

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

5-(4-Phenoxyphenyl)-1,3,4-thiadiazol-2-amine

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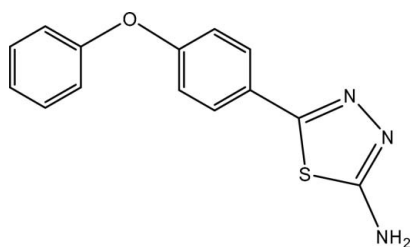
Received 5 April 2009; accepted 7 April 2009

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.051; wR factor = 0.141; data-to-parameter ratio = 13.6.

The title compound, $\text{C}_{14}\text{H}_{11}\text{N}_3\text{OS}$, was synthesized by the reaction of phenoxybenzoic acid and thiosemicarbazide. The thiadiazole ring makes dihedral angles of 0.99 (16) and 86.53 (18) $^\circ$, respectively, with the benzene and phenyl rings. The dihedral angle between the benzene and phenyl rings is 87.17 (19) $^\circ$. Intramolecular $\text{C}-\text{H}\cdots\text{S}$ contacts are present. In the crystal, intermolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds link the molecules.

Related literature

For the fungicidal and herbicidal activities of thiadiazole derivatives, see: Chen *et al.* (2000); Kidwai *et al.* (2000); Vicentini *et al.* (1998). For their insecticidal activities, see: Arun *et al.* (1999); Wasfy *et al.* (1996). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$\text{C}_{14}\text{H}_{11}\text{N}_3\text{OS}$
 $M_r = 269.32$
 Monoclinic, $P2_1/c$

$a = 13.409$ (3) Å
 $b = 10.582$ (2) Å
 $c = 9.5710$ (19) Å

$\beta = 108.58$ (3) $^\circ$
 $V = 1287.3$ (4) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 0.25$ mm⁻¹
 $T = 293$ K
 $0.30 \times 0.20 \times 0.20$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.930$, $T_{\max} = 0.953$
 2438 measured reflections

2336 independent reflections
 1596 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$
 3 standard reflections every 200 reflections
 intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.141$
 $S = 1.00$
 2336 reflections

172 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.22$ e Å⁻³
 $\Delta\rho_{\min} = -0.22$ e Å⁻³

Table 1
 Hydrogen-bond geometry (Å, $^\circ$).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|-------|-------------|-------------|---------------|
| $\text{N3}-\text{H3A}\cdots\text{N2}^{\text{i}}$ | 0.86 | 2.21 | 3.042 (4) | 162 |
| $\text{N3}-\text{H3B}\cdots\text{N1}^{\text{ii}}$ | 0.86 | 2.26 | 3.094 (3) | 163 |
| $\text{C9}-\text{H9A}\cdots\text{S}$ | 0.93 | 2.72 | 3.133 (4) | 108 |

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1989); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); 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: *SHELXL97*.

The authors gratefully acknowledge Professor Hua-Qin Wang of the Analysis Center, Nanjing University, for providing the Enraf–Nonius CAD-4 diffractometer for this research project.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2760).

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supplementary materials

Acta Cryst. (2009). E65, o1044 [doi:10.1107/S1600536809013257]

5-(4-Phenoxyphenyl)-1,3,4-thiadiazol-2-amine

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Comment

Thiadiazole derivatives containing the thiazolidinone unit are of great interest because of their chemical and pharmaceutical properties. Some derivatives have fungicidal and herbicidal activities (Chen *et al.*, 2000; Kidwai *et al.*, 2000; Vicentini *et al.*, 1998); some show insecticidal activities (Arun *et al.*, 1999; Wasfy *et al.*, 1996). We report here the crystal structure of the title compound, (I).

The molecular structure of (I) is shown in Fig. 1, in which the bond lengths (Allen *et al.*, 1987) and angles are generally within normal ranges. The thiadiazole ring makes dihedral angles of 0.99 (16)° and 86.53 (18)° with the benzene and phenyl rings, respectively. The dihedral angle between the benzene and phenyl rings is 87.17 (19)°. There are intramolecular C—H···S contacts (Fig. 1), and intermolecular N—H···N hydrogen bonds, linking the molecules into chains along the *b* axis (Fig. 2).

