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4-(4-Chlorophenyl)-6-(methylsulfanyl)-pyrimidin-2-amine

Qi-Hua Zhao,* Li-Nan Li and Kun-Miao Wang

School of Chemical Science and Technology, Key Laboratory of Medicinal Chemistry for Natural Resources, Ministry of Education, Yunnan University, Kunming 650091, People's Republic of China

Correspondence e-mail: qhzhao@ynu.edu.cn

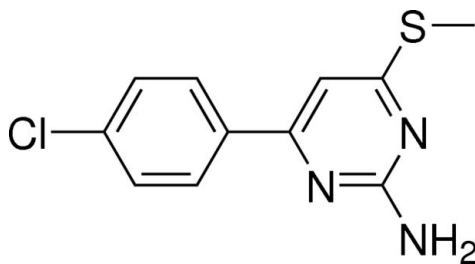
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.049; wR factor = 0.096; data-to-parameter ratio = 19.3.

In the title compound, $\text{C}_{11}\text{H}_{10}\text{ClN}_3\text{S}$, the dihedral angle between the benzene and pyrimidine rings is $3.99(4)^\circ$. In the crystal, intermolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds link the molecules into ribbons of $R_2^2(8)$ rings parallel to $[100]$. Weak $\text{C}-\text{H}\cdots\text{S}$ contacts connect adjacent ribbons into a two-dimensional undulating layer-like structure extending parallel to (110) . The benzene and pyrimidine rings of adjacent molecules have the offset face-to-face $\pi-\pi$ stacking interactions in a zigzag fashion along the c axis, with perpendicular ring distances of 3.463 and 3.639 Å, and a dihedral angle between the planes of $3.99(2)^\circ$. The distance between the ring centroids is 4.420(2) Å.

Related literature

For the synthesis of pyrimidine-5-carbaldehydes from α -formylaroylketene dithioacetals, see: Mathews & Asokan (2007). For the synthesis of a 6-aryl aminopyrimidine compound, see: Lin *et al.* (2008). For the application of organic compounds as ligands, see: Li *et al.* (2007). For the importance aminopyrimidine compounds in the synthesis of complexes, see: Cui & Lan (2007). For a review of intermolecular $\text{C}-\text{H}\cdots\text{S}$ contacts, see: Taylor & Kennard (1982). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_{11}\text{H}_{10}\text{ClN}_3\text{S}$
 $M_r = 251.73$
 Orthorhombic, $P2_12_12_1$
 $a = 6.8148(11)$ Å
 $b = 10.6107(16)$ Å
 $c = 16.509(3)$ Å
 $V = 1193.7(3)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.47$ mm⁻¹
 $T = 293$ K
 $0.25 \times 0.14 \times 0.08$ mm

Data collection

Bruker APEXII 1K CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.925$, $T_{\max} = 0.964$
 7825 measured reflections
 2800 independent reflections
 1841 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.050$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.096$
 $S = 1.01$
 2800 reflections
 145 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.19$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.20$ e Å⁻³
 Absolute structure: Flack (1983),
 1061 Friedel pairs
 Flack parameter: 0.02 (10)

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{N3}-\text{H3A}\cdots\text{N2}^{\text{i}}$ | 0.86 | 2.31 | 3.095 (3) | 152 |
| $\text{N3}-\text{H3B}\cdots\text{N1}^{\text{ii}}$ | 0.86 | 2.21 | 3.045 (3) | 164 |
| $\text{C11}-\text{H11A}\cdots\text{S1}^{\text{iii}}$ | 0.96 | 2.93 | 3.859 (4) | 163 |

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{5}{2}, -z + 2$; (ii) $x - \frac{1}{2}, -y + \frac{5}{2}, -z + 2$; (iii) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 2$.

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

We acknowledge the National Natural Science Foundation of China for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2183).

