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1-(2,2-Dimethylcyclopropylcarbonyl)-3-(2-pyridyl)thiourea

Jing Wang, Li Tian* and Shang-Yuan Liu

College of Chemistry and Life Science, Tianjin Normal University, Tianjin 300074, People's Republic of China
Correspondence e-mail: lilytianli@gmail.com

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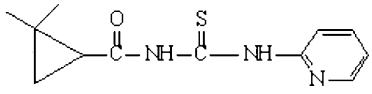
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.003 Å; R factor = 0.042; wR factor = 0.121; data-to-parameter ratio = 15.2.

In the molecule of the title compound, $C_{12}H_{15}N_3OS$, an intramolecular N—H···O hydrogen bond causes the formation of a planar six-membered ring (*A*). Dihedral angles between this and the cyclopropane (B) and pyridine (C) rings are: *A*/*B* = 79.14 (3)°, *A*/*C* = 14.60 (2)° and *B*/*C* = 83.45 (3)°. In the crystal structure, intermolecular N—H···N hydrogen bonds link the molecules.

Related literature

For general background, see: Langcake *et al.* (1983); Adams & Yang (1979); Nadler *et al.* (1988); Kamala & Rao (1989); Elbert *et al.* (2000). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{12}H_{15}N_3OS$
M_r = 249.33
Orthorhombic, *Pbca*
a = 13.785 (5) Å
b = 10.664 (4) Å
c = 18.233 (6) Å
V = 2680.2 (16) Å^3
Z = 8
Mo *K*α radiation
μ = 0.23 mm^{-1}
T = 294 (2) K
0.24 × 0.22 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.737, T_{max} = 0.950
13556 measured reflections
2371 independent reflections
1825 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.121
S = 1.06
2371 reflections
156 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.50 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O1	0.86	1.93	2.648 (2)	141
N3—H3*A*···N1^{i}	0.86	2.13	2.982 (3)	170

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); 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, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2302).

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supplementary materials

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1-(2,2-Dimethylcyclopropylcarbonyl)-3-(2-pyridyl)thiourea

J. Wang, L. Tian and S.-Y. Liu

Comment

Cyclopropane derivatives have several biological activities. 2,2-Dichloro-3,3 -dimethylcyclopropanecarboxylic acid is an effective inducer against the rice blast fungus (Langcake *et al.*, 1983). 1-Aminocyclopropane-1-carboxylic acid (ACC) is an intermediate in the biosynthesis of the ripening hormone ethylene (Adams & Yang, 1979), a component of bacterial phytotoxines, and azetidine-2 -carboxylic acid (Nadler *et al.*, 1988). Thus, it is very important to synthesize other new compounds containing cyclopropane, and study their biological activities. Acyl thiourea derivatives have many biological activities, for example, they have been used as bactericides, fungicides and insecticides in many plants (Kamala & Rao, 1989). A pyridine ring is often used as an active component in pesticide discovery (Elbert *et al.*, 2000). The title compound, (I), contains all these three active parts and may show some insecticidal activity. It was characterized by ^{1}H NMR and elemental analysis, and we report herein its crystal structure.

In the molecule of the title compound, (I), (Fig. 1) the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). The intramolecular N—H···O hydrogen bond (Table 1) causes to the formation of a six-membered planar ring A (H2A/N2/C6/N3/C7/O1). Rings B (C8—C10) and C (N1/C1—C5) are, of course, planar and the dihedral angles between them are A/B = 79.14 (3)°, A/C = 14.60 (2)° and B/C = 83.45 (3)°.

In the crystal structure, intermolecular N—H···N hydrogen bonds (Table 1) link the molecules (Fig. 2). The intra- and intermolecular hydrogen bonds seem to be effective in the stabilization of the crystal structure.

Experimental

To a solution of NaSCN (0.49 g, 6 mmol) in anhydrous acetonitrile (10 ml) was added dropwise a solution of 2,2-dimethyl-cycloprpopanecarbonyl chloride (0.60 g, 4.5 mmol) in anhyrous acetonitrile (3 ml) at room temperature. The reaction mixture was kept at room temperature for half an hour and then at 333 K for 3 h. The solution was cooled, filtered and concentrated to about 4 ml. The residue was added dropwise to a solution of 2-aminopyridine (0.42 g, 4.5 mmol) in anhydrous acetonitrile (8 ml) at room temperature. The rection mixture refluxed for 5 h, and then was concentrated. The residue was separated by silica gel chromatography to afford the title compound, (I). Yellow single crystals were grown from a solution of AcOEt-cyclohexane (1:4).

