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(E)-2-Furyl methyl ketone 2,4-dinitrophenylhydrazone

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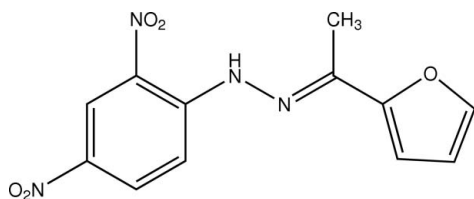
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.038; wR factor = 0.112; data-to-parameter ratio = 14.9.

Crystals of the title compound, $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_5$, were obtained from a condensation reaction of 2,4-dinitrophenylhydrazine and 2-furyl methyl ketone. The molecule displays a nearly planar structure, and the furan ring is slightly twisted by a dihedral angle of $12.62(6)^\circ$ with respect to the phenylhydrazone plane. The face-to-face separation of $3.287(7)$ Å between parallel benzene rings of adjacent molecules indicates the existence of π - π stacking between dinitrophenyl rings in the crystal structure.

Related literature

For general background, see: Okabe *et al.* (1993); Shan *et al.* (2003a, 2006). For related structures, see: Vickery *et al.* (1985); Fan *et al.* (2004); Shan *et al.* (2003b).



Experimental

Crystal data

$\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_5$
 $M_r = 290.24$
 Monoclinic, $P2_1/c$

$a = 9.8917(8)$ Å
 $b = 12.8477(15)$ Å
 $c = 10.6549(12)$ Å

$\beta = 111.63(2)^\circ$
 $V = 1258.7(3)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 0.12$ mm⁻¹
 $T = 293(2)$ K
 $0.36 \times 0.23 \times 0.18$ mm

Data collection

Rigaku R-Axis RAPID IP diffractometer
 Absorption correction: none
 12121 measured reflections

2858 independent reflections
 1784 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.111$
 $S = 1.03$
 2858 reflections

192 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.21$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.17$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|-------|-------------|-------------|---------------|
| $\text{N3}-\text{H3}\cdots\text{O1}$ | 0.86 | 1.97 | 2.6063 (15) | 130 |
| $\text{C9}-\text{H9}\cdots\text{O4}^i$ | 0.93 | 2.41 | 3.334 (2) | 172 |
| $\text{C11}-\text{H11}\cdots\text{O2}^{ii}$ | 0.93 | 2.41 | 3.1530 (19) | 137 |

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2233).

References

- Altomare, A., Casciarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
 Fan, Z., Shan, S., Hu, W.-X. & Xu, D.-J. (2004). *Acta Cryst.* **E60**, o1102–o1104.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
 Okabe, N., Nakamura, T. & Fukuda, H. (1993). *Acta Cryst.* **C49**, 1678–1680.
 Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
 Rigaku/MS (2002). *CrystalStructure*. Rigaku/MS, The Woodlands, Texas, USA.
 Shan, S., Fan, Z. & Xu, D.-J. (2006). *Acta Cryst.* **E62**, o1123–o1125.
 Shan, S., Xu, D.-J. & Hu, W.-X. (2003b). *Acta Cryst.* **E59**, o838–o840.
 Shan, S., Xu, D.-J., Hung, C.-H., Wu, J.-Y. & Chiang, M. Y. (2003a). *Acta Cryst.* **C59**, o135–o136.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Vickery, B., Willey, G. R. & Drew, M. G. B. (1985). *Acta Cryst.* **C41**, 1072–1075.

supplementary materials

Acta Cryst. (2008). E64, o1153 [doi:10.1107/S1600536808015122]

(E)-2-Furyl methyl ketone 2,4-dinitrophenylhydrazone

S. Shan, Y.-L. Tian, S.-H. Wang, W.-L. Wang and Y.-L. Xu

Comment

As some phenylhydrazone derivatives have shown to be potentially DNA damaging and mutagenic agents (Okabe *et al.*, 1993), a series of new phenylhydrazone derivatives have been synthesized in our laboratory (Shan *et al.*, 2003a; Shan *et al.*, 2006). As part of the ongoing investigation, the title compound has recently been prepared and its crystal structure is reported here.

