Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# (*E*)-*N*′-(3,5-Dibromo-2-hydroxybenzylidene)-2-nitrobenzohydrazide methanol solvate

**Heng-Yu Qian[a]* and Da-Ping Qu[b]**

[a]Key Laboratory of Surface and Interface Science of Henan, School of Material & Chemical Engineering, Zhengzhou University of Light Industry, Zhengzhou 450002, People's Republic of China, and [b]Department of Chemistry, Dalian Teacher College, Dalian 116000, People's Republic of China
Correspondence e-mail: hengyu_qian@126.com

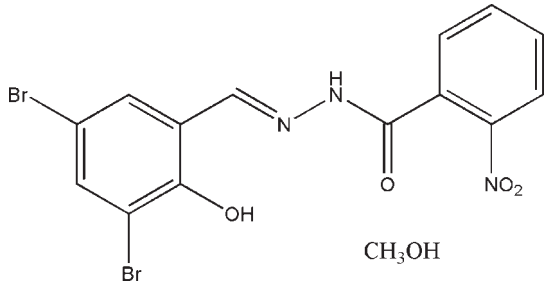
Received 19 August 2009; accepted 19 August 2009

Key indicators: single-crystal X-ray study; $T$ = 298 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.036; $wR$ factor = 0.094; data-to-parameter ratio = 16.3.

In the title compound, $C_{14}H_9Br_2N_3O_4\cdot CH_3OH$, the Schiff base molecule adopts an $E$ geometry with respect to the C=N bond and the benzene rings are oriented at a dihedral angle of 45.3 (2)°. An intramolecular O—H···N hydrogen bond helps to establish the conformation. In the crystal, the methanol solvent molecule is linked to the Schiff base molecule through an O—H···O hydrogen bond and intermolecular N—H···O hydrogen bonds link the components to form layers parallel to the *bc* direction.

## Related literature

For our previous work in this area, see: Yin, Qian *et al.* (2007); Yin, Guo *et al.* (2007); Qian *et al.* (2009).




## Experimental

### Crystal data

$C_{14}H_9Br_2N_3O_4\cdot CH_4O$
$M_r$ = 475.10
Monoclinic, $C2/c$
$a$ = 18.981 (1) Å
$b$ = 10.054 (2) Å
$c$ = 19.746 (2) Å
$\beta$ = 110.974 (2)°
$V$ = 3518.6 (8) Å$^3$
$Z$ = 8
Mo $K\alpha$ radiation
$\mu$ = 4.64 mm$^{-1}$
$T$ = 298 K
0.18 × 0.17 × 0.16 mm

### Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min}$ = 0.490, $T_{max}$ = 0.524
10461 measured reflections
3784 independent reflections
2670 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.041

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.094
$S$ = 1.02
3784 reflections
232 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.36 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.66 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1···N1 | 0.82 | 1.87 | 2.587 (3) | 146 |
| O5—H5···O2 | 0.82 | 1.94 | 2.735 (4) | 165 |
| N2—H2···O5$^{i}$ | 0.893 (10) | 1.958 (13) | 2.840 (3) | 169 (4) |

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

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*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5053).

## References

Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Qian, H., Yin, Z. & Yao, Z. (2009). *Acta Cryst.* E**65**, o2155.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Yin, Z., Guo, S., Qian, H. & Feng, Y. (2007). *Acta Cryst.* E**63**, o4407.
Yin, Z.-G., Qian, H.-Y., Jie, H. & Yu-Li, F. (2007). *Acta Cryst.* E**63**, o4406.

# supplementary materials

*Acta Cryst.* (2009). E**65**, o2237 [ **doi:10.1107/S160053680903311X** ]

# (*E*)-*N*'-(3,5-Dibromo-2-hydroxybenzylidene)-2-nitrobenzohydrazide methanol solvate

**H.-Y. Qian and D.-P. Qu**

## Comment

As part of our ongoing studies of Schiff bases (Yin, Qian *et al.*, 2007; Yin, Guo *et al.*, 2007; Qian *et al.*, 2009), we now report the synthesis and structure of the title compound, (I), (Fig. 1).

The Schiff base molecule adopts an *E* geometry with respect to the C=N bond, and there forms an intramolecular O—H···N hydrogen bond. The two benzene rings forms a dihedral angle of 45.3 (2)°. The dihedral angle between the O3/N3/O4 plane and the C9—C14 benzene ring is 37.1 (2)°. The methanol molecule is linked to the Schiff base molecule through the O—H···O hydrogen bond (Table 1). In the crystal structure, molecules are linked through intermolecular N—H···O hydrogen bonds (Table 1) to form layers parallel to the *bc* direction (Fig. 2).