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Bruker (2004). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
 Cui, R.-H. & Lan, Y.-Q. (2007). *Acta Cryst.* **E63**, o4515.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Li, S.-L., Liu, J. & Ma, J.-F. (2007). *Acta Cryst.* **E63**, o4509.
 Lin, J., Liu, Y.-J., Yan, S.-J., Niu, Y.-F., Zheng, H. & Huang, R. (2008). CN Patent No. 101302203A.
 Mathews, A. & Asokan, C. V. (2007). *Tetrahedron*, **63**, 7845–7849.
 Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
 Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

supplementary materials

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4-(4-Chlorophenyl)-6-(methylsulfanyl)pyrimidin-2-amine

Q.-H. Zhao, L.-N. Li and K.-M. Wang

Comment

In recent years, aminopyrimidine compounds have shown predominant bioactivity and played an important role in the drug synthesis (Mathews & Asokan, 2007). Meanwhile, these organic compounds can be used as new organic N-donor ligands, which can construct a wide range of coordination polymers with novel architectures and special properties. The selection and synthesis of proper ligands are the most important tasks (Li *et al.*, 2007; Cui & Lan, 2007). Herein, the crystal structure of the title compound is reported. Its synthetic method followed the procedure given by Lin *et al.*, (2008).

In the title compound (Fig. 1), all atoms are almost in the same plane and the largest distortion from the mean plane being 0.3127 Å for C11, atoms S1 and C11 being 0.1338 (6) and 0.1251 (5) Å out-of-plane. The two aromatic rings of the molecule make a dihedral angle of 3.99 (4)°.

In the crystal structure, there are two kinds of hydrogen bonds. One group is N3—H3A···N2, N3—H3B···N1, and the other is C11—H11A···S1 (Fig. 2 and Table 1). The strong intermolecular N—H···N hydrogen bonds link the molecules into ribbons of R²₂(8) rings (Bernstein *et al.* 1995) parallel to [1 0 0]. The weak intermolecular C—H···S contacts connect the adjacent ribbons into a two-dimensional waved layer-like structure extending parallel to (1 1 0). Similar geometric parameters (H···S = 2.916 Å, angle C—H···S = 164.9%) were discussed for a possible intermolecular C—H···S contact by Taylor & Kennard (1982). The phenyl and pyrimidine rings of adjacent molecules exhibit π — π stacking interactions in a zig-zag fashion along the *c* axis with perpendicular ring distances of 3.463 Å and 3.639 Å, and the dihedral angle α being 3.99°. The distance between the ring centroids Cg1···Cg2^{iv} amounts to 4.420 (2) Å. Cg1 and Cg2 represent the centroids of the pyrimidine and phenyl rings. The symmetry code: (iv = -1 + x, y, z). The intermolecular forces construct a three-dimensional supramolecular architecture in the crystal.

Experimental

All chemicals used were commercially available. We first got the title compound using the reported method (Lin *et al.*, 2008). After that 1 mmol (0.025 g) 4-(4-Chlorophenyl)-6-(methylthio)pyrimidin-2-amine was dissolved in a mixture of 15 ml methyl cyanide and 5 ml water. Then the solution was stirred for 40 min at room temperature. The solvent was removed gradually for a few weeks and faint yellow crystals for X-ray data collection were obtained by the slow evaporation method.

Refinement

H atoms bonded to C and N atoms were calculated geometrically and allowed to ride on the C and N atoms with distance restraints of C—H = 0.93 Å and N—H = 0.86 Å, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$.

Figures

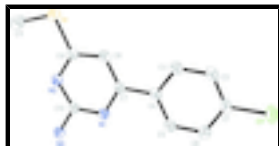


Fig. 1. The molecular structure of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

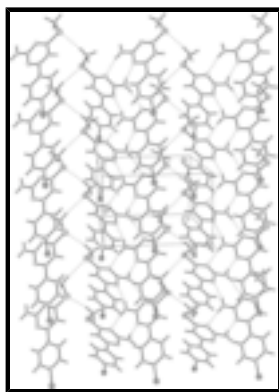


Fig. 2. The crystal packing diagram of the title compound, showing hydrogen bonds along the *ab* plane.