The molecular structure of the title compound is shown in Fig. 1. The molecule displays an approximately planar structure, the furan ring is slightly twisted with respect to the phenylhydrazone plane with a dihedral angle of 12.62 (6)°. The N4—C7 bond distance (Table 1) indicates a typical C=N double bond. The molecule assumes an E configuration with the phenylhydrazine and furan located on the opposite sides of the C=N bond. An intramolecular hydrogen bond is observed between the N3-imino and the adjacent N1-nitro groups; such a hydrogen bonding is a common feature in *o*-nitrophenylhydrazine compounds (Vickery *et al.*, 1985; Fan *et al.*, 2004).

A partially overlapped arrangement of parallel benzene rings of adjacent molecules is illustrated in Fig. 2. The face-to-face separation of 3.287 (7) Å strongly indicates the existence of π - π stacking between parallel dinitrophenyl rings of adjacent molecules in the crystal. It agrees with that found in a related dinitrophenylhydrazine compound, isobutylaldehyde 2,4-dinitrophenylhydrazone (Shan *et al.*, 2003b).

The crystal structure also contains intermolecular weak C—H \cdots O hydrogen bonding (Table 2).

Experimental

2,4-Dinitrophenylhydrazine (0.4 g, 2 mmol) was dissolved in ethanol (10 ml), and H₂SO₄ solution (98%, 0.5 ml) was slowly added to the ethanol solution with stirring. The solution was heated at 333 K for several min until the solution cleared. 2-Furyl methylketone (0.22 g, 2 mmol) was added to the above solution with continuous stirring, and the mixture was refluxed for 30 min. When the solution had cooled to room temperature brown powder crystals appeared. The powder crystals were separated and washed with water three times. Recrystallization from an absolute ethanol solution yielded well shaped single crystals.

Refinement

Methyl H atoms were placed in calculated positions with C—H = 0.96 Å and the torsion angle was refined to fit the electron density, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. Other H atoms were placed in calculated positions with C—H = 0.93 and N—H = 0.86 Å, and refined in riding mode, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$.

Figures

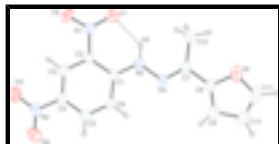


Fig. 1. The molecular structure of the title compound with 30% probability displacement ellipsoids for non-H atoms.

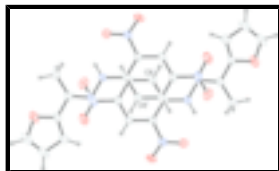


Fig. 2. A diagram showing the overlapped arrangement of parallel benzene rings of neighboring molecules [symmetry code: (i) $1 - x, 1 - y, 1 - z$].

(E)-2-Furyl methyl ketone 2,4-dinitrophenylhydrazone

Crystal data

$C_{12}H_{10}N_4O_5$

$M_r = 290.24$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 9.8917\ (8)\ \text{\AA}$

$b = 12.8477\ (15)\ \text{\AA}$

$c = 10.6549\ (12)\ \text{\AA}$

$\beta = 111.63\ (2)^\circ$

$V = 1258.7\ (3)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 600$

$D_x = 1.532\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 5266 reflections

$\theta = 3.2\text{--}26.0^\circ$

$\mu = 0.12\ \text{mm}^{-1}$

$T = 293\ (2)\ \text{K}$

Prism, brown

$0.36 \times 0.23 \times 0.18\ \text{mm}$

Data collection

Rigaku R-Axis RAPID IP
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: $10.00\ \text{pixels mm}^{-1}$

$T = 293\ (2)\ \text{K}$

ω scans

Absorption correction: none

12121 measured reflections

2858 independent reflections

1784 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\text{max}} = 27.4^\circ$

$\theta_{\text{min}} = 3.2^\circ$

$h = -12 \rightarrow 12$

$k = -16 \rightarrow 16$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0649P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$

| | |
|--|---|
| $wR(F^2) = 0.111$ | $(\Delta/\sigma)_{\max} < 0.001$ |
| $S = 1.03$ | $\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$ |
| 2858 reflections | $\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$ |
| 192 parameters | Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$ |
| Primary atom site location: structure-invariant direct methods | Extinction coefficient: 0.0047 (11) |
| Secondary atom site location: difference Fourier map | |

