

(E)-4-Hydroxy-N'-(3-hydroxy-4-methoxybenzylidene)benzohydrazide

Hoong-Kun Fun,^{a,*} Jirapa Horkaew^b and Suchada Chantrapromma^c

^aX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, ^bDepartment of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand, and ^cCrystal Materials Research Unit, Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand

Correspondence e-mail: hkfun@usm.my

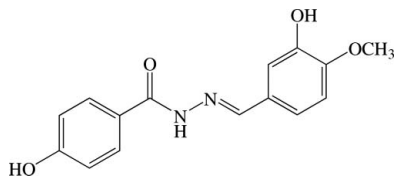
Received 6 September 2011; accepted 8 September 2011

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.041; wR factor = 0.125; data-to-parameter ratio = 20.5.

The molecule of the title benzohydrazide derivative, $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_4$, exists in a *trans* conformation with respect to the $\text{C}=\text{N}$ double bond and is twisted, the dihedral angle between the two benzene rings being 24.17 (6)°. The methoxy group is almost co-planar with respect to the attached benzene ring [$\text{C}_m-\text{O}-\text{C}-\text{C}$ ($m = \text{methyl}$) = -1.45 (17)°]. In the crystal, the molecules are linked by $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds into sheets parallel to the *bc* plane. These sheets are further connected into a three-dimensional network by weak $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\pi$ interactions.

Related literature

For bond-length data, see: Allen *et al.* (1987). For related structures, see: Li & Ban (2009); Zhang (2011). For background to and applications of benzohydrazide derivatives, see: Bedia *et al.* (2006); Bhole & Bhusari (2009); Loncle *et al.* (2004); Raj *et al.* (2007). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer, (1986).



* Thomson Reuters ResearcherID: A-3561-2009.

† Thomson Reuters ResearcherID: A-5085-2009. Additional correspondence author, email: suchada.c@psu.ac.th.

Experimental

Crystal data

$\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_4$
 $M_r = 286.28$
 Monoclinic, $P2_1/c$
 $a = 10.7484$ (5) Å
 $b = 9.4669$ (4) Å
 $c = 15.7198$ (5) Å
 $\beta = 122.166$ (2)°
 $V = 1354.04$ (10) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹
 $T = 100$ K
 $0.42 \times 0.29 \times 0.19$ mm

Data collection

Bruker APEX DUO CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2009)
 $T_{\min} = 0.958$, $T_{\max} = 0.981$
 16525 measured reflections
 3910 independent reflections
 3438 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.125$
 $S = 1.03$
 3910 reflections
 191 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.45$ e Å⁻³
 $\Delta\rho_{\min} = -0.49$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C1–C6 ring.

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{N1}-\text{H1A}\cdots\text{O3}^{\text{i}}$ | 0.88 | 2.30 | 2.9798 (12) | 134 |
| $\text{N1}-\text{H1A}\cdots\text{O4}^{\text{i}}$ | 0.88 | 2.53 | 3.3542 (12) | 156 |
| $\text{O2}-\text{H2A}\cdots\text{O1}^{\text{ii}}$ | 0.84 | 1.89 | 2.7259 (11) | 174 |
| $\text{O3}-\text{H3A}\cdots\text{O1}^{\text{iii}}$ | 0.84 | 1.88 | 2.6762 (13) | 157 |
| $\text{C10}-\text{H10A}\cdots\text{O2}^{\text{iv}}$ | 0.95 | 2.58 | 3.4786 (14) | 158 |
| $\text{C15}-\text{H15B}\cdots\text{Cg1}^{\text{v}}$ | 0.98 | 2.85 | 3.7211 (16) | 149 |

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); 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 and PLATON (Spek, 2009).

JH thanks the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Commission on Higher Education, Ministry of Education, for financial support. The authors thank the Prince of Songkla University and Universiti Sains Malaysia for the Research University Grant No. 1001/PFIZIK/811160.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6400).

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
 Bedia, K.-K., Elçin, O., Seda, U., Fatma, K., Nathaly, S., Sevim, R. & Dimoglo, A. (2006). *Eur. J. Med. Chem.* **41**, 1253–1261.
 Bhole, R. P. & Bhusari, K. P. (2009). *QSAR Comb. Sci.* **28**, 1405–1417.
 Bruker (2009). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.

