compounds can be obtained, such as aldehydes and their nucleophilic addition products. In view of these observations and our continued interest in the synthesis of biologically active heterocyclic compounds, we thought it worthwhile to synthesize new fused heterocyclic compounds which possess a dichloromethyl group as the biological activities may be improved many times over that of their parent compounds when incorporating biologically active groups that might interact with the microstructure of the cell.

In the molecule of (I) (Fig. 1), both the five-membered triazole ring as well as the thiadiazole ring are each planar, and the angle between both rings is bascically zero, thus indicating sp^2 hybridization for all carbon and nitrogen atoms of the heterocyclic rings. The short C—N bond lengths of 1.286 (3), 1.307 (3) and 1.299 (3) for N1—C2, C4—N4, and C3—N3, respectively, suggest partially localized double bonds localized as shown in scheme 1.

In the solid state each two molecules of (I) are arranged around an inversion center to form pairs of weakly π-π stacked dimers (symmetry operator 1/2-x, 1/2-y, -z), the centroid-to-centroid distances between the thiadiazole and triazole rings of neigboring molecules are 3.8520 (15) Å. Within the plane of the planar rings (I) forms another type of a loosely connected centrosymmetric dimers via close intermolecular contacts between the nitrogen atoms N3 and the sulfur atom S1 of neighboring molecules with N—S distances of 2.847 (2) Å (symmetry operator 1/2-x, 3/2-y, -z). This type of close contacts of chalcogens when with a more electronegative atom such as nitrogen or oxygen is not untypical and the interaction is usually interpreted as the donation of a nitrogen lone pair into the chalcogen-centered antibonding orbitals (Cozzolino *et al.*, 2005).

Experimental

A mixture of thiocarbohydrazide (0.03 mol) and butyric acid (0.03 mol) was refluxed for 4 h. Then the solution was cooled , and unreacted butyric acid was completely removed in vacuo. The resulting 3-propyl-4-amino-5-mercapto-1,2,4-triazole was first purified by reprecipitation using ethanol. Then, a mixture of 3-propyl-4-amino-5-mercapto-1,2,4-triazole (5.0 mmol) and dichloroacetic acid (5.5 mmol) in phosphorous oxychloride (20 ml) was heated to reflux for 7 h. The reaction mixture was poured gradually onto crushed ice with stirring. Some solid potassium carbonate was added to the mixture with stirring, then a appropriate amount of solid potassium hydroxide was added till the pH value was 8. The separated solid after standing overnight was filtered, washed with cold water, dried, and recrystallized from absolute alcohol to afford the title compounds 3-propyl-6-dichloromethyl-1,2,4-triazolo[3,4-b]- 1,3,4-thiadiazole [m.p. 340-341 K] in about 58.9% yield. IR (KBr): 2973, 2920 (RH), 1628 (C=N), 1513, 1464 (aromatic ring skeleton vibration), 1258 (N—N=C), 812, 739 (C—Cl), 695 (C—S—C) cm^{-1}. ^{1}H NMR (DMSO-d$_6$): 0.96 (t, 3H, -CH$_2$), 1.76-1.84 (m, 2H, -CH$_2$-), 2.97-3.02 (m, 2H, -CH$_2$-), 5.22, 8.03 (s, H, -CHCl$_2$) ppm. ^{13}C NMR (DMSO-d$_6$): 13.56 (-CH$_3$), 19.67, 26.18, 39.42 (-CH$_2$-), 64.46 (-CHCl$_2$), 147.93, 152.70, 167.04 (fused heterocycle carbon) ppm.

Refinement

All H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of Csp^2—H = 0.93 Å with U_{iso}=1.2U_{eq}(parent atom), and Csp^3—H = 0.96 or 0.97 Å with U_{iso}=1.5U_{eq}(parent atom).

Figures

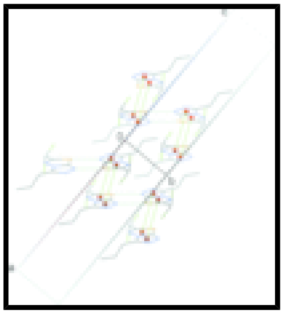
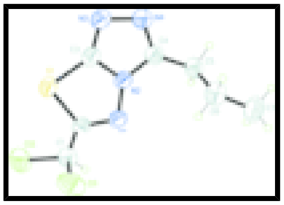


Fig. 1 The molecular structure of (I) with the atom numbering scheme, showing displacement ellipsoids at the 30% probability level.
Fig. 2 Packing diagram for (I), showing the short contacts between N3 and S1 (blue dashed lines) and the π-π stacking interactions (green dotted lines).