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)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| O1 | 0.13582 (13) | 0.43547 (8) | 0.14104 (11) | 0.0648 (4) |
| O2 | 0.15573 (13) | 0.27996 (8) | 0.22020 (12) | 0.0648 (4) |
| O3 | 0.44159 (13) | 0.19704 (8) | 0.66737 (13) | 0.0660 (4) |
| O4 | 0.52296 (15) | 0.31707 (10) | 0.81753 (13) | 0.0742 (4) |
| O5 | 0.09817 (11) | 0.93990 (8) | 0.18361 (12) | 0.0566 (3) |
| N1 | 0.17859 (13) | 0.37357 (9) | 0.23615 (12) | 0.0452 (3) |
| N2 | 0.45693 (14) | 0.28930 (10) | 0.70150 (14) | 0.0498 (3) |
| N3 | 0.21841 (13) | 0.59367 (8) | 0.30483 (12) | 0.0412 (3) |
| H3 | 0.1757 | 0.5753 | 0.2219 | 0.049* |
| N4 | 0.22992 (13) | 0.69747 (8) | 0.33900 (12) | 0.0411 (3) |
| C1 | 0.27421 (13) | 0.52042 (9) | 0.40146 (14) | 0.0349 (3) |
| C2 | 0.25858 (14) | 0.41229 (10) | 0.37100 (14) | 0.0368 (3) |
| C3 | 0.31897 (14) | 0.33809 (10) | 0.46968 (15) | 0.0406 (3) |
| H3A | 0.3085 | 0.2677 | 0.4478 | 0.049* |
| C4 | 0.39417 (14) | 0.36870 (10) | 0.59975 (15) | 0.0403 (3) |
| C5 | 0.40955 (15) | 0.47424 (11) | 0.63469 (15) | 0.0412 (3) |
| H5 | 0.4597 | 0.4940 | 0.7238 | 0.049* |
| C6 | 0.35072 (14) | 0.54818 (10) | 0.53751 (14) | 0.0393 (3) |
| H6 | 0.3613 | 0.6182 | 0.5615 | 0.047* |
| C7 | 0.16518 (14) | 0.76093 (10) | 0.24031 (14) | 0.0395 (3) |
| C8 | 0.18273 (16) | 0.87045 (10) | 0.27796 (16) | 0.0431 (4) |
| C9 | 0.26625 (19) | 0.92158 (12) | 0.38905 (18) | 0.0586 (4) |
| H9 | 0.3329 | 0.8926 | 0.4674 | 0.070* |
| C10 | 0.2326 (2) | 1.02927 (13) | 0.3632 (2) | 0.0691 (5) |