4-(4-Chlorophenyl)-6-(methylsulfanyl)pyrimidin-2-amine

Crystal data

$C_{11}H_{10}ClN_3S$

$M_r = 251.73$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 6.8148$ (11) Å

$b = 10.6107$ (16) Å

$c = 16.509$ (3) Å

$V = 1193.7$ (3) Å³

$Z = 4$

$F_{000} = 520$

$D_x = 1.401$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3984 reflections

$\theta = 2.3$ – 28.4°

$\mu = 0.47$ mm⁻¹

$T = 293$ K

Block, yellow

$0.25 \times 0.14 \times 0.08$ mm

Data collection

Bruker APEXII 1K CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293$ K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.925$, $T_{\max} = 0.964$

7825 measured reflections

2800 independent reflections

1841 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.050$

$\theta_{\max} = 28.4^\circ$

$\theta_{\min} = 2.3^\circ$

$h = -8 \rightarrow 8$

$k = -13 \rightarrow 11$

$l = -21 \rightarrow 22$

Refinement

| | |
|--|--|
| Refinement on F^2 | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.049$ | $w = 1/[\sigma^2(F_o^2) + (0.036P)^2]$ |
| $wR(F^2) = 0.096$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.01$ | $(\Delta/\sigma)_{\max} < 0.001$ |
| 2800 reflections | $\Delta\rho_{\max} = 0.19 \text{ e } \text{\AA}^{-3}$ |
| 145 parameters | $\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none |
| Secondary atom site location: difference Fourier map | Absolute structure: Flack (1983), 1061 Friedel pairs |
| | Flack parameter: 0.02 (10) |

Special details

Experimental. 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.

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|---------------|--------------|--------------|----------------------------------|
| C11 | 1.15208 (14) | 1.01534 (10) | 0.62970 (5) | 0.0694 (3) |
| S1 | -0.01688 (13) | 0.85410 (8) | 0.91781 (5) | 0.0522 (2) |
| N1 | 0.4426 (3) | 1.1541 (2) | 0.89640 (13) | 0.0357 (6) |
| N2 | 0.1442 (4) | 1.0763 (2) | 0.95722 (13) | 0.0338 (6) |
| N3 | 0.2824 (4) | 1.2627 (2) | 0.99649 (16) | 0.0423 (6) |
| H3A | 0.3713 | 1.3201 | 0.9931 | 0.051* |
| H3B | 0.1880 | 1.2708 | 1.0307 | 0.051* |
| C1 | 0.9466 (5) | 1.0272 (3) | 0.69138 (17) | 0.0454 (8) |
| C2 | 0.8052 (5) | 0.9354 (3) | 0.68825 (18) | 0.0508 (9) |
| H2B | 0.8186 | 0.8682 | 0.6526 | 0.061* |
| C3 | 0.6427 (5) | 0.9430 (3) | 0.73817 (19) | 0.0473 (8) |
| H3C | 0.5474 | 0.8803 | 0.7359 | 0.057* |
| C4 | 0.6197 (4) | 1.0437 (3) | 0.79209 (16) | 0.0359 (7) |