6-Dichloromethyl-3-propyl-1,2,4-triazolo[3,4-b][1,3,4]thiadiazole

Crystal data

$C_7H_8Cl_2N_4S$	F_{000} = 1024
M_r = 251.13	D_x = 1.584 Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 2080 reflections
a = 21.116 (4) Å	θ = 2.5–25.0°
b = 5.1836 (9) Å	μ = 0.78 mm^{-1}
c = 19.781 (3) Å	T = 298 (2) K
β = 103.440 (3)°	Rod, colorless

$V = 2105.8$ (6) Å^3	0.35 × 0.19 × 0.18 mm
$Z = 8$	

Data collection

Bruker APEX area-detector diffractometer	1880 independent reflections
Radiation source: fine-focus sealed tube	1678 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.020$
$T = 298(2)$ K	$\theta_{\text{max}} = 25.2°$
φ and ω scans	$\theta_{\text{min}} = 2.0°$
Absorption correction: multi-scan (SADABS; Bruker, 2002)	$h = -20\rightarrow24$
$T_{\text{min}} = 0.772$, $T_{\text{max}} = 0.872$	$k = -6\rightarrow6$
5254 measured reflections	$l = -23\rightarrow21$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2 + 2.565P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$wR(F^2) = 0.101$	$\Delta\rho_{\text{max}} = 0.40$ e Å^{-3}
$S = 1.06$	$\Delta\rho_{\text{min}} = -0.30$ e Å^{-3}
1880 reflections	Extinction correction: none
128 parameters	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: inferred from neighbouring sites	

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.

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 > 2sigma(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}
S1	0.19565 (3)	0.03777 (12)	0.90696 (3)	0.0436 (2)

Cl1	0.17703 (4)	0.25892 (16)	0.72291 (3)	0.0635 (3)
Cl2	0.09661 (4)	0.4437 (2)	0.81287 (4)	0.0754 (3)
N1	0.28183 (9)	0.3513 (4)	0.87479 (10)	0.0403 (5)
N2	0.31298 (9)	0.1848 (4)	0.92536 (10)	0.0388 (5)
N3	0.31385 (10)	−0.1427 (4)	0.99590 (11)	0.0511 (6)
N4	0.37773 (11)	−0.0510 (4)	1.00200 (12)	0.0519 (6)
C1	0.17588 (12)	0.4254 (5)	0.80105 (13)	0.0427 (6)
H1	0.1920	0.6011	0.7976	0.051*
C2	0.22106 (11)	0.2914 (4)	0.86033 (12)	0.0373 (5)
C3	0.27697 (12)	0.0023 (5)	0.94926 (12)	0.0408 (6)
C4	0.37629 (12)	0.1447 (5)	0.96000 (12)	0.0442 (6)
C5	0.43185 (12)	0.2989 (5)	0.94811 (13)	0.0486 (6)
H5A	0.4706	0.2527	0.9830	0.058*
H5B	0.4231	0.4801	0.9542	0.058*
C6	0.44528 (14)	0.2615 (6)	0.87671 (16)	0.0564 (7)
H6A	0.4586	0.0845	0.8722	0.068*
H6B	0.4055	0.2914	0.8416	0.068*
C7	0.49772 (15)	0.4413 (7)	0.86391 (18)	0.0708 (9)
H7A	0.4853	0.6167	0.8696	0.106*
H7B	0.5031	0.4170	0.8175	0.106*
H7C	0.5380	0.4044	0.8965	0.106*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0417 (4)	0.0432 (4)	0.0470 (4)	−0.0081 (3)	0.0126 (3)	0.0023 (3)
Cl1	0.0646 (5)	0.0792 (5)	0.0429 (4)	0.0160 (4)	0.0047 (3)	−0.0107 (3)
Cl2	0.0481 (4)	0.1088 (7)	0.0736 (5)	0.0196 (4)	0.0228 (4)	0.0109 (5)
N1	0.0439 (11)	0.0403 (11)	0.0374 (11)	−0.0030 (9)	0.0109 (8)	0.0041 (9)
N2	0.0417 (11)	0.0381 (11)	0.0362 (10)	−0.0054 (9)	0.0085 (8)	0.0031 (8)
N3	0.0512 (13)	0.0497 (13)	0.0510 (13)	−0.0063 (10)	0.0091 (10)	0.0119 (11)
N4	0.0496 (13)	0.0537 (13)	0.0497 (13)	−0.0028 (10)	0.0065 (10)	0.0080 (11)
C1	0.0424 (13)	0.0409 (13)	0.0459 (14)	0.0030 (11)	0.0122 (11)	−0.0030 (11)
C2	0.0413 (13)	0.0366 (12)	0.0360 (12)	−0.0032 (10)	0.0131 (10)	−0.0025 (10)
C3	0.0432 (13)	0.0405 (13)	0.0403 (13)	−0.0069 (11)	0.0128 (10)	−0.0008 (10)
C4	0.0413 (13)	0.0499 (15)	0.0399 (13)	−0.0033 (11)	0.0063 (10)	−0.0004 (11)
C5	0.0397 (13)	0.0518 (15)	0.0524 (15)	−0.0084 (11)	0.0072 (11)	−0.0021 (12)
C6	0.0539 (16)	0.0562 (17)	0.0619 (18)	−0.0044 (13)	0.0192 (13)	−0.0025 (13)
C7	0.0619 (19)	0.077 (2)	0.083 (2)	−0.0040 (16)	0.0351 (17)	0.0057 (18)

