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# (*E*)-*N*′-(2-Chloro-5-nitrobenzylidene)-3-methoxybenzohydrazide monohydrate

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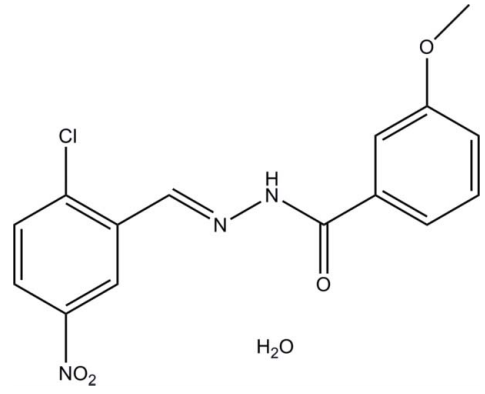
Key indicators: single-crystal X-ray study; $T$ = 298 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.061; $wR$ factor = 0.185; data-to-parameter ratio = 14.7.

In the hydrazone molecule of the title compound, $C_{15}H_{12}ClN_3O_4\cdot H_2O$, the two benzene rings form a dihedral angle of 3.6 (1)°. In the crystal structure, the solvent water molecules are involved in the formation of intermolecular N—H···O and O—H···N hydrogen bonds, which link the molecules into double ribbons extending along the $b$ axis. Intermolecular $\pi$–$\pi$ interactions between the aromatic rings [centroid–centroid distances = 3.712 (3) and 3.672 (3) Å] link these ribbons further into layers parallel to the $ab$ plane.

## Related literature

For the crystal structures of hydrazones recently reported by us, see: Liu & You (2010*a*,*b*,*c*); Liu & Wang (2010*a*,*b*); Sun *et al.* (2011).




## Experimental

### Crystal data

$C_{15}H_{12}ClN_3O_4\cdot H_2O$ $M_r$ = 351.74
Triclinic, $P\overline{1}$
$a$ = 7.176 (2) Å
$b$ = 7.179 (2) Å
$c$ = 15.395 (4) Å
$\alpha$ = 83.820 (18)°
$\beta$ = 89.953 (18)°
$\gamma$ = 80.190 (18)°
$V$ = 776.8 (4) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.28 mm$^{-1}$
$T$ = 298 K
0.23 × 0.21 × 0.20 mm

### Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min}$ = 0.939, $T_{max}$ = 0.947
4678 measured reflections
3267 independent reflections
2015 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.032

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.185
$S$ = 1.02
3267 reflections
222 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.36 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.48 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H2···O5 | 0.90 (1) | 1.92 (1) | 2.813 (4) | 169 (4) |
| O5—H5$B$···O1$^{iii}$ | 0.84 (1) | 2.03 (2) | 2.783 (3) | 150 (4) |
| O5—H5$A$···O1$^{iv}$ | 0.84 (1) | 2.30 (3) | 3.004 (4) | 142 (3) |

Symmetry codes: (iii) $x, y+1, z$; (iv) $-x+1, -y+1, -z+2$.

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; 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: CV5103).

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# supplementary materials

*Acta Cryst.* (2011). E**67**, o1625 [ **doi:10.1107/S1600536811020769** ]

# (*E*)-*N*'-(2-Chloro-5-nitrobenzylidene)-3-methoxybenzohydrazide monohydrate

**S.-Y. Liu and X.-L. Wang**

## Comment

In continuation of our structural studies of hydrazone derivatives (Liu & You, 2010*a*,*b*,*c*; Liu & Wang, 2010*a*,*b*; Sun *et al.*, 2011), we present here the title compound (I) (Fig. 1).

In the hydrazone molecule of (I) , two benzene rings form a dihedral angle of 3.6 (1)°. In the crystal structure, the crystalline water molecules are involved in formation of intermolecular N—H···O and O—H···O hydrogen bonds (Table 2), which link the molecules into doubled ribbons extended along *b* axis (Fig. 2). Intermolecular π–π interactions (Table 1) between the aromatic rings link further these ribbons into layers parallel to *ab* plane.

## Experimental

The title compound was prepared by the condensation reaction of 2-chloro-5-nitrobenzaldehyde (1.0 mmol, 0.185 g) and 3-methoxybenzohydrazide (1.0 mmol, 0.166 g) in methanol (50 ml) at ambient temperature. Colourless block-shaped single crystals suitable for X-ray structural determination were obtained by slow evaporation of the solution for a few days.