- Li, C.-M. & Ban, H.-Y. (2009). *Acta Cryst.* **E65**, o876.
- Loncle, C., Brunel, J. M., Vidal, N., Dherbomez, M. & Letourneux, Y. (2004). *Eur. J. Med. Chem.* **39**, 1067–1071.
- Raj, K. K. V., Narayana, B., Ashalatha, B. V., Kumari, N. S. & Sarojini, B. K. (2007). *Eur. J. Med. Chem.* **42**, 425–429.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Zhang, Z. (2011). *Acta Cryst.* **E67**, o300.

supplementary materials

Acta Cryst. (2011). E67, o2644–o2645 [doi:10.1107/S1600536811036579]

(*E*)-4-Hydroxy-*N'*-(3-hydroxy-4-methoxybenzylidene)benzohydrazide

H.-K. Fun, J. Horkaew and S. Chantrapromma

Comment

Benzohydrazide derivatives have a wide variety of biological properties, such as antibacterial (Bhole & Bhusari, 2009), antifungal (Loncle *et al.*, 2004), antitubecular (Bedia *et al.*, 2006) and antiproliferative (Raj *et al.*, 2007) activities.

These interesting properties lead us to synthesize the title compound (I), which contains hydroxyl and methoxy substituents, in order to study and compare its biological properties with other related benzohydrazide derivatives. Herein the crystal structure of (I) is reported.

The molecule of the title benzohydrazide derivative (Fig. 1), C₁₅H₁₄N₂O₄, exists in a *trans*-configuration with respect to the C8=N2 bond [1.2811 (13) Å] and the torsion angle N1–N2–C8–C9 = 178.77 (9)°. The molecule is twisted with the dihedral angle between the two benzene rings being 24.17 (6)°. Atom O1, C7, N1, N2 and C8 of the middle bridge lie nearly on the same plane with the torsion angle O1–C7–N1–N2 = -3.15 (14)°. The mean plane through this middle bridge makes the dihedral angles of 4.82 (7) and 25.95 (7)° with the C1–C6 and C9–C14 benzene rings, respectively. The methoxy group is almost co-planar with the attached benzene ring with the torsion angle C15–O4–C12–C13 = -1.45 (17)°. Bond distances are of normal values (Allen *et al.*, 1987) and are comparable with related structures (Li & Ban, 2009; Zhang, 2011).

In the crystal packing (Fig. 2), the molecules are linked by N—H···O and O—H···O hydrogen bonds (Table 1) into sheets parallel to the *bc* plane and these sheets are further connected into three dimensional network. The crystal is stabilized N—H···O and O—H···O hydrogen bonds together with C—H···O weak interaction. C—H···π weak interaction (Table 1) was also observed.

Experimental

The title compound (I) was prepared by dissolving 4-hydroxybenzohydrazide (0.1 mmol, 0.15 g) in ethanol (15 ml). A solution of 3-hydroxy-4-methoxybenzaldehyde (0.1 mmol, 0.15 g) in ethanol (15 ml) was then added slowly to the reaction. The mixture was refluxed for around 5 hr. The solution was then cooled to room temperature. Colorless blocks of (I) were obtained after slow evaporation of the solvent at room temperature after several days, Mp. 516 K (decompose).

Refinement

All H atoms were positioned geometrically and allowed to ride on their parent atoms, with d(O-H) = 0.84 Å, d(N-H) = 0.88 Å, d(C-H) = 0.95 Å for aromatic and CH and 0.98 Å for CH₃ atoms. The U_{iso} values were constrained to be 1.5 U_{eq} of the carrier atom for methyl H atoms and 1.2 U_{eq} for the remaining H atoms. A rotating group model was used for the methyl groups. The highest residual electron density peak is located at 0.70 Å from C1 and the deepest hole is located at 0.21 Å from H2A.

Figures

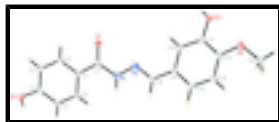


Fig. 1. The molecular structure of the title compound, showing 50% probability displacement ellipsoids.

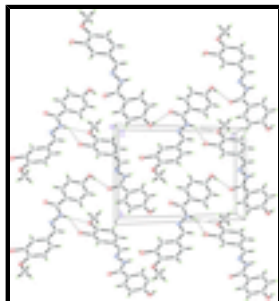


Fig. 2. The crystal packing of the title compound viewed along the *a* axis, Hydrogen bonds were shown as dashed lines.