Geometric parameters (Å, °)

S1—C3	1.736 (3)	C1—H1	0.9800
S1—C2	1.760 (2)	C4—C5	1.483 (3)
Cl1—C1	1.775 (2)	C5—C6	1.516 (4)
Cl2—C1	1.746 (2)	C5—H5A	0.9700
N1—C2	1.286 (3)	C5—H5B	0.9700
N1—N2	1.368 (3)	C6—C7	1.513 (4)
N2—C3	1.365 (3)	C6—H6A	0.9700

N2—C4	1.369 (3)	C6—H6B	0.9700
N3—C3	1.299 (3)	C7—H7A	0.9600
N3—N4	1.409 (3)	C7—H7B	0.9600
N4—C4	1.307 (3)	C7—H7C	0.9600
C1—C2	1.499 (3)		

C3—S1—C2	86.78 (11)	N4—C4—C5	128.1 (2)
C2—N1—N2	107.21 (18)	N2—C4—C5	123.7 (2)
C3—N2—N1	118.59 (19)	C4—C5—C6	113.9 (2)
C3—N2—C4	106.2 (2)	C4—C5—H5A	108.8
N1—N2—C4	135.2 (2)	C6—C5—H5A	108.8
C3—N3—N4	105.6 (2)	C4—C5—H5B	108.8
C4—N4—N3	109.1 (2)	C6—C5—H5B	108.8
C2—C1—Cl2	112.10 (17)	H5A—C5—H5B	107.7
C2—C1—Cl1	108.72 (17)	C7—C6—C5	112.3 (2)
Cl2—C1—Cl1	110.52 (14)	C7—C6—H6A	109.1
C2—C1—H1	108.5	C5—C6—H6A	109.1
Cl2—C1—H1	108.5	C7—C6—H6B	109.1
Cl1—C1—H1	108.5	C5—C6—H6B	109.1
N1—C2—C1	118.9 (2)	H6A—C6—H6B	107.9
N1—C2—S1	118.26 (18)	C6—C7—H7A	109.5
C1—C2—S1	122.67 (17)	C6—C7—H7B	109.5
N3—C3—N2	110.9 (2)	H7A—C7—H7B	109.5
N3—C3—S1	140.0 (2)	C6—C7—H7C	109.5
N2—C3—S1	109.12 (17)	H7A—C7—H7C	109.5
N4—C4—N2	108.2 (2)	H7B—C7—H7C	109.5