Experimental

Phenoxybenzoic acid (5 mmol) and thiosemicarbazide (5 mmol) were added in toluene (50 ml), which is heated under reflux for 4 h. The reaction mixture was left to cool to room temperature, poured into ice water, filtered, and the filter cake was crystallized from acetone to give pure compound (I) [m.p. 513–514 K]. Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of an acetone solution.

Refinement

All H atoms were placed geometrically at the distances of C—H = 0.93 Å and N—H = 0.86 Å, and included in the refinement in riding motion approximation with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the carrier atom.

Figures

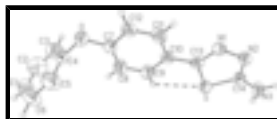


Fig. 1. A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate the intramolecular C—H···S contact.

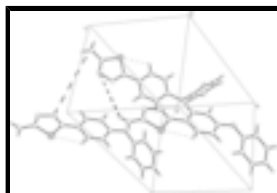


Fig. 2. Partial packing view showing the hydrogen-bonded network. Dashed lines indicate intermolecular N—H···N hydrogen bonds.

5-(4-Phenoxyphenyl)-1,3,4-thiadiazol-2-amine

Crystal data

| | |
|--------------------------------|---|
| $C_{14}H_{11}N_3OS$ | $F_{000} = 560$ |
| $M_r = 269.32$ | $D_x = 1.390 \text{ Mg m}^{-3}$ |
| Monoclinic, $P2_1/c$ | Melting point: 542 K |
| Hall symbol: -P 2ybc | Mo $K\alpha$ radiation |
| $a = 13.409 (3) \text{ \AA}$ | $\lambda = 0.71073 \text{ \AA}$ |
| $b = 10.582 (2) \text{ \AA}$ | Cell parameters from 25 reflections |
| $c = 9.5710 (19) \text{ \AA}$ | $\theta = 10\text{--}13^\circ$ |
| $\beta = 108.58 (3)^\circ$ | $\mu = 0.25 \text{ mm}^{-1}$ |
| $V = 1287.3 (4) \text{ \AA}^3$ | $T = 293 \text{ K}$ |
| $Z = 4$ | Block, colourless |
| | $0.30 \times 0.20 \times 0.20 \text{ mm}$ |

Data collection

| | |
|---|------------------------------------|
| Enraf-Nonius CAD-4 diffractometer | $R_{\text{int}} = 0.032$ |
| Radiation source: fine-focus sealed tube | $\theta_{\text{max}} = 25.3^\circ$ |
| Monochromator: graphite | $\theta_{\text{min}} = 2.5^\circ$ |
| $T = 293 \text{ K}$ | $h = 0 \rightarrow 16$ |
| $\omega/2\theta$ scans | $k = 0 \rightarrow 12$ |
| Absorption correction: ψ scan (North <i>et al.</i> , 1968) | $l = -11 \rightarrow 10$ |
| $T_{\text{min}} = 0.930$, $T_{\text{max}} = 0.953$ | 3 standard reflections |
| 2438 measured reflections | every 200 reflections |
| 2336 independent reflections | intensity decay: 1% |
| 1596 reflections with $I > 2\sigma(I)$ | |