## Refinement

N- and O-bound H atoms were located from a difference Fourier map and refined with $U_{iso}$(H) fixed to 0.08 and with the N—H distance restrained to 0.90 (1) Å and O—H distances restrained to 0.84 (1). The remaining H atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H distances of 0.93–0.96 Å, and with $U_{iso}$(H) = 1.2–1.5$U_{eq}$(C).

## Figures

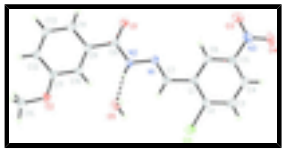

Fig. 1. The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms are shown as spheres of arbitrary radius. Hydrogen bond is shown as a dashed line.

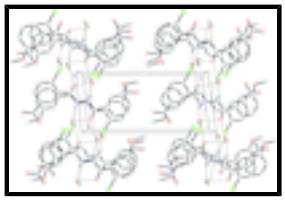

Fig. 2. A portion of the crystal packing viewed along the *a* axis. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted.

**(*E*)-*N*'-(2-Chloro-5-nitrobenzylidene)-3-methoxybenzohydrazide monohydrate**

*Crystal data*

| | |
|---|---|
| $C_{15}H_{12}ClN_3O_4 \cdot H_2O$ | $Z = 2$ |
| $M_r = 351.74$ | $F(000) = 364$ |
| Triclinic, $P\overline{1}$ | $D_x = 1.504$ Mg m$^{-3}$ |
| $a = 7.176$ (2) Å | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $b = 7.179$ (2) Å | Cell parameters from 887 reflections |
| $c = 15.395$ (4) Å | $\theta = 2.8$–$25.3°$ |
| $\alpha = 83.820$ (18)° | $\mu = 0.28$ mm$^{-1}$ |
| $\beta = 89.953$ (18)° | $T = 298$ K |
| $\gamma = 80.190$ (18)° | Block, colourless |
| $V = 776.8$ (4) Å$^3$ | 0.23 × 0.21 × 0.20 mm |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 3267 independent reflections |
| Radiation source: fine-focus sealed tube | 2015 reflections with $I > 2\sigma(I)$ |
| graphite | $R_{int} = 0.032$ |
| ω scans | $\theta_{max} = 27.0°$, $\theta_{min} = 1.3°$ |
| Absorption correction: multi-scan (*SADABS*; Bruker, 2001) | $h = -9 \rightarrow 9$ |
| $T_{min} = 0.939$, $T_{max} = 0.947$ | $k = -8 \rightarrow 9$ |
| 4678 measured reflections | $l = -19 \rightarrow 19$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.061$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.185$ | H atoms treated by a mixture of independent and constrained refinement |
| $S = 1.02$ | $w = 1/[\sigma^2(F_o^2) + (0.0928P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 3267 reflections | $(\Delta/\sigma)_{max} < 0.001$ |
| 222 parameters | $\Delta\rho_{max} = 0.36$ e Å$^{-3}$ |
| 4 restraints | $\Delta\rho_{min} = -0.48$ e Å$^{-3}$ |