supplementary materials

| | | | | |
|------|-------------|------------|--------------|-------------|
| C5 | 0.7638 (5) | 1.1359 (3) | 0.79272 (17) | 0.0427 (8) |
| H5A | 0.7502 | 1.2044 | 0.8274 | 0.051* |
| C6 | 0.9275 (5) | 1.1292 (3) | 0.74324 (18) | 0.0484 (9) |
| H6A | 1.0228 | 1.1919 | 0.7448 | 0.058* |
| C7 | 0.4499 (4) | 1.0503 (3) | 0.84876 (16) | 0.0343 (7) |
| C8 | 0.3107 (5) | 0.9576 (3) | 0.85466 (18) | 0.0438 (8) |
| H8A | 0.3171 | 0.8859 | 0.8224 | 0.053* |
| C9 | 0.1589 (4) | 0.9737 (3) | 0.91043 (17) | 0.0366 (7) |
| C10 | 0.2911 (4) | 1.1611 (3) | 0.94864 (16) | 0.0333 (7) |
| C11 | -0.1656 (6) | 0.9020 (4) | 1.0015 (2) | 0.0811 (13) |
| H11A | -0.2674 | 0.8410 | 1.0102 | 0.122* |
| H11B | -0.2235 | 0.9826 | 0.9900 | 0.122* |
| H11C | -0.0858 | 0.9083 | 1.0493 | 0.122* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C11 | 0.0647 (6) | 0.0800 (7) | 0.0634 (6) | 0.0144 (6) | 0.0276 (5) | -0.0046 (5) |
| S1 | 0.0488 (5) | 0.0391 (4) | 0.0686 (5) | -0.0083 (5) | 0.0010 (5) | -0.0064 (5) |
| N1 | 0.0339 (13) | 0.0370 (14) | 0.0361 (13) | 0.0013 (12) | 0.0010 (10) | -0.0044 (12) |
| N2 | 0.0334 (13) | 0.0344 (14) | 0.0336 (13) | 0.0003 (12) | -0.0039 (11) | -0.0010 (12) |
| N3 | 0.0381 (16) | 0.0411 (16) | 0.0476 (14) | -0.0054 (12) | 0.0095 (13) | -0.0139 (13) |
| C1 | 0.048 (2) | 0.053 (2) | 0.0349 (16) | 0.0154 (18) | 0.0071 (15) | 0.0003 (16) |
| C2 | 0.056 (2) | 0.049 (2) | 0.0468 (19) | 0.0101 (18) | 0.0025 (18) | -0.0163 (17) |
| C3 | 0.045 (2) | 0.046 (2) | 0.0516 (19) | 0.0008 (17) | -0.0012 (17) | -0.0137 (17) |
| C4 | 0.0367 (18) | 0.0368 (18) | 0.0344 (15) | 0.0061 (14) | -0.0056 (13) | -0.0035 (14) |
| C5 | 0.0501 (19) | 0.0398 (19) | 0.0381 (17) | 0.0023 (18) | 0.0065 (15) | -0.0044 (16) |
| C6 | 0.051 (2) | 0.049 (2) | 0.0446 (18) | -0.0049 (17) | 0.0095 (16) | -0.0024 (17) |
| C7 | 0.0310 (17) | 0.0373 (18) | 0.0347 (15) | 0.0058 (14) | -0.0033 (12) | -0.0044 (14) |
| C8 | 0.044 (2) | 0.0382 (19) | 0.0489 (19) | -0.0005 (16) | 0.0015 (15) | -0.0105 (15) |
| C9 | 0.0346 (16) | 0.0341 (17) | 0.0411 (16) | 0.0000 (14) | -0.0101 (15) | 0.0027 (15) |
| C10 | 0.0319 (16) | 0.0346 (18) | 0.0334 (15) | 0.0036 (14) | -0.0043 (12) | -0.0021 (14) |
| C11 | 0.077 (3) | 0.065 (3) | 0.101 (3) | -0.021 (2) | 0.037 (3) | -0.001 (2) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|--------|-----------|----------|-----------|
| C11—C1 | 1.736 (3) | C3—C4 | 1.400 (4) |
| S1—C9 | 1.750 (3) | C3—H3C | 0.9300 |
| S1—C11 | 1.788 (4) | C4—C5 | 1.387 (4) |
| N1—C10 | 1.347 (3) | C4—C7 | 1.490 (4) |
| N1—C7 | 1.354 (3) | C5—C6 | 1.384 (4) |
| N2—C9 | 1.339 (3) | C5—H5A | 0.9300 |
| N2—C10 | 1.353 (4) | C6—H6A | 0.9300 |
| N3—C10 | 1.338 (4) | C7—C8 | 1.370 (4) |
| N3—H3A | 0.8600 | C8—C9 | 1.395 (4) |
| N3—H3B | 0.8600 | C8—H8A | 0.9300 |
| C1—C2 | 1.371 (5) | C11—H11A | 0.9600 |
| C1—C6 | 1.386 (4) | C11—H11B | 0.9600 |
| C2—C3 | 1.383 (4) | C11—H11C | 0.9600 |