Refinement

| | |
|--|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.051$ | H-atom parameters constrained |
| $wR(F^2) = 0.141$ | $w = 1/[\sigma^2(F_o^2) + (0.074P)^2 + 0.12P]$ |
| $S = 1.00$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 2336 reflections | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 172 parameters | $\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$ |
| | 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 $F^2 > \sigma(F^2)$ 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)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|-------------|-------------|-------------|----------------------------------|
| S | 0.07308 (7) | 0.15388 (7) | 0.18224 (8) | 0.0444 (3) |
| O | 0.3343 (2) | -0.0997 (2) | -0.2453 (3) | 0.0751 (8) |
| N1 | 0.0991 (2) | -0.0816 (2) | 0.2420 (3) | 0.0438 (6) |
| N2 | 0.0458 (2) | -0.0359 (2) | 0.3336 (3) | 0.0450 (6) |
| N3 | -0.0237 (2) | 0.1545 (2) | 0.3882 (3) | 0.0564 (7) |
| H3A | -0.0449 | 0.1197 | 0.4550 | 0.068* |
| H3B | -0.0344 | 0.2337 | 0.3693 | 0.068* |
| C1 | 0.4549 (4) | 0.1716 (4) | -0.4561 (5) | 0.0764 (12) |
| H1B | 0.4826 | 0.2314 | -0.5046 | 0.092* |
| C2 | 0.3629 (4) | 0.1137 (4) | -0.5265 (5) | 0.0870 (13) |
| H2B | 0.3273 | 0.1343 | -0.6242 | 0.104* |
| C3 | 0.3208 (3) | 0.0249 (4) | -0.4566 (5) | 0.0729 (11) |
| H3C | 0.2572 | -0.0142 | -0.5061 | 0.087* |
| C4 | 0.3732 (3) | -0.0048 (3) | -0.3145 (4) | 0.0526 (8) |
| C5 | 0.4662 (3) | 0.0517 (4) | -0.2422 (4) | 0.0721 (11) |
| H5A | 0.5027 | 0.0301 | -0.1451 | 0.086* |
| C6 | 0.5062 (3) | 0.1415 (4) | -0.3144 (5) | 0.0834 (13) |
| H6A | 0.5691 | 0.1818 | -0.2648 | 0.100* |
| C7 | 0.2835 (3) | -0.0671 (3) | -0.1459 (4) | 0.0501 (8) |
| C8 | 0.2482 (3) | 0.0534 (3) | -0.1339 (4) | 0.0586 (9) |
| H8A | 0.2603 | 0.1185 | -0.1918 | 0.070* |
| C9 | 0.1947 (3) | 0.0763 (3) | -0.0349 (4) | 0.0537 (9) |
| H9A | 0.1701 | 0.1573 | -0.0272 | 0.064* |
| C10 | 0.1769 (2) | -0.0194 (3) | 0.0532 (3) | 0.0383 (7) |
| C11 | 0.2148 (2) | -0.1399 (3) | 0.0400 (4) | 0.0481 (8) |
| H11A | 0.2044 | -0.2051 | 0.0989 | 0.058* |
| C12 | 0.2673 (2) | -0.1634 (3) | -0.0592 (4) | 0.0516 (8) |
| H12A | 0.2919 | -0.2443 | -0.0677 | 0.062* |
| C13 | 0.1199 (2) | 0.0043 (3) | 0.1577 (3) | 0.0375 (7) |
| C14 | 0.0255 (2) | 0.0854 (3) | 0.3138 (3) | 0.0406 (7) |

supplementary materials

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|-------------|--------------|
| S | 0.0627 (5) | 0.0291 (4) | 0.0463 (4) | 0.0030 (4) | 0.0244 (4) | 0.0026 (3) |
| O | 0.101 (2) | 0.0436 (14) | 0.115 (2) | -0.0098 (13) | 0.0814 (18) | -0.0134 (14) |
| N1 | 0.0596 (16) | 0.0287 (13) | 0.0480 (14) | 0.0027 (11) | 0.0241 (12) | 0.0010 (11) |
| N2 | 0.0619 (17) | 0.0319 (13) | 0.0483 (15) | 0.0004 (12) | 0.0274 (13) | 0.0014 (11) |
| N3 | 0.091 (2) | 0.0384 (14) | 0.0525 (15) | 0.0099 (14) | 0.0404 (15) | 0.0044 (13) |
| C1 | 0.085 (3) | 0.072 (3) | 0.082 (3) | -0.004 (2) | 0.040 (2) | 0.017 (2) |
| C2 | 0.097 (3) | 0.081 (3) | 0.070 (3) | 0.009 (3) | 0.008 (2) | 0.018 (2) |
| C3 | 0.052 (2) | 0.066 (3) | 0.088 (3) | -0.0005 (19) | 0.005 (2) | -0.004 (2) |
| C4 | 0.057 (2) | 0.0439 (18) | 0.069 (2) | -0.0033 (16) | 0.0369 (18) | -0.0102 (17) |
| C5 | 0.081 (3) | 0.084 (3) | 0.049 (2) | -0.020 (2) | 0.0162 (19) | 0.0017 (19) |
| C6 | 0.068 (3) | 0.095 (3) | 0.086 (3) | -0.035 (2) | 0.021 (2) | 0.006 (3) |
| C7 | 0.055 (2) | 0.0393 (18) | 0.067 (2) | -0.0050 (15) | 0.0341 (17) | -0.0090 (16) |
| C8 | 0.079 (2) | 0.0385 (18) | 0.075 (2) | 0.0031 (16) | 0.049 (2) | 0.0069 (16) |
| C9 | 0.074 (2) | 0.0316 (16) | 0.069 (2) | 0.0056 (16) | 0.0412 (19) | 0.0000 (15) |
| C10 | 0.0392 (16) | 0.0307 (15) | 0.0458 (16) | -0.0012 (12) | 0.0147 (13) | -0.0015 (12) |
| C11 | 0.0474 (18) | 0.0367 (17) | 0.065 (2) | 0.0023 (14) | 0.0253 (16) | 0.0064 (15) |
| C12 | 0.0516 (19) | 0.0341 (16) | 0.077 (2) | -0.0005 (14) | 0.0322 (17) | -0.0031 (16) |
| C13 | 0.0410 (16) | 0.0299 (14) | 0.0392 (15) | -0.0004 (12) | 0.0093 (13) | 0.0004 (12) |
| C14 | 0.0527 (19) | 0.0329 (16) | 0.0358 (15) | -0.0009 (13) | 0.0137 (14) | -0.0029 (12) |