Refinement

H atoms were positioned geometrically with N—H = 0.86 Å (for NH), C—H = 0.93, 0.98, 0.97 and 0.96 Å for aromatic, methine, methylene and methyl H atoms, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C,*N*), where x = 1.5 for methyl H, and x = 1.2 for all other H atoms.

Figures

Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. Hydrogen bonds are shown as dashed lines.

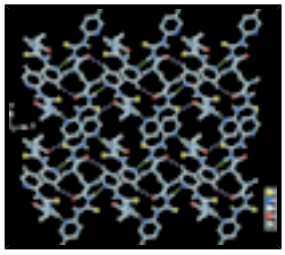

Fig. 2. A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

Fig. 3. The formation of the title compound.

1-(2,2-Dimethylcyclopropylcarbonyl)-3-(2-pyridyl)thiourea

Crystal data

$C_{12}H_{15}N_3OS$	D_x = 1.236 Mg m^{-3}
M_r = 249.33	Melting point: 365 K
Orthorhombic, *Pbca*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2ac 2ab	Cell parameters from 3793 reflections
a = 13.785 (5) Å	θ = 2.2–23.3º
b = 10.664 (4) Å	μ = 0.23 mm^{-1}
c = 18.233 (6) Å	*T* = 294 (2) K
V = 2680.2 (16) Å^3	Block, colorless
Z = 8	0.24 × 0.22 × 0.20 mm
F_{000} = 1056	

Data collection

Bruker SMART CCD area-detector diffractometer	2371 independent reflections
Radiation source: fine-focus sealed tube	1825 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.024
T = 294(2) K	θ_{max} = 25.0º
φ and ω scans	θ_{min} = 2.2º
Absorption correction: multi-scan (SADABS; Bruker, 1997)	*h* = −16→15
T_{min} = 0.737, T_{max} = 0.950	*k* = −12→10
13556 measured reflections	*l* = −21→21

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.121$

$S = 1.06$

2371 reflections

156 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0509P)^2 + 1.1474P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.49$ e Å^{-3}

$\Delta\rho_{min} = -0.50$ e Å^{-3}

Extinction correction: SHELXL97

Extinction coefficient: 0.0045 (6)

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 $F^2 > 2$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}
S1	0.20197 (6)	0.31298 (7)	0.39880 (4)	0.0880 (3)
N1	0.06932 (13)	0.68893 (15)	0.47218 (10)	0.0573 (5)
N2	0.17241 (13)	0.52421 (15)	0.47711 (9)	0.0540 (4)
H2A	0.1972	0.5695	0.5113	0.065*
N3	0.29367 (13)	0.39256 (16)	0.51506 (10)	0.0562 (4)
H3A	0.3287	0.3279	0.5056	0.067*
O1	0.28019 (13)	0.55553 (14)	0.59591 (9)	0.0729 (5)
C1	0.03215 (16)	0.5184 (2)	0.39285 (12)	0.0603 (6)
H1	0.0484	0.4401	0.3741	0.072*
C2	−0.04982 (17)	0.5802 (2)	0.36940 (14)	0.0669 (6)
H2	−0.0898	0.5435	0.3343	0.080*
C3	−0.07274 (17)	0.6952 (2)	0.39747 (13)	0.0639 (6)
H3	−0.1282	0.7378	0.3826	0.077*
C4	−0.01104 (17)	0.7452 (2)	0.44817 (13)	0.0637 (6)
H4	−0.0260	0.8237	0.4672	0.076*
C5	0.08957 (14)	0.57576 (17)	0.44482 (11)	0.0483 (5)
C6	0.22019 (15)	0.41698 (19)	0.46441 (11)	0.0533 (5)
C7	0.31854 (17)	0.45635 (19)	0.57795 (13)	0.0580 (5)
C8	0.39334 (18)	0.3926 (2)	0.62153 (13)	0.0682 (6)
H8	0.4317	0.3302	0.5948	0.082*
C9	0.37782 (19)	0.3640 (2)	0.70296 (13)	0.0662 (6)
C10	0.4473 (2)	0.4617 (3)	0.68099 (15)	0.0853 (8)