## Experimental

2-Nitrobenzohydrazide (1 mmol, 0.181 g) and 3,5-dibromosalicylaldehyde (1 mmol, 0.280 g) were dissolved in anhydrous methanol (15 ml). The mixture was stirred for several minutes at room temperature. The product was isolated and recrystallized from methanol, colourless blocks of (I) were obtained after five days.

## Refinement

The imino H atom was located in a difference map and its positional parameters were refined with a fixed isotropic thermal parameter of 0.08 Å$^2$. Other H atoms were positioned geometrically and refined as riding with C—H = 0.93 Å (aromatic) and 0.96 Å (methyl), O—H = 0.82 Å, and with $U_{iso}$(H) = 1.2$U_{eq}$(C) and 1.5$U_{eq}$(C15 and O).

## Figures

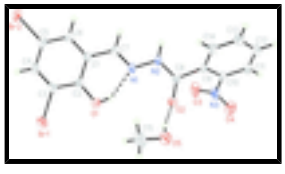


Fig. 1. The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonding is shown as dashed lines.

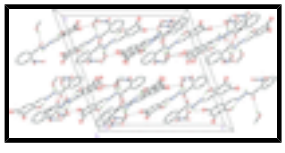


Fig. 2. The molecular packing of the title compound, viewed along the *b* axis. Hydrogen bonding is shown in dashed lines.

**(*E*)-*N*'-(3,5-Dibromo-2-hydroxybenzylidene)-2-nitrobenzohydrazide methanol solvate**

*Crystal data*

| | |
|---|---|
| $C_{14}H_9Br_2N_3O_4·CH_4O$ | $F_{000}$ = 1872 |
| $M_r$ = 475.10 | $D_x$ = 1.794 Mg m$^{-3}$ |
| Monoclinic, *C*2/*c* | Mo *K*α radiation, λ = 0.71073 Å |
| Hall symbol: -C 2yc | Cell parameters from 3081 reflections |
| *a* = 18.981 (1) Å | θ = 2.7–25.0º |
| *b* = 10.054 (2) Å | μ = 4.64 mm$^{-1}$ |
| *c* = 19.746 (2) Å | *T* = 298 K |
| β = 110.974 (2)º | Block, colourless |
| *V* = 3518.6 (8) Å$^3$ | 0.18 × 0.17 × 0.16 mm |
| *Z* = 8 | |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD diffractometer | 3784 independent reflections |
| Radiation source: fine-focus sealed tube | 2670 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int}$ = 0.041 |
| *T* = 298 K | $\theta_{max}$ = 26.9º |
| ω scans | $\theta_{min}$ = 2.2º |
| Absorption correction: multi-scan (SADABS; Bruker, 2001) | *h* = −24→20 |
| $T_{min}$ = 0.490, $T_{max}$ = 0.524 | *k* = −12→12 |
| 10461 measured reflections | *l* = −19→25 |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.036 | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2)$ = 0.094 | $w = 1/[\sigma^2(F_o^2) + (0.0488P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| *S* = 1.02 | $(\Delta/\sigma)_{max} < 0.001$ |
| 3784 reflections | $\Delta\rho_{max}$ = 0.36 e Å$^{-3}$ |
| 232 parameters | $\Delta\rho_{min}$ = −0.65 e Å$^{-3}$ |
| 1 restraint | Extinction correction: none |
| Primary atom site location: structure-invariant direct methods | |