(*E*)-4-Hydroxy-*N'*-(3-hydroxy-4-methoxybenzylidene)benzohydrazide

Crystal data

$C_{15}H_{14}N_2O_4$

$M_r = 286.28$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 10.7484\ (5)\ \text{\AA}$

$b = 9.4669\ (4)\ \text{\AA}$

$c = 15.7198\ (5)\ \text{\AA}$

$\beta = 122.166\ (2)^\circ$

$V = 1354.04\ (10)\ \text{\AA}^3$

$Z = 4$

$F(000) = 600$

$D_x = 1.404\ \text{Mg m}^{-3}$

Melting point = 516 (decompose)–516 K

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3910 reflections

$\theta = 2.2\text{--}30.0^\circ$

$\mu = 0.10\ \text{mm}^{-1}$

$T = 100\ \text{K}$

Block, colorless

$0.42 \times 0.29 \times 0.19\ \text{mm}$

Data collection

Bruker APEX DUO CCD
diffractometer

Radiation source: sealed tube
graphite

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2009)

$T_{\min} = 0.958$, $T_{\max} = 0.981$

16525 measured reflections

3910 independent reflections

3438 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 30.0^\circ$, $\theta_{\min} = 2.2^\circ$

$h = -14 \rightarrow 15$

$k = -13 \rightarrow 13$

$l = -22 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

$$R[F^2 > 2\sigma(F^2)] = 0.041$$

$$wR(F^2) = 0.125$$

$$S = 1.03$$

3910 reflections

191 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0719P)^2 + 0.4766P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.45 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.49 \text{ e } \text{\AA}^{-3}$$

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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 $F^2 > 2\sigma(F^2)$ 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> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|-------------|----------------------------------|
| O1 | 0.43925 (8) | 1.18018 (8) | 0.58385 (5) | 0.01852 (17) |
| O2 | 0.49471 (9) | 1.47445 (8) | 0.24675 (6) | 0.01967 (17) |
| H2A | 0.4792 | 1.4316 | 0.1952 | 0.030* |
| O3 | 0.26685 (8) | 0.66939 (8) | 0.80751 (6) | 0.01987 (17) |
| H3A | 0.3556 | 0.6774 | 0.8260 | 0.030* |
| O4 | 0.01675 (9) | 0.54612 (9) | 0.72204 (6) | 0.02306 (18) |
| N1 | 0.28428 (10) | 1.03431 (9) | 0.45801 (6) | 0.01717 (18) |
| H1A | 0.2380 | 1.0104 | 0.3942 | 0.021* |
| N2 | 0.26221 (9) | 0.96119 (9) | 0.52515 (6) | 0.01676 (18) |
| C1 | 0.40755 (10) | 1.22076 (10) | 0.42422 (7) | 0.01464 (18) |
| C2 | 0.50952 (12) | 1.33110 (12) | 0.46469 (8) | 0.0208 (2) |
| H2B | 0.5603 | 1.3494 | 0.5348 | 0.025* |
| C3 | 0.53774 (12) | 1.41401 (12) | 0.40453 (8) | 0.0229 (2) |
| H3B | 0.6071 | 1.4888 | 0.4334 | 0.027* |
| C4 | 0.46467 (10) | 1.38813 (10) | 0.30166 (7) | 0.01553 (19) |
| C5 | 0.36654 (12) | 1.27532 (12) | 0.26061 (8) | 0.0210 (2) |
| H5A | 0.3193 | 1.2547 | 0.1910 | 0.025* |
| C6 | 0.33780 (12) | 1.19320 (12) | 0.32125 (8) | 0.0208 (2) |
| H6A | 0.2699 | 1.1173 | 0.2925 | 0.025* |
| C7 | 0.37956 (10) | 1.14385 (10) | 0.49418 (7) | 0.01477 (18) |
| C8 | 0.15580 (12) | 0.87261 (12) | 0.48512 (8) | 0.0204 (2) |