H10A	0.5158	0.4435	0.6869	0.102*
H10B	0.4295	0.5483	0.6901	0.102*
C11	0.4160 (3)	0.2389 (2)	0.72840 (16)	0.0987 (10)
H11A	0.4792	0.2251	0.7080	0.148*
H11B	0.3729	0.1736	0.7125	0.148*
H11C	0.4200	0.2384	0.7810	0.148*
C12	0.2849 (2)	0.4015 (3)	0.73987 (16)	0.0930 (9)
H12A	0.2951	0.4065	0.7919	0.139*
H12B	0.2358	0.3402	0.7296	0.139*
H12C	0.2645	0.4818	0.7218	0.139*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.1028 (6)	0.0876 (5)	0.0736 (4)	0.0359 (4)	−0.0289 (4)	−0.0302 (4)
N1	0.0604 (11)	0.0481 (10)	0.0633 (11)	0.0035 (8)	−0.0025 (9)	0.0014 (8)
N2	0.0589 (11)	0.0453 (9)	0.0578 (10)	0.0006 (8)	−0.0089 (8)	−0.0005 (8)
N3	0.0603 (11)	0.0498 (9)	0.0585 (10)	0.0080 (8)	−0.0079 (8)	−0.0016 (8)
O1	0.0922 (12)	0.0477 (9)	0.0788 (11)	0.0052 (8)	−0.0285 (9)	−0.0096 (8)
C1	0.0607 (13)	0.0535 (12)	0.0666 (14)	0.0020 (10)	−0.0064 (11)	−0.0032 (10)
C2	0.0616 (14)	0.0668 (14)	0.0723 (15)	0.0002 (11)	−0.0125 (12)	0.0005 (12)
C3	0.0530 (13)	0.0641 (14)	0.0746 (15)	0.0041 (10)	−0.0014 (11)	0.0110 (12)
C4	0.0662 (14)	0.0500 (12)	0.0750 (14)	0.0073 (11)	0.0027 (12)	0.0020 (11)
C5	0.0507 (11)	0.0443 (10)	0.0500 (11)	−0.0022 (9)	0.0036 (9)	0.0079 (9)
C6	0.0575 (13)	0.0521 (12)	0.0503 (11)	0.0018 (10)	−0.0005 (9)	0.0045 (9)
C7	0.0634 (13)	0.0463 (12)	0.0642 (13)	−0.0039 (10)	−0.0111 (10)	0.0014 (10)
C8	0.0709 (15)	0.0659 (14)	0.0680 (14)	0.0114 (12)	−0.0183 (12)	−0.0063 (11)
C9	0.0790 (17)	0.0526 (12)	0.0671 (14)	0.0036 (11)	−0.0261 (12)	−0.0049 (11)
C10	0.0817 (18)	0.0794 (17)	0.0947 (19)	−0.0100 (14)	−0.0385 (15)	0.0026 (15)
C11	0.140 (3)	0.0620 (15)	0.094 (2)	0.0146 (17)	−0.0489 (19)	0.0006 (14)
C12	0.098 (2)	0.108 (2)	0.0722 (18)	0.0091 (18)	−0.0160 (15)	0.0025 (16)

Geometric parameters (Å, °)

S1—C6	1.651 (2)	C4—H4	0.9300
N1—C4	1.334 (3)	C7—C8	1.469 (3)
N1—C5	1.335 (2)	C8—C10	1.507 (3)
N2—C6	1.340 (3)	C8—H8	0.9800
N2—C5	1.397 (3)	C9—C8	1.531 (3)
N2—H2A	0.8600	C9—C10	1.471 (4)
N3—C7	1.377 (3)	C9—C11	1.507 (3)
N3—C6	1.395 (3)	C9—C12	1.501 (4)
N3—H3A	0.8600	C10—H10A	0.9700
O1—C7	1.227 (3)	C10—H10B	0.9700
C1—C2	1.376 (3)	C11—H11A	0.9600
C1—C5	1.378 (3)	C11—H11B	0.9600
C1—H1	0.9300	C11—H11C	0.9600
C2—H2	0.9300	C12—H12A	0.9600
C3—C4	1.365 (3)	C12—H12B	0.9600