*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 ($Å^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Br1 | 0.07056 (2) | 0.15611 (4) | 0.382792 (19) | 0.05768 (14) |
| Br2 | 0.14655 (2) | 0.69346 (4) | 0.365230 (19) | 0.06064 (15) |
| O1 | 0.16461 (14) | 0.1962 (2) | 0.53986 (11) | 0.0507 (6) |
| H1 | 0.1901 | 0.2081 | 0.5828 | 0.076* |
| O2 | 0.26477 (13) | 0.1296 (2) | 0.74915 (11) | 0.0556 (6) |
| O3 | 0.42343 (15) | 0.0570 (3) | 0.78985 (13) | 0.0758 (8) |
| O4 | 0.43759 (18) | −0.0577 (3) | 0.88592 (14) | 0.0873 (9) |
| O5 | 0.12161 (14) | 0.0782 (2) | 0.74447 (13) | 0.0640 (7) |
| H5 | 0.1605 | 0.1003 | 0.7384 | 0.096* |
| N1 | 0.25316 (14) | 0.3244 (2) | 0.65150 (13) | 0.0403 (6) |
| N2 | 0.30067 (15) | 0.3314 (2) | 0.72253 (13) | 0.0421 (6) |
| N3 | 0.42213 (15) | 0.0446 (3) | 0.85052 (15) | 0.0526 (7) |
| C1 | 0.20261 (16) | 0.4236 (3) | 0.53512 (14) | 0.0357 (6) |
| C2 | 0.16312 (16) | 0.3082 (3) | 0.50269 (15) | 0.0369 (7) |
| C3 | 0.12163 (17) | 0.3109 (3) | 0.42817 (15) | 0.0391 (7) |
| C4 | 0.11755 (16) | 0.4237 (3) | 0.38783 (15) | 0.0429 (7) |
| H4 | 0.0893 | 0.4242 | 0.3384 | 0.052* |
| C5 | 0.15566 (17) | 0.5361 (3) | 0.42122 (15) | 0.0422 (7) |
| C6 | 0.19789 (16) | 0.5366 (3) | 0.49391 (15) | 0.0405 (7) |
| H6 | 0.2235 | 0.6133 | 0.5156 | 0.049* |
| C7 | 0.24867 (16) | 0.4255 (3) | 0.61175 (15) | 0.0390 (7) |
| H7 | 0.2753 | 0.5021 | 0.6320 | 0.047* |
| C8 | 0.30280 (16) | 0.2312 (3) | 0.76752 (16) | 0.0384 (7) |
| C9 | 0.35228 (16) | 0.2548 (3) | 0.84468 (15) | 0.0365 (7) |
| C10 | 0.40432 (17) | 0.1623 (3) | 0.88545 (15) | 0.0391 (7) |
| C11 | 0.4444 (2) | 0.1791 (3) | 0.95794 (16) | 0.0517 (9) |
| H11 | 0.4787 | 0.1150 | 0.9840 | 0.062* |
| C12 | 0.4331 (2) | 0.2913 (4) | 0.99107 (18) | 0.0608 (10) |
| H12 | 0.4601 | 0.3039 | 1.0402 | 0.073* |
| C13 | 0.3827 (2) | 0.3856 (4) | 0.95328 (18) | 0.0622 (10) |
| H13 | 0.3756 | 0.4621 | 0.9766 | 0.075* |
| C14 | 0.34200 (19) | 0.3670 (3) | 0.87998 (16) | 0.0494 (8) |
| H14 | 0.3074 | 0.4312 | 0.8544 | 0.059* |

| | | | | |
|---|---|---|---|---|
| C15 | 0.0603 (2) | 0.1292 (4) | 0.6894 (2) | 0.0898 (15) |
| H15A | 0.0148 | 0.0934 | 0.6928 | 0.135* |
| H15B | 0.0634 | 0.1056 | 0.6435 | 0.135* |
| H15C | 0.0599 | 0.2243 | 0.6937 | 0.135* |
| H2 | 0.3299 (18) | 0.403 (2) | 0.7369 (19) | 0.080* |