| | | | |
|------------|-------------|---------------|-----------|
| C2—H2B | 0.9300 | | |
| C9—S1—C11 | 103.63 (16) | C5—C6—C1 | 118.7 (3) |
| C10—N1—C7 | 116.4 (2) | C5—C6—H6A | 120.6 |
| C9—N2—C10 | 115.1 (2) | C1—C6—H6A | 120.6 |
| C10—N3—H3A | 120.0 | N1—C7—C8 | 121.1 (3) |
| C10—N3—H3B | 120.0 | N1—C7—C4 | 115.6 (2) |
| H3A—N3—H3B | 120.0 | C8—C7—C4 | 123.3 (3) |
| C2—C1—C6 | 120.8 (3) | C7—C8—C9 | 118.2 (3) |
| C2—C1—C11 | 119.6 (3) | C7—C8—H8A | 120.9 |
| C6—C1—C11 | 119.7 (3) | C9—C8—H8A | 120.9 |
| C1—C2—C3 | 120.0 (3) | N2—C9—C8 | 122.4 (3) |
| C1—C2—H2B | 120.0 | N2—C9—S1 | 119.9 (2) |
| C3—C2—H2B | 120.0 | C8—C9—S1 | 117.7 (2) |
| C2—C3—C4 | 120.8 (3) | N3—C10—N1 | 117.1 (3) |
| C2—C3—H3C | 119.6 | N3—C10—N2 | 116.2 (2) |
| C4—C3—H3C | 119.6 | N1—C10—N2 | 126.7 (3) |
| C5—C4—C3 | 117.7 (3) | S1—C11—H11A | 109.5 |
| C5—C4—C7 | 120.8 (3) | S1—C11—H11B | 109.5 |
| C3—C4—C7 | 121.4 (3) | H11A—C11—H11B | 109.5 |
| C6—C5—C4 | 122.0 (3) | S1—C11—H11C | 109.5 |
| C6—C5—H5A | 119.0 | H11A—C11—H11C | 109.5 |
| C4—C5—H5A | 119.0 | H11B—C11—H11C | 109.5 |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|------------------------------|-------------|---------------|-----------------------|-------------------------|
| N3—H3A...N2 ⁱ | 0.86 | 2.31 | 3.095 (3) | 152 |
| N3—H3B...N1 ⁱⁱ | 0.86 | 2.21 | 3.045 (3) | 164 |
| C11—H11A...S1 ⁱⁱⁱ | 0.96 | 2.93 | 3.859 (4) | 163 |

Symmetry codes: (i) $x+1/2, -y+5/2, -z+2$; (ii) $x-1/2, -y+5/2, -z+2$; (iii) $x-1/2, -y+3/2, -z+2$.

Fig. 1

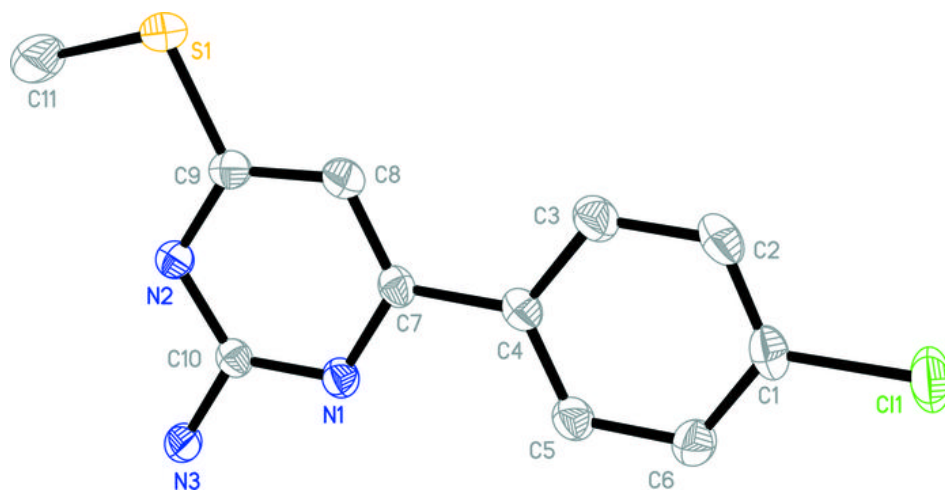


Fig. 2