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

| | | | |
|------------|------------|-----------|-----------|
| S—C14 | 1.740 (3) | C3—H3C | 0.9300 |
| S—C13 | 1.746 (3) | C4—C5 | 1.357 (5) |
| O—C7 | 1.378 (4) | C5—C6 | 1.380 (5) |
| O—C4 | 1.393 (4) | C5—H5A | 0.9300 |
| N1—C13 | 1.303 (4) | C6—H6A | 0.9300 |
| N1—N2 | 1.383 (3) | C7—C12 | 1.374 (4) |
| N2—C14 | 1.314 (4) | C7—C8 | 1.378 (4) |
| N3—C14 | 1.333 (4) | C8—C9 | 1.381 (4) |
| N3—H3A | 0.8600 | C8—H8A | 0.9300 |
| N3—H3B | 0.8600 | C9—C10 | 1.386 (4) |
| C1—C6 | 1.349 (5) | C9—H9A | 0.9300 |
| C1—C2 | 1.349 (6) | C10—C11 | 1.393 (4) |
| C1—H1B | 0.9300 | C10—C13 | 1.462 (4) |
| C2—C3 | 1.375 (6) | C11—C12 | 1.373 (4) |
| C2—H2B | 0.9300 | C11—H11A | 0.9300 |
| C3—C4 | 1.354 (5) | C12—H12A | 0.9300 |
| C14—S—C13 | 87.14 (13) | C12—C7—C8 | 120.7 (3) |
| C7—O—C4 | 119.3 (2) | C12—C7—O | 116.0 (3) |
| C13—N1—N2 | 113.8 (2) | C8—C7—O | 123.2 (3) |
| C14—N2—N1 | 112.0 (2) | C7—C8—C9 | 119.2 (3) |
| C14—N3—H3A | 120.0 | C7—C8—H8A | 120.4 |
| C14—N3—H3B | 120.0 | C9—C8—H8A | 120.4 |