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

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.0549 (2) | 0.0620 (2) | 0.0483 (2) | −0.01531 (16) | 0.00887 (17) | −0.01568 (16) |
| Br2 | 0.0684 (3) | 0.0597 (2) | 0.0450 (2) | 0.00128 (17) | 0.00967 (18) | 0.02143 (16) |
| O1 | 0.0630 (16) | 0.0411 (12) | 0.0378 (12) | −0.0092 (10) | 0.0055 (11) | 0.0045 (10) |
| O2 | 0.0565 (15) | 0.0490 (13) | 0.0457 (13) | −0.0159 (11) | −0.0007 (11) | 0.0061 (10) |
| O3 | 0.095 (2) | 0.091 (2) | 0.0403 (15) | 0.0193 (16) | 0.0228 (14) | −0.0040 (13) |
| O4 | 0.131 (3) | 0.0544 (16) | 0.0632 (17) | 0.0358 (16) | 0.0182 (17) | 0.0122 (14) |
| O5 | 0.0643 (17) | 0.0531 (15) | 0.0629 (15) | 0.0092 (13) | 0.0086 (13) | 0.0013 (12) |
| N1 | 0.0377 (15) | 0.0457 (15) | 0.0276 (12) | −0.0015 (10) | −0.0005 (11) | 0.0039 (10) |
| N2 | 0.0436 (16) | 0.0422 (15) | 0.0268 (12) | −0.0059 (11) | −0.0041 (11) | 0.0071 (11) |
| N3 | 0.0528 (18) | 0.0576 (18) | 0.0380 (16) | 0.0095 (13) | 0.0051 (13) | 0.0014 (13) |
| C1 | 0.0332 (17) | 0.0404 (16) | 0.0293 (14) | −0.0005 (12) | 0.0062 (12) | 0.0007 (12) |
| C2 | 0.0336 (17) | 0.0408 (16) | 0.0339 (15) | 0.0000 (12) | 0.0091 (13) | 0.0012 (13) |
| C3 | 0.0345 (17) | 0.0461 (17) | 0.0333 (16) | −0.0041 (12) | 0.0080 (13) | −0.0061 (13) |
| C4 | 0.0366 (18) | 0.061 (2) | 0.0263 (15) | 0.0010 (14) | 0.0054 (13) | 0.0032 (14) |
| C5 | 0.0431 (19) | 0.0491 (19) | 0.0317 (15) | 0.0051 (13) | 0.0100 (13) | 0.0102 (13) |
| C6 | 0.0414 (18) | 0.0387 (17) | 0.0362 (16) | −0.0008 (13) | 0.0075 (13) | 0.0038 (13) |
| C7 | 0.0398 (18) | 0.0382 (16) | 0.0313 (15) | −0.0013 (12) | 0.0034 (13) | 0.0032 (13) |
| C8 | 0.0325 (17) | 0.0425 (17) | 0.0343 (15) | 0.0014 (13) | 0.0049 (13) | 0.0040 (13) |
| C9 | 0.0386 (17) | 0.0378 (15) | 0.0308 (14) | −0.0031 (12) | 0.0097 (13) | 0.0061 (12) |
| C10 | 0.0412 (19) | 0.0422 (17) | 0.0300 (15) | −0.0001 (12) | 0.0078 (13) | 0.0036 (12) |
| C11 | 0.055 (2) | 0.058 (2) | 0.0309 (17) | 0.0027 (15) | 0.0018 (15) | 0.0105 (15) |
| C12 | 0.081 (3) | 0.064 (2) | 0.0268 (16) | −0.0072 (19) | 0.0065 (17) | −0.0010 (16) |
| C13 | 0.093 (3) | 0.051 (2) | 0.041 (2) | −0.0017 (19) | 0.022 (2) | −0.0061 (16) |
| C14 | 0.059 (2) | 0.0438 (19) | 0.0419 (19) | 0.0029 (15) | 0.0138 (17) | 0.0044 (14) |
| C15 | 0.080 (3) | 0.075 (3) | 0.081 (3) | 0.018 (2) | −0.013 (3) | −0.005 (2) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Br1—C3 | 1.882 (3) | C4—C5 | 1.377 (4) |
| Br2—C5 | 1.902 (3) | C4—H4 | 0.9300 |
| O1—C2 | 1.338 (3) | C5—C6 | 1.371 (4) |
| O1—H1 | 0.8200 | C6—H6 | 0.9300 |
| O2—C8 | 1.228 (4) | C7—H7 | 0.9300 |
| O3—N3 | 1.214 (3) | C8—C9 | 1.495 (4) |
| O4—N3 | 1.218 (4) | C9—C14 | 1.376 (5) |
| O5—C15 | 1.376 (4) | C9—C10 | 1.385 (4) |
| O5—H5 | 0.8200 | C10—C11 | 1.370 (4) |
| N1—C7 | 1.269 (4) | C11—C12 | 1.359 (5) |
| N1—N2 | 1.371 (3) | C11—H11 | 0.9300 |
| N2—C8 | 1.335 (4) | C12—C13 | 1.364 (5) |