supplementary materials

| | | | | |
|------|--------------|--------------|--------------|------------|
| H10 | 0.2734 | 1.0842 | 0.4218 | 0.083* |
| C11 | 0.1335 (2) | 1.03623 (12) | 0.2414 (2) | 0.0662 (5) |
| H11 | 0.0926 | 1.0983 | 0.1997 | 0.079* |
| C12 | 0.07984 (19) | 0.73130 (12) | 0.09826 (17) | 0.0556 (4) |
| H12A | 0.1447 | 0.7073 | 0.0560 | 0.083* |
| H12B | 0.0268 | 0.7907 | 0.0502 | 0.083* |
| H12C | 0.0130 | 0.6767 | 0.0968 | 0.083* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|------------|-------------|-------------|-------------|-------------|
| O1 | 0.0920 (9) | 0.0420 (6) | 0.0438 (7) | -0.0007 (6) | 0.0055 (6) | -0.0006 (5) |
| O2 | 0.0836 (8) | 0.0323 (6) | 0.0615 (8) | -0.0105 (5) | 0.0068 (6) | -0.0098 (5) |
| O3 | 0.0778 (8) | 0.0408 (6) | 0.0728 (9) | 0.0058 (5) | 0.0200 (7) | 0.0147 (5) |
| O4 | 0.0884 (9) | 0.0708 (8) | 0.0459 (8) | 0.0053 (7) | 0.0041 (7) | 0.0107 (6) |
| O5 | 0.0572 (6) | 0.0371 (6) | 0.0754 (8) | 0.0069 (5) | 0.0242 (6) | 0.0136 (5) |
| N1 | 0.0513 (7) | 0.0333 (6) | 0.0443 (8) | -0.0020 (5) | 0.0096 (6) | -0.0035 (5) |
| N2 | 0.0510 (7) | 0.0468 (8) | 0.0489 (9) | 0.0030 (6) | 0.0151 (6) | 0.0111 (6) |
| N3 | 0.0510 (7) | 0.0272 (5) | 0.0399 (7) | -0.0003 (5) | 0.0103 (5) | -0.0014 (5) |
| N4 | 0.0490 (7) | 0.0263 (6) | 0.0468 (7) | -0.0013 (5) | 0.0164 (6) | -0.0013 (5) |
| C1 | 0.0349 (7) | 0.0296 (6) | 0.0404 (8) | -0.0010 (5) | 0.0142 (6) | -0.0009 (5) |
| C2 | 0.0373 (7) | 0.0305 (6) | 0.0400 (8) | -0.0020 (5) | 0.0112 (6) | -0.0026 (5) |
| C3 | 0.0411 (7) | 0.0297 (6) | 0.0492 (9) | -0.0020 (5) | 0.0147 (7) | 0.0013 (6) |
| C4 | 0.0395 (7) | 0.0372 (7) | 0.0434 (9) | 0.0017 (6) | 0.0146 (6) | 0.0064 (6) |
| C5 | 0.0421 (7) | 0.0439 (8) | 0.0366 (8) | -0.0028 (6) | 0.0132 (6) | -0.0034 (6) |
| C6 | 0.0433 (7) | 0.0316 (7) | 0.0448 (9) | -0.0023 (6) | 0.0181 (6) | -0.0047 (6) |
| C7 | 0.0428 (7) | 0.0343 (7) | 0.0427 (8) | -0.0003 (6) | 0.0171 (6) | 0.0024 (6) |
| C8 | 0.0507 (8) | 0.0319 (7) | 0.0496 (9) | 0.0045 (6) | 0.0220 (7) | 0.0084 (6) |
| C9 | 0.0800 (11) | 0.0390 (8) | 0.0549 (10) | -0.0056 (8) | 0.0227 (9) | -0.0049 (7) |
| C10 | 0.0959 (14) | 0.0354 (8) | 0.0892 (15) | -0.0106 (8) | 0.0495 (13) | -0.0130 (9) |
| C11 | 0.0762 (12) | 0.0289 (8) | 0.1072 (18) | 0.0051 (8) | 0.0499 (13) | 0.0085 (9) |
| C12 | 0.0682 (10) | 0.0446 (8) | 0.0471 (10) | 0.0010 (8) | 0.0133 (8) | 0.0036 (7) |

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

| | | | |
|--------|-------------|----------|-------------|
| O1—N1 | 1.2338 (16) | C3—H3A | 0.9300 |
| O2—N1 | 1.2239 (15) | C4—C5 | 1.3995 (19) |
| O3—N2 | 1.2327 (17) | C5—C6 | 1.367 (2) |
| O4—N2 | 1.2194 (18) | C5—H5 | 0.9300 |
| O5—C11 | 1.369 (2) | C6—H6 | 0.9300 |
| O5—C8 | 1.3735 (18) | C7—C8 | 1.4560 (19) |
| N1—C2 | 1.4491 (18) | C7—C12 | 1.485 (2) |
| N2—C4 | 1.4510 (18) | C8—C9 | 1.339 (2) |
| N3—C1 | 1.3533 (17) | C9—C10 | 1.426 (2) |
| N3—N4 | 1.3760 (15) | C9—H9 | 0.9300 |
| N3—H3 | 0.8600 | C10—C11 | 1.309 (3) |
| N4—C7 | 1.2977 (18) | C10—H10 | 0.9300 |
| C1—C6 | 1.4115 (19) | C11—H11 | 0.9300 |
| C1—C2 | 1.4221 (17) | C12—H12A | 0.9600 |