Fig. 1

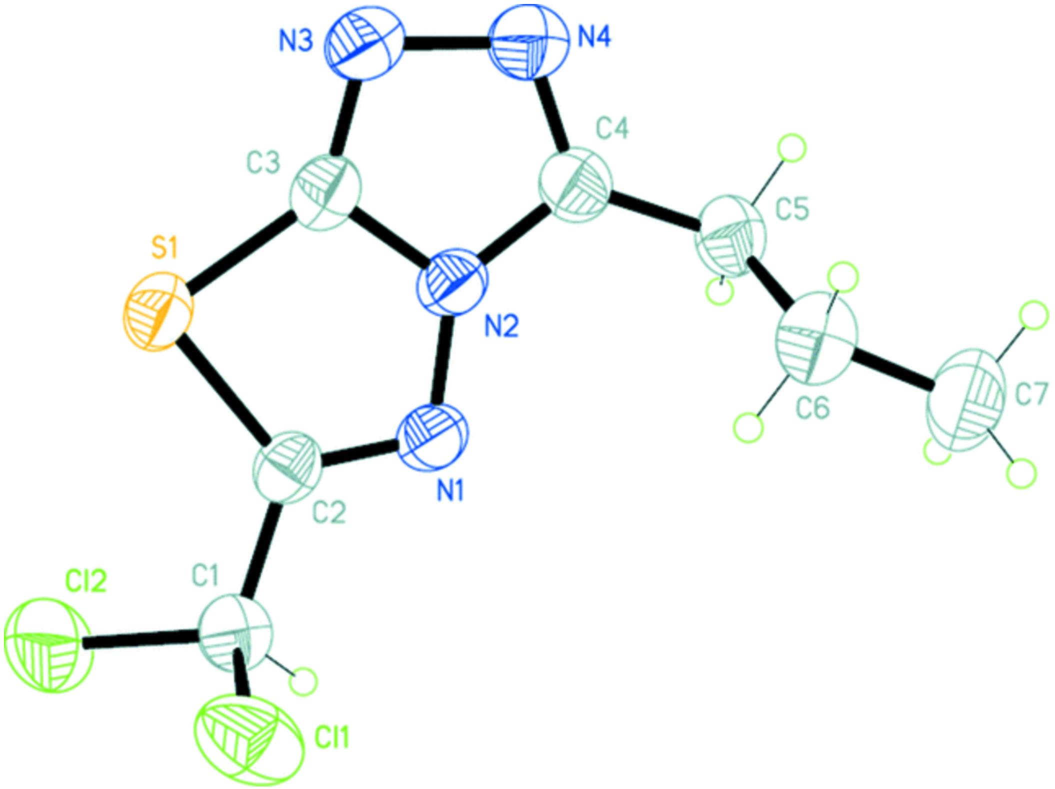


Fig. 2

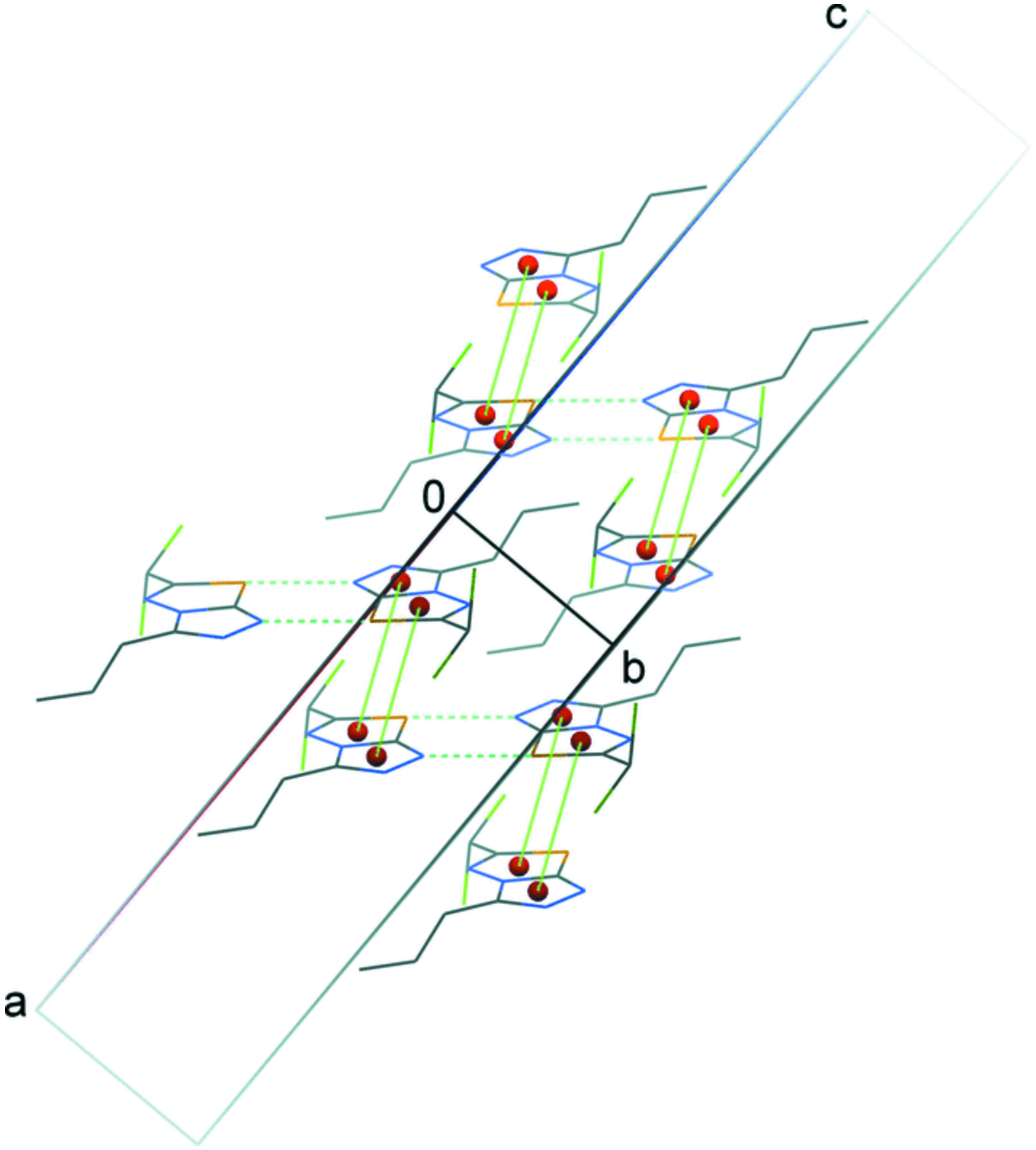


Fig. 3