supplementary materials

| | | | | |
|------|---------------|--------------|--------------|--------------|
| H8A | 0.0982 | 0.8631 | 0.4141 | 0.024* |
| C9 | 0.12146 (11) | 0.78585 (11) | 0.54692 (8) | 0.0189 (2) |
| C10 | 0.21899 (10) | 0.77112 (10) | 0.65114 (7) | 0.01542 (19) |
| H10A | 0.3115 | 0.8176 | 0.6838 | 0.019* |
| C11 | 0.18034 (10) | 0.68906 (10) | 0.70614 (7) | 0.01506 (19) |
| C12 | 0.04194 (11) | 0.62256 (11) | 0.65889 (8) | 0.0189 (2) |
| C13 | -0.05414 (13) | 0.63664 (15) | 0.55581 (9) | 0.0306 (3) |
| H13A | -0.1475 | 0.5918 | 0.5232 | 0.037* |
| C14 | -0.01309 (13) | 0.71667 (15) | 0.50042 (9) | 0.0312 (3) |
| H14A | -0.0781 | 0.7241 | 0.4297 | 0.037* |
| C15 | -0.12259 (13) | 0.47708 (14) | 0.67802 (10) | 0.0297 (3) |
| H15D | -0.1294 | 0.4289 | 0.7306 | 0.045* |
| H15A | -0.1325 | 0.4077 | 0.6285 | 0.045* |
| H15B | -0.2014 | 0.5473 | 0.6448 | 0.045* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|------------|------------|-------------|------------|-------------|
| O1 | 0.0209 (3) | 0.0232 (4) | 0.0119 (3) | -0.0039 (3) | 0.0090 (3) | -0.0025 (3) |
| O2 | 0.0247 (4) | 0.0215 (4) | 0.0148 (3) | -0.0043 (3) | 0.0119 (3) | 0.0004 (3) |
| O3 | 0.0180 (3) | 0.0263 (4) | 0.0132 (3) | -0.0006 (3) | 0.0069 (3) | 0.0032 (3) |
| O4 | 0.0221 (4) | 0.0259 (4) | 0.0225 (4) | -0.0044 (3) | 0.0128 (3) | 0.0058 (3) |
| N1 | 0.0221 (4) | 0.0188 (4) | 0.0119 (4) | -0.0044 (3) | 0.0100 (3) | -0.0008 (3) |
| N2 | 0.0198 (4) | 0.0186 (4) | 0.0146 (4) | 0.0001 (3) | 0.0110 (3) | 0.0020 (3) |
| C1 | 0.0162 (4) | 0.0159 (4) | 0.0129 (4) | -0.0002 (3) | 0.0085 (3) | -0.0002 (3) |
| C2 | 0.0222 (5) | 0.0248 (5) | 0.0121 (4) | -0.0074 (4) | 0.0069 (4) | -0.0013 (4) |
| C3 | 0.0244 (5) | 0.0265 (5) | 0.0142 (5) | -0.0107 (4) | 0.0079 (4) | -0.0018 (4) |
| C4 | 0.0170 (4) | 0.0172 (4) | 0.0142 (4) | 0.0007 (3) | 0.0096 (3) | 0.0014 (3) |
| C5 | 0.0263 (5) | 0.0244 (5) | 0.0131 (4) | -0.0077 (4) | 0.0111 (4) | -0.0040 (4) |
| C6 | 0.0265 (5) | 0.0221 (5) | 0.0155 (5) | -0.0097 (4) | 0.0124 (4) | -0.0055 (4) |
| C7 | 0.0158 (4) | 0.0163 (4) | 0.0130 (4) | 0.0009 (3) | 0.0081 (3) | 0.0004 (3) |
| C8 | 0.0211 (5) | 0.0246 (5) | 0.0141 (4) | -0.0031 (4) | 0.0084 (4) | 0.0021 (4) |
| C9 | 0.0184 (4) | 0.0219 (5) | 0.0153 (4) | -0.0030 (3) | 0.0083 (4) | 0.0023 (3) |
| C10 | 0.0146 (4) | 0.0165 (4) | 0.0154 (4) | -0.0009 (3) | 0.0081 (3) | -0.0003 (3) |
| C11 | 0.0155 (4) | 0.0156 (4) | 0.0137 (4) | 0.0017 (3) | 0.0076 (3) | 0.0006 (3) |
| C12 | 0.0189 (4) | 0.0199 (5) | 0.0189 (5) | -0.0023 (3) | 0.0106 (4) | 0.0030 (4) |
| C13 | 0.0200 (5) | 0.0428 (7) | 0.0205 (5) | -0.0137 (5) | 0.0050 (4) | 0.0054 (5) |
| C14 | 0.0225 (5) | 0.0452 (7) | 0.0158 (5) | -0.0128 (5) | 0.0032 (4) | 0.0066 (5) |
| C15 | 0.0267 (5) | 0.0295 (6) | 0.0348 (6) | -0.0092 (4) | 0.0177 (5) | 0.0038 (5) |