*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 $F^2 > 2\text{sigma}(F^2)$ 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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cl1 | 0.05788 (14) | 1.03926 (12) | 1.12824 (6) | 0.0525 (3) |
| N1 | 0.2400 (4) | 0.5012 (4) | 1.03085 (15) | 0.0348 (6) |
| N2 | 0.2787 (4) | 0.5246 (3) | 0.94318 (16) | 0.0350 (6) |
| N3 | 0.1926 (5) | 0.3190 (5) | 1.36258 (19) | 0.0543 (8) |
| O1 | 0.3018 (4) | 0.2107 (3) | 0.93423 (15) | 0.0486 (6) |
| O2 | 0.2513 (4) | 0.8041 (4) | 0.63274 (15) | 0.0594 (8) |
| O3 | 0.2584 (5) | 0.1707 (4) | 1.33358 (19) | 0.0750 (9) |
| O4 | 0.1633 (5) | 0.3291 (4) | 1.44026 (17) | 0.0838 (10) |
| O5 | 0.4570 (3) | 0.8422 (3) | 0.90264 (16) | 0.0475 (6)* |
| C1 | 0.1635 (4) | 0.6554 (4) | 1.15934 (19) | 0.0322 (7) |
| C2 | 0.0887 (4) | 0.8238 (4) | 1.1940 (2) | 0.0350 (7) |
| C3 | 0.0387 (5) | 0.8259 (5) | 1.2810 (2) | 0.0435 (8) |
| H3 | −0.0148 | 0.9392 | 1.3021 | 0.052* |
| C4 | 0.0690 (5) | 0.6595 (5) | 1.3356 (2) | 0.0448 (8) |
| H4 | 0.0350 | 0.6582 | 1.3940 | 0.054* |
| C5 | 0.1506 (5) | 0.4938 (5) | 1.3029 (2) | 0.0373 (8) |
| C6 | 0.1960 (4) | 0.4882 (4) | 1.2159 (2) | 0.0356 (7) |
| H6 | 0.2478 | 0.3738 | 1.1954 | 0.043* |
| C7 | 0.2063 (4) | 0.6559 (4) | 1.0662 (2) | 0.0362 (7) |
| H7 | 0.2088 | 0.7708 | 1.0323 | 0.043* |
| C8 | 0.3063 (4) | 0.3706 (4) | 0.8984 (2) | 0.0335 (7) |
| C9 | 0.3373 (4) | 0.4103 (4) | 0.8024 (2) | 0.0327 (7) |
| C10 | 0.2874 (4) | 0.5904 (4) | 0.7584 (2) | 0.0366 (7) |
| H10 | 0.2378 | 0.6916 | 0.7892 | 0.044* |
| C11 | 0.3104 (5) | 0.6216 (5) | 0.6691 (2) | 0.0397 (8) |
| C12 | 0.3870 (5) | 0.4713 (5) | 0.6231 (2) | 0.0449 (8) |
| H12 | 0.4035 | 0.4907 | 0.5631 | 0.054* |
| C13 | 0.4381 (5) | 0.2933 (5) | 0.6678 (2) | 0.0462 (9) |
| H13 | 0.4893 | 0.1925 | 0.6371 | 0.055* |
| C14 | 0.4157 (5) | 0.2598 (5) | 0.7561 (2) | 0.0396 (8) |
| H14 | 0.4524 | 0.1383 | 0.7849 | 0.048* |
| C15 | 0.2835 (6) | 0.8508 (6) | 0.5424 (2) | 0.0683 (12) |
| H15A | 0.4162 | 0.8194 | 0.5312 | 0.103* |
| H15B | 0.2414 | 0.9844 | 0.5267 | 0.103* |
| H15C | 0.2148 | 0.7799 | 0.5083 | 0.103* |
| H2 | 0.334 (5) | 0.624 (4) | 0.923 (3) | 0.080* |
| H5A | 0.563 (3) | 0.822 (5) | 0.928 (2) | 0.080* |
| H5B | 0.382 (4) | 0.931 (4) | 0.921 (2) | 0.080* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cl1 | 0.0666 (7) | 0.0353 (5) | 0.0513 (6) | 0.0039 (4) | 0.0017 (4) | −0.0056 (4) |
| N1 | 0.0430 (16) | 0.0342 (14) | 0.0266 (13) | −0.0046 (12) | 0.0026 (11) | −0.0043 (11) |
| N2 | 0.0474 (17) | 0.0316 (14) | 0.0263 (13) | −0.0060 (12) | 0.0050 (12) | −0.0053 (11) |
| N3 | 0.069 (2) | 0.057 (2) | 0.0384 (18) | −0.0204 (17) | −0.0057 (15) | 0.0042 (15) |
| O1 | 0.0780 (18) | 0.0293 (12) | 0.0386 (13) | −0.0088 (12) | 0.0036 (12) | −0.0046 (10) |
| O2 | 0.085 (2) | 0.0501 (15) | 0.0335 (13) | 0.0100 (14) | 0.0089 (13) | 0.0051 (11) |
| O3 | 0.114 (3) | 0.0452 (16) | 0.0614 (19) | −0.0077 (17) | −0.0034 (17) | 0.0033 (14) |
| O4 | 0.133 (3) | 0.086 (2) | 0.0292 (14) | −0.021 (2) | 0.0034 (16) | 0.0090 (14) |
| C1 | 0.0302 (16) | 0.0331 (16) | 0.0331 (16) | −0.0038 (13) | −0.0005 (13) | −0.0062 (13) |
| C2 | 0.0334 (17) | 0.0363 (17) | 0.0347 (17) | −0.0030 (13) | −0.0015 (13) | −0.0053 (13) |
| C3 | 0.044 (2) | 0.045 (2) | 0.0417 (19) | −0.0018 (16) | 0.0014 (16) | −0.0174 (16) |
| C4 | 0.048 (2) | 0.060 (2) | 0.0297 (17) | −0.0132 (17) | 0.0049 (15) | −0.0131 (16) |
| C5 | 0.0391 (19) | 0.0415 (18) | 0.0330 (17) | −0.0134 (15) | −0.0025 (14) | −0.0011 (14) |
| C6 | 0.0389 (18) | 0.0356 (17) | 0.0325 (16) | −0.0047 (14) | 0.0004 (14) | −0.0072 (13) |
| C7 | 0.0397 (18) | 0.0320 (16) | 0.0342 (16) | −0.0009 (14) | 0.0045 (14) | −0.0008 (13) |
| C8 | 0.0372 (18) | 0.0305 (16) | 0.0331 (16) | −0.0044 (13) | 0.0001 (13) | −0.0059 (13) |
| C9 | 0.0309 (17) | 0.0351 (16) | 0.0334 (16) | −0.0064 (13) | 0.0002 (13) | −0.0080 (13) |
| C10 | 0.0410 (19) | 0.0355 (17) | 0.0319 (16) | 0.0000 (14) | 0.0021 (14) | −0.0080 (13) |
| C11 | 0.0392 (19) | 0.0416 (18) | 0.0365 (18) | −0.0020 (15) | 0.0026 (15) | −0.0036 (14) |
| C12 | 0.051 (2) | 0.054 (2) | 0.0320 (17) | −0.0110 (17) | 0.0133 (16) | −0.0106 (15) |
| C13 | 0.056 (2) | 0.0410 (19) | 0.045 (2) | −0.0088 (16) | 0.0150 (17) | −0.0183 (15) |
| C14 | 0.046 (2) | 0.0347 (17) | 0.0379 (18) | −0.0044 (15) | 0.0032 (15) | −0.0066 (14) |
| C15 | 0.096 (3) | 0.067 (3) | 0.036 (2) | −0.005 (2) | 0.004 (2) | 0.0071 (19) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cl1—C2 | 1.735 (3) | C4—C5 | 1.380 (5) |
| N1—C7 | 1.275 (4) | C4—H4 | 0.9300 |
| N1—N2 | 1.376 (3) | C5—C6 | 1.381 (4) |
| N2—C8 | 1.351 (4) | C6—H6 | 0.9300 |
| N2—H2 | 0.902 (10) | C7—H7 | 0.9300 |
| N3—O3 | 1.219 (4) | C8—C9 | 1.499 (4) |
| N3—O4 | 1.222 (4) | C9—C10 | 1.383 (4) |
| N3—C5 | 1.461 (4) | C9—C14 | 1.396 (4) |
| O1—C8 | 1.225 (3) | C10—C11 | 1.383 (4) |
| O2—C11 | 1.365 (4) | C10—H10 | 0.9300 |
| O2—C15 | 1.424 (4) | C11—C12 | 1.389 (5) |
| O5—H5A | 0.837 (10) | C12—C13 | 1.376 (5) |
| O5—H5B | 0.835 (10) | C12—H12 | 0.9300 |
| C1—C6 | 1.391 (4) | C13—C14 | 1.369 (5) |
| C1—C2 | 1.397 (4) | C13—H13 | 0.9300 |
| C1—C7 | 1.467 (4) | C14—H14 | 0.9300 |
| C2—C3 | 1.388 (4) | C15—H15A | 0.9600 |
| C3—C4 | 1.370 (5) | C15—H15B | 0.9600 |
| C3—H3 | 0.9300 | C15—H15C | 0.9600 |