| | | | |
|---|---|---|---|
| N2—H2 | 0.893 (10) | C12—H12 | 0.9300 |
| N3—C10 | 1.469 (4) | C13—C14 | 1.388 (4) |
| C1—C6 | 1.382 (4) | C13—H13 | 0.9300 |
| C1—C2 | 1.405 (4) | C14—H14 | 0.9300 |
| C1—C7 | 1.452 (4) | C15—H15A | 0.9600 |
| C2—C3 | 1.399 (4) | C15—H15B | 0.9600 |
| C3—C4 | 1.372 (4) | C15—H15C | 0.9600 |
| C2—O1—H1 | 109.5 | C1—C7—H7 | 119.5 |
| C15—O5—H5 | 109.5 | O2—C8—N2 | 123.8 (3) |
| C7—N1—N2 | 117.7 (2) | O2—C8—C9 | 121.4 (3) |
| C8—N2—N1 | 119.6 (2) | N2—C8—C9 | 114.6 (3) |
| C8—N2—H2 | 122 (2) | C14—C9—C10 | 117.2 (3) |
| N1—N2—H2 | 118 (2) | C14—C9—C8 | 119.7 (3) |
| O3—N3—O4 | 124.6 (3) | C10—C9—C8 | 122.9 (3) |
| O3—N3—C10 | 118.0 (3) | C11—C10—C9 | 122.6 (3) |
| O4—N3—C10 | 117.3 (3) | C11—C10—N3 | 117.0 (3) |
| C6—C1—C2 | 120.0 (3) | C9—C10—N3 | 120.3 (3) |
| C6—C1—C7 | 119.4 (3) | C12—C11—C10 | 118.7 (3) |
| C2—C1—C7 | 120.7 (3) | C12—C11—H11 | 120.6 |
| O1—C2—C3 | 119.1 (3) | C10—C11—H11 | 120.6 |
| O1—C2—C1 | 122.8 (2) | C11—C12—C13 | 121.0 (3) |
| C3—C2—C1 | 118.1 (3) | C11—C12—H12 | 119.5 |
| C4—C3—C2 | 121.4 (3) | C13—C12—H12 | 119.5 |
| C4—C3—Br1 | 119.6 (2) | C12—C13—C14 | 119.8 (3) |
| C2—C3—Br1 | 119.0 (2) | C12—C13—H13 | 120.1 |
| C3—C4—C5 | 119.3 (3) | C14—C13—H13 | 120.1 |
| C3—C4—H4 | 120.3 | C9—C14—C13 | 120.8 (3) |
| C5—C4—H4 | 120.3 | C9—C14—H14 | 119.6 |
| C6—C5—C4 | 121.0 (3) | C13—C14—H14 | 119.6 |
| C6—C5—Br2 | 120.2 (2) | O5—C15—H15A | 109.5 |
| C4—C5—Br2 | 118.8 (2) | O5—C15—H15B | 109.5 |
| C5—C6—C1 | 120.3 (3) | H15A—C15—H15B | 109.5 |
| C5—C6—H6 | 119.9 | O5—C15—H15C | 109.5 |
| C1—C6—H6 | 119.9 | H15A—C15—H15C | 109.5 |
| N1—C7—C1 | 121.1 (3) | H15B—C15—H15C | 109.5 |
| N1—C7—H7 | 119.5 | | |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1···N1 | 0.82 | 1.87 | 2.587 (3) | 146 |
| O5—H5···O2 | 0.82 | 1.94 | 2.735 (4) | 165 |
| N2—H2···O5$^{i}$ | 0.893 (10) | 1.958 (13) | 2.840 (3) | 169 (4) |

Symmetry codes: (i) −*x*+1/2, *y*+1/2, −*z*+3/2.

**Fig. 1**

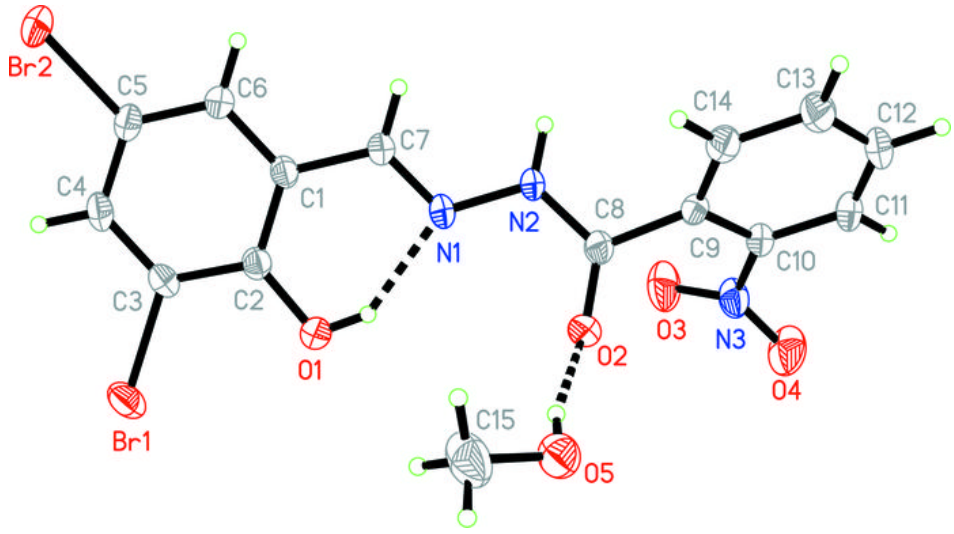

Br2
C5
C6
C7
C4
C1
N1
N2
C8
C14
C13
C12
C9
C10
C11
C3
C2
O1
O3
N3
O2
O4
Br1
C15
O5

**Fig. 2**