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

| | | | |
|--------|-------------|--------|-------------|
| O1—C7 | 1.2465 (12) | C4—C5 | 1.3946 (14) |
| O2—C4 | 1.3468 (12) | C5—C6 | 1.3864 (14) |
| O2—H2A | 0.8400 | C5—H5A | 0.9500 |
| O3—C11 | 1.3642 (12) | C6—H6A | 0.9500 |
| O3—H3A | 0.8400 | C8—C9 | 1.4616 (14) |
| O4—C12 | 1.3671 (12) | C8—H8A | 0.9500 |
| O4—C15 | 1.4302 (13) | C9—C14 | 1.3889 (15) |

| | | | |
|-------------|--------------|----------------|-------------|
| N1—C7 | 1.3518 (13) | C9—C10 | 1.4049 (13) |
| N1—N2 | 1.3841 (11) | C10—C11 | 1.3804 (13) |
| N1—H1A | 0.8800 | C10—H10A | 0.9500 |
| N2—C8 | 1.2811 (13) | C11—C12 | 1.4087 (14) |
| C1—C2 | 1.3981 (13) | C12—C13 | 1.3886 (15) |
| C1—C6 | 1.3992 (13) | C13—C14 | 1.3913 (16) |
| C1—C7 | 1.4774 (13) | C13—H13A | 0.9500 |
| C2—C3 | 1.3813 (14) | C14—H14A | 0.9500 |
| C2—H2B | 0.9500 | C15—H15D | 0.9800 |
| C3—C4 | 1.3927 (14) | C15—H15A | 0.9800 |
| C3—H3B | 0.9500 | C15—H15B | 0.9800 |
| C4—O2—H2A | 109.5 | N2—C8—C9 | 121.12 (9) |
| C11—O3—H3A | 109.5 | N2—C8—H8A | 119.4 |
| C12—O4—C15 | 116.86 (9) | C9—C8—H8A | 119.4 |
| C7—N1—N2 | 117.51 (8) | C14—C9—C10 | 119.23 (10) |
| C7—N1—H1A | 121.2 | C14—C9—C8 | 118.41 (9) |
| N2—N1—H1A | 121.2 | C10—C9—C8 | 122.36 (9) |
| C8—N2—N1 | 115.06 (8) | C11—C10—C9 | 119.98 (9) |
| C2—C1—C6 | 118.24 (9) | C11—C10—H10A | 120.0 |
| C2—C1—C7 | 116.77 (9) | C9—C10—H10A | 120.0 |
| C6—C1—C7 | 124.97 (9) | O3—C11—C10 | 124.27 (9) |
| C3—C2—C1 | 121.18 (9) | O3—C11—C12 | 115.25 (9) |
| C3—C2—H2B | 119.4 | C10—C11—C12 | 120.44 (9) |
| C1—C2—H2B | 119.4 | O4—C12—C13 | 125.91 (9) |
| C2—C3—C4 | 120.09 (9) | O4—C12—C11 | 114.55 (9) |
| C2—C3—H3B | 120.0 | C13—C12—C11 | 119.53 (9) |
| C4—C3—H3B | 120.0 | C12—C13—C14 | 119.73 (10) |
| O2—C4—C3 | 117.26 (9) | C12—C13—H13A | 120.1 |
| O2—C4—C5 | 123.26 (9) | C14—C13—H13A | 120.1 |
| C3—C4—C5 | 119.48 (9) | C9—C14—C13 | 121.04 (10) |
| C6—C5—C4 | 120.11 (9) | C9—C14—H14A | 119.5 |
| C6—C5—H5A | 119.9 | C13—C14—H14A | 119.5 |
| C4—C5—H5A | 119.9 | O4—C15—H15D | 109.5 |
| C5—C6—C1 | 120.83 (9) | O4—C15—H15A | 109.5 |
| C5—C6—H6A | 119.6 | H15D—C15—H15A | 109.5 |
| C1—C6—H6A | 119.6 | O4—C15—H15B | 109.5 |
| O1—C7—N1 | 120.39 (9) | H15D—C15—H15B | 109.5 |
| O1—C7—C1 | 121.31 (9) | H15A—C15—H15B | 109.5 |
| N1—C7—C1 | 118.28 (8) | | |
| C7—N1—N2—C8 | 170.09 (9) | N2—C8—C9—C14 | 165.34 (12) |
| C6—C1—C2—C3 | 2.04 (16) | N2—C8—C9—C10 | -14.19 (17) |
| C7—C1—C2—C3 | -176.66 (10) | C14—C9—C10—C11 | -0.25 (16) |
| C1—C2—C3—C4 | -0.29 (18) | C8—C9—C10—C11 | 179.28 (10) |
| C2—C3—C4—O2 | 178.66 (10) | C9—C10—C11—O3 | -179.40 (9) |
| C2—C3—C4—C5 | -2.01 (17) | C9—C10—C11—C12 | -1.60 (15) |
| O2—C4—C5—C6 | -178.17 (10) | C15—O4—C12—C13 | -1.45 (17) |
| C3—C4—C5—C6 | 2.53 (16) | C15—O4—C12—C11 | 179.62 (10) |
| C4—C5—C6—C1 | -0.77 (17) | O3—C11—C12—O4 | -1.13 (13) |