| | | | |
|---|---|---|---|
| Cg1···Cg2$^{i}$ | 3.712 (3) | Cg1···Cg2$^{ii}$ | 3.672 (3) |
| C7—N1—N2 | 114.2 (2) | C1—C7—H7 | 119.5 |
| C8—N2—N1 | 119.0 (2) | O1—C8—N2 | 121.7 (3) |
| C8—N2—H2 | 118 (3) | O1—C8—C9 | 122.8 (3) |
| N1—N2—H2 | 118 (3) | N2—C8—C9 | 115.5 (3) |
| O3—N3—O4 | 122.8 (3) | C10—C9—C14 | 119.4 (3) |
| O3—N3—C5 | 119.1 (3) | C10—C9—C8 | 121.9 (3) |
| O4—N3—C5 | 118.1 (3) | C14—C9—C8 | 118.7 (3) |
| C11—O2—C15 | 118.6 (3) | C9—C10—C11 | 120.7 (3) |
| H5A—O5—H5B | 113 (2) | C9—C10—H10 | 119.7 |
| C6—C1—C2 | 117.9 (3) | C11—C10—H10 | 119.7 |
| C6—C1—C7 | 121.3 (3) | O2—C11—C10 | 115.3 (3) |
| C2—C1—C7 | 120.8 (3) | O2—C11—C12 | 124.9 (3) |
| C3—C2—C1 | 121.9 (3) | C10—C11—C12 | 119.8 (3) |
| C3—C2—Cl1 | 117.9 (2) | C13—C12—C11 | 118.9 (3) |
| C1—C2—Cl1 | 120.2 (2) | C13—C12—H12 | 120.5 |
| C4—C3—C2 | 119.4 (3) | C11—C12—H12 | 120.5 |
| C4—C3—H3 | 120.3 | C14—C13—C12 | 122.0 (3) |
| C2—C3—H3 | 120.3 | C14—C13—H13 | 119.0 |
| C3—C4—C5 | 119.1 (3) | C12—C13—H13 | 119.0 |
| C3—C4—H4 | 120.5 | C13—C14—C9 | 119.2 (3) |
| C5—C4—H4 | 120.5 | C13—C14—H14 | 120.4 |
| C4—C5—C6 | 122.3 (3) | C9—C14—H14 | 120.4 |
| C4—C5—N3 | 118.8 (3) | O2—C15—H15A | 109.5 |
| C6—C5—N3 | 119.0 (3) | O2—C15—H15B | 109.5 |
| C5—C6—C1 | 119.3 (3) | H15A—C15—H15B | 109.5 |
| C5—C6—H6 | 120.3 | O2—C15—H15C | 109.5 |
| C1—C6—H6 | 120.3 | H15A—C15—H15C | 109.5 |
| N1—C7—C1 | 121.0 (3) | H15B—C15—H15C | 109.5 |
| N1—C7—H7 | 119.5 | | |