C3—C2	1.366 (3)	C12—H12C	0.9600
C3—H3	0.9300		
C4—N1—C5	117.24 (19)	C7—C8—C9	121.3 (2)
C6—N2—C5	131.66 (18)	C10—C8—C9	57.90 (16)
C6—N2—H2A	114.2	C7—C8—H8	115.1
C5—N2—H2A	114.2	C10—C8—H8	115.1
C7—N3—C6	129.78 (18)	C9—C8—H8	115.1
C7—N3—H3A	115.1	C10—C9—C12	119.3 (2)
C6—N3—H3A	115.1	C10—C9—C11	118.9 (2)
C2—C1—C5	118.2 (2)	C12—C9—C11	113.3 (3)
C2—C1—H1	120.9	C10—C9—C8	60.25 (17)
C5—C1—H1	120.9	C12—C9—C8	120.1 (2)
C3—C2—C1	120.2 (2)	C11—C9—C8	115.2 (2)
C3—C2—H2	119.9	C9—C10—C8	61.85 (17)
C1—C2—H2	119.9	C9—C10—H10A	117.6
C4—C3—C2	117.4 (2)	C8—C10—H10A	117.6
C4—C3—H3	121.3	C9—C10—H10B	117.6
C2—C3—H3	121.3	C8—C10—H10B	117.6
N1—C4—C3	124.4 (2)	H10A—C10—H10B	114.7
N1—C4—H4	117.8	C9—C11—H11A	109.5
C3—C4—H4	117.8	C9—C11—H11B	109.5
N1—C5—C1	122.53 (19)	H11A—C11—H11B	109.5
N1—C5—N2	111.65 (18)	C9—C11—H11C	109.5
C1—C5—N2	125.78 (19)	H11A—C11—H11C	109.5
N2—C6—N3	113.69 (17)	H11B—C11—H11C	109.5
N2—C6—S1	128.60 (16)	C9—C12—H12A	109.5
N3—C6—S1	117.70 (15)	C9—C12—H12B	109.5
O1—C7—N3	122.8 (2)	H12A—C12—H12B	109.5
O1—C7—C8	123.8 (2)	C9—C12—H12C	109.5
N3—C7—C8	113.38 (19)	H12A—C12—H12C	109.5
C7—C8—C10	120.7 (2)	H12B—C12—H12C	109.5
C5—N1—C4—C3	−0.6 (3)	C4—C3—C2—C1	0.7 (4)
C4—N1—C5—C1	1.3 (3)	C2—C3—C4—N1	−0.4 (4)
C4—N1—C5—N2	−176.82 (18)	O1—C7—C8—C10	−16.7 (4)
C6—N2—C5—N1	−176.9 (2)	N3—C7—C8—C10	164.6 (2)
C6—N2—C5—C1	5.1 (3)	O1—C7—C8—C9	52.1 (3)
C5—N2—C6—N3	−172.60 (19)	N3—C7—C8—C9	−126.7 (2)
C5—N2—C6—S1	6.5 (3)	C7—C8—C10—C9	109.9 (3)
C7—N3—C6—N2	5.6 (3)	C10—C9—C8—C7	−108.9 (3)
C7—N3—C6—S1	−173.64 (18)	C12—C9—C8—C7	−0.2 (3)
C6—N3—C7—O1	−5.6 (4)	C11—C9—C8—C7	140.9 (2)
C6—N3—C7—C8	173.2 (2)	C12—C9—C8—C10	108.7 (3)
C5—C1—C2—C3	0.0 (3)	C11—C9—C8—C10	−110.3 (3)
C2—C1—C5—N1	−1.0 (3)	C12—C9—C10—C8	−109.9 (2)
C2—C1—C5—N2	176.8 (2)	C11—C9—C10—C8	104.2 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