| | | | |
|---------------|------------|-----------------|------------|
| H3A—N3—H3B | 120.0 | C8—C9—C10 | 121.1 (3) |
| C6—C1—C2 | 119.2 (4) | C8—C9—H9A | 119.4 |
| C6—C1—H1B | 120.4 | C10—C9—H9A | 119.4 |
| C2—C1—H1B | 120.4 | C9—C10—C11 | 118.4 (3) |
| C1—C2—C3 | 121.2 (4) | C9—C10—C13 | 121.3 (3) |
| C1—C2—H2B | 119.4 | C11—C10—C13 | 120.3 (3) |
| C3—C2—H2B | 119.4 | C12—C11—C10 | 120.7 (3) |
| C4—C3—C2 | 119.0 (4) | C12—C11—H11A | 119.6 |
| C4—C3—H3C | 120.5 | C10—C11—H11A | 119.6 |
| C2—C3—H3C | 120.5 | C11—C12—C7 | 119.9 (3) |
| C3—C4—C5 | 120.6 (3) | C11—C12—H12A | 120.1 |
| C3—C4—O | 119.5 (3) | C7—C12—H12A | 120.1 |
| C5—C4—O | 119.9 (3) | N1—C13—C10 | 124.5 (3) |
| C4—C5—C6 | 119.2 (4) | N1—C13—S | 113.1 (2) |
| C4—C5—H5A | 120.4 | C10—C13—S | 122.4 (2) |
| C6—C5—H5A | 120.4 | N2—C14—N3 | 125.0 (3) |
| C1—C6—C5 | 120.7 (4) | N2—C14—S | 113.9 (2) |
| C1—C6—H6A | 119.6 | N3—C14—S | 121.1 (2) |
| C5—C6—H6A | 119.6 | | |
| C13—N1—N2—C14 | 1.2 (4) | C9—C10—C11—C12 | -0.7 (5) |
| C6—C1—C2—C3 | -0.1 (7) | C13—C10—C11—C12 | 179.2 (3) |
| C1—C2—C3—C4 | -0.2 (7) | C10—C11—C12—C7 | 0.4 (5) |
| C2—C3—C4—C5 | -0.3 (6) | C8—C7—C12—C11 | 0.5 (5) |
| C2—C3—C4—O | -176.4 (3) | O—C7—C12—C11 | -178.2 (3) |
| C7—O—C4—C3 | -103.8 (4) | N2—N1—C13—C10 | 178.9 (3) |
| C7—O—C4—C5 | 80.0 (4) | N2—N1—C13—S | -0.7 (3) |
| C3—C4—C5—C6 | 1.0 (6) | C9—C10—C13—N1 | 178.9 (3) |
| O—C4—C5—C6 | 177.1 (4) | C11—C10—C13—N1 | -1.0 (4) |
| C2—C1—C6—C5 | 0.8 (7) | C9—C10—C13—S | -1.6 (4) |
| C4—C5—C6—C1 | -1.3 (7) | C11—C10—C13—S | 178.6 (2) |
| C4—O—C7—C12 | -166.5 (3) | C14—S—C13—N1 | 0.1 (2) |
| C4—O—C7—C8 | 14.8 (5) | C14—S—C13—C10 | -179.6 (2) |
| C12—C7—C8—C9 | -1.0 (6) | N1—N2—C14—N3 | -179.2 (3) |
| O—C7—C8—C9 | 177.6 (3) | N1—N2—C14—S | -1.2 (3) |
| C7—C8—C9—C10 | 0.7 (5) | C13—S—C14—N2 | 0.6 (2) |
| C8—C9—C10—C11 | 0.2 (5) | C13—S—C14—N3 | 178.7 (3) |
| C8—C9—C10—C13 | -179.7 (3) | | |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------------|-------|-------------|-------------|---------------|
| N3—H3A \cdots N2 ⁱ | 0.86 | 2.21 | 3.042 (4) | 162 |
| N3—H3B \cdots N1 ⁱⁱ | 0.86 | 2.26 | 3.094 (3) | 163 |
| C9—H9A \cdots S | 0.93 | 2.72 | 3.133 (4) | 108 |

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

Fig. 1

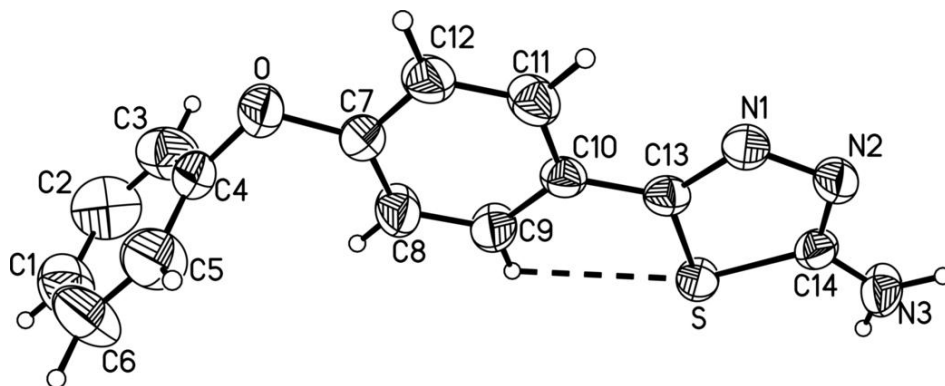


Fig. 2