supplementary materials

| | | | |
|-------------|--------------|-----------------|--------------|
| C2—C1—C6—C5 | -1.50 (16) | C10—C11—C12—O4 | -179.13 (9) |
| C7—C1—C6—C5 | 177.08 (10) | O3—C11—C12—C13 | 179.87 (11) |
| N2—N1—C7—O1 | -3.15 (14) | C10—C11—C12—C13 | 1.87 (16) |
| N2—N1—C7—C1 | 178.39 (8) | O4—C12—C13—C14 | -179.17 (12) |
| C2—C1—C7—O1 | 3.16 (14) | C11—C12—C13—C14 | -0.3 (2) |
| C6—C1—C7—O1 | -175.44 (10) | C10—C9—C14—C13 | 1.8 (2) |
| C2—C1—C7—N1 | -178.39 (9) | C8—C9—C14—C13 | -177.71 (13) |
| C6—C1—C7—N1 | 3.01 (15) | C12—C13—C14—C9 | -1.6 (2) |
| N1—N2—C8—C9 | 178.77 (9) | | |

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

Cg1 is the centroid of the C1—C6 ring.

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|-------|-------------|-------------|---------------|
| N1—H1A \cdots O3 ⁱ | 0.88 | 2.30 | 2.9798 (12) | 134 |
| N1—H1A \cdots O4 ⁱ | 0.88 | 2.53 | 3.3542 (12) | 156 |
| O2—H2A \cdots O1 ⁱⁱ | 0.84 | 1.89 | 2.7259 (11) | 174 |
| O3—H3A \cdots O1 ⁱⁱⁱ | 0.84 | 1.88 | 2.6762 (13) | 157 |
| C10—H10A \cdots O2 ^{iv} | 0.95 | 2.58 | 3.4786 (14) | 158 |
| C15—H15B \cdots Cg1 ^v | 0.98 | 2.85 | 3.7211 (16) | 149 |

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

Fig. 1

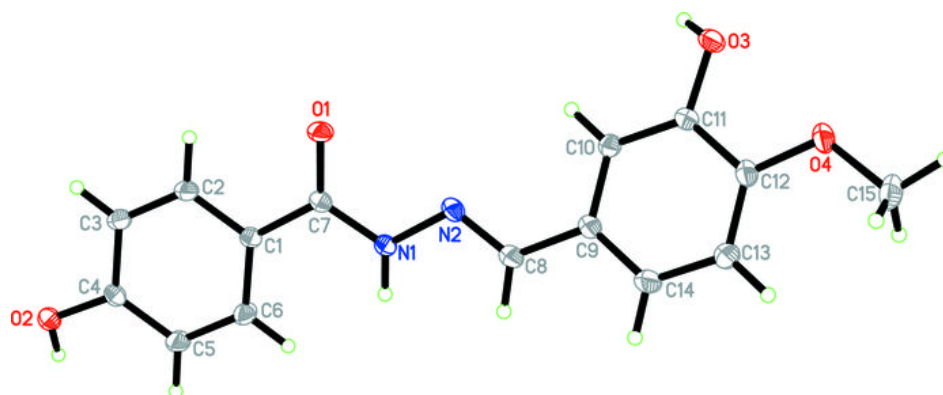


Fig. 2