N2—H2A···O1	0.86	1.93	2.648 (2)	141
N3—H3A···N1^{i}	0.86	2.13	2.982 (3)	170

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

Fig. 1

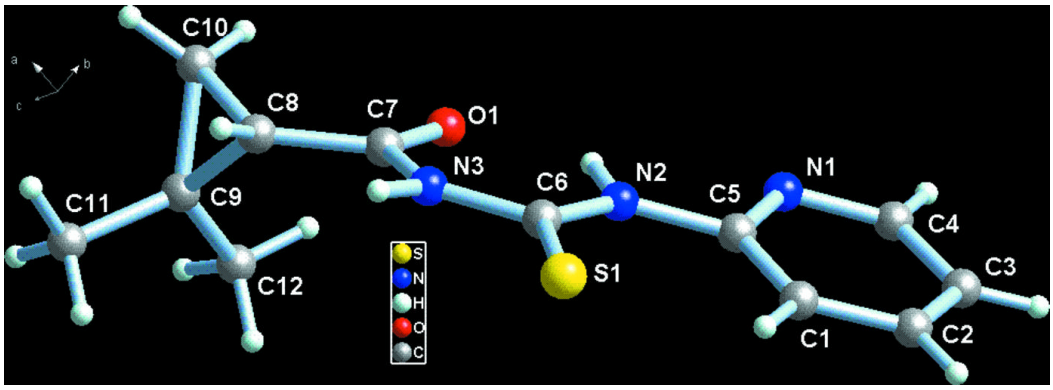

Fig. 2

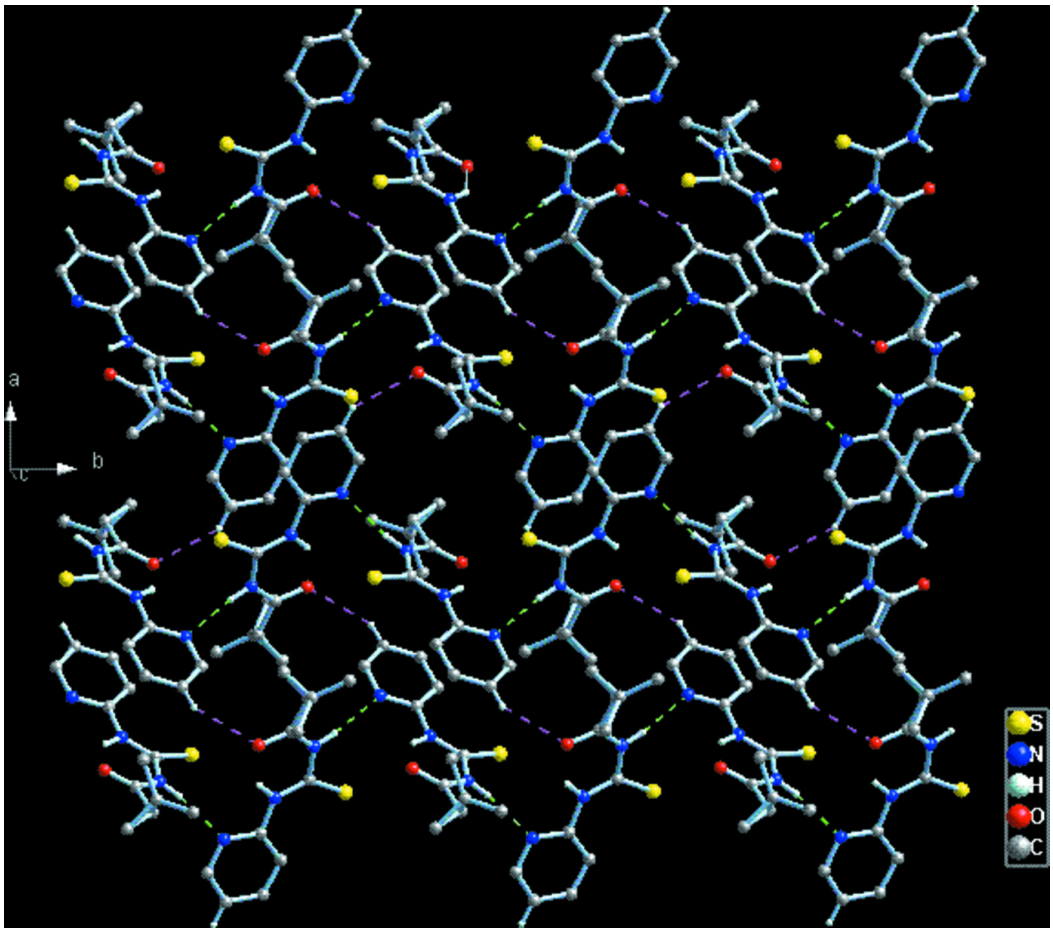

Fig. 3