| | | | |
|-----------|-------------|---------------|-------------|
| C2—C3 | 1.3813 (19) | C12—H12B | 0.9600 |
| C3—C4 | 1.367 (2) | C12—H12C | 0.9600 |
| C11—O5—C8 | 105.81 (13) | C4—C5—H5 | 120.1 |
| O2—N1—O1 | 121.97 (13) | C5—C6—C1 | 121.31 (13) |
| O2—N1—C2 | 118.71 (12) | C5—C6—H6 | 119.3 |
| O1—N1—C2 | 119.32 (11) | C1—C6—H6 | 119.3 |
| O4—N2—O3 | 122.83 (14) | N4—C7—C8 | 114.26 (13) |
| O4—N2—C4 | 118.26 (13) | N4—C7—C12 | 126.16 (13) |
| O3—N2—C4 | 118.91 (14) | C8—C7—C12 | 119.58 (12) |
| C1—N3—N4 | 120.13 (12) | C9—C8—O5 | 109.82 (13) |
| C1—N3—H3 | 119.9 | C9—C8—C7 | 133.59 (14) |
| N4—N3—H3 | 119.9 | O5—C8—C7 | 116.59 (13) |
| C7—N4—N3 | 115.25 (12) | C8—C9—C10 | 106.32 (17) |
| N3—C1—C6 | 121.30 (12) | C8—C9—H9 | 126.8 |
| N3—C1—C2 | 121.75 (13) | C10—C9—H9 | 126.8 |
| C6—C1—C2 | 116.95 (12) | C11—C10—C9 | 107.09 (16) |
| C3—C2—C1 | 121.36 (13) | C11—C10—H10 | 126.5 |
| C3—C2—N1 | 116.28 (12) | C9—C10—H10 | 126.5 |
| C1—C2—N1 | 122.37 (12) | C10—C11—O5 | 110.96 (14) |
| C4—C3—C2 | 119.62 (13) | C10—C11—H11 | 124.5 |
| C4—C3—H3A | 120.2 | O5—C11—H11 | 124.5 |
| C2—C3—H3A | 120.2 | C7—C12—H12A | 109.5 |
| C3—C4—C5 | 120.90 (13) | C7—C12—H12B | 109.5 |
| C3—C4—N2 | 118.57 (13) | H12A—C12—H12B | 109.5 |
| C5—C4—N2 | 120.52 (13) | C7—C12—H12C | 109.5 |
| C6—C5—C4 | 119.84 (13) | H12A—C12—H12C | 109.5 |
| C6—C5—H5 | 120.1 | H12B—C12—H12C | 109.5 |

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|-------|-------------|-------------|---------------|
| N3—H3 \cdots O1 | 0.86 | 1.97 | 2.6063 (15) | 130 |
| C9—H9 \cdots O4 ⁱ | 0.93 | 2.41 | 3.334 (2) | 172 |
| C11—H11 \cdots O2 ⁱⁱ | 0.93 | 2.41 | 3.1530 (19) | 137 |

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

Fig. 1

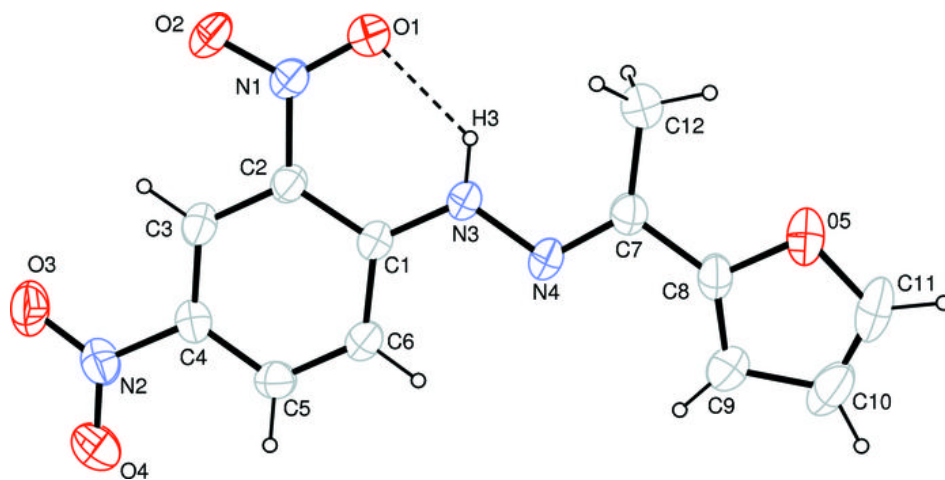


Fig. 2