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

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2···O5 | 0.90 (1) | 1.92 (1) | 2.813 (4) | 169 (4) |
| O5—H5B···O1$^{iii}$ | 0.84 (1) | 2.03 (2) | 2.783 (3) | 150 (4) |
| O5—H5A···O1$^{iv}$ | 0.84 (1) | 2.30 (3) | 3.004 (4) | 142 (3) |

Symmetry codes: (iii) *x*, *y*+1, *z*; (iv) −*x*+1, −*y*+1, −*z*+2.

**Fig. 1**

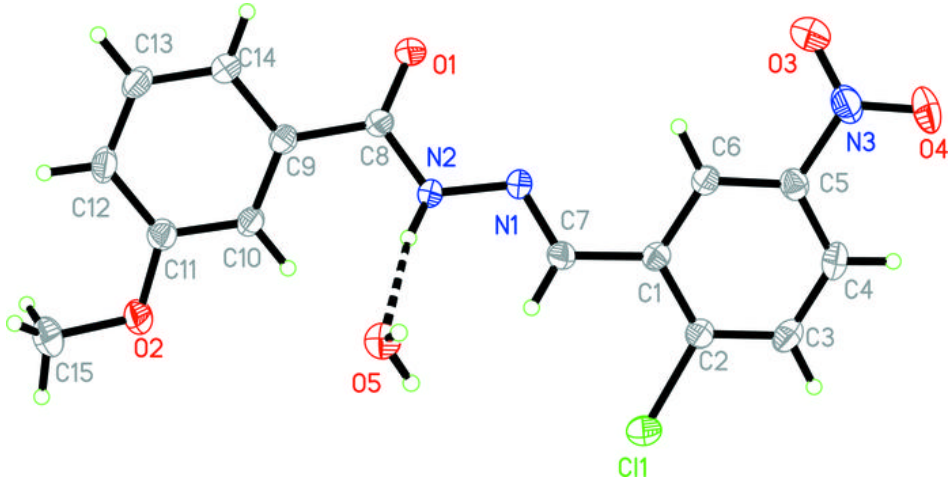
C13
C14
O1
O3
N3
O4
C6
C5
C8
N2
C9
C12
N1
C7
C11
C10
C1
C4
O2
C3
C15
O5
C2
Cl1

**Fig. 2**