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(E)-2-[(2-Hydroxy-5-nitrophenyl)- iminoethyl]-4-nitrophenolate

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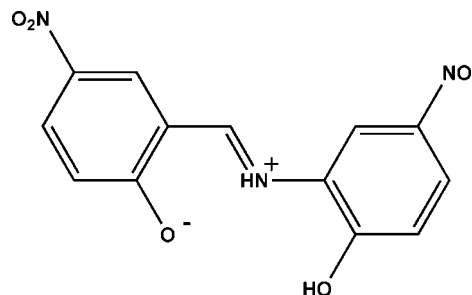
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 Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.041; wR factor = 0.129; data-to-parameter ratio = 12.4.

The title molecule, $\text{C}_{13}\text{H}_9\text{N}_3\text{O}_6$, consists of a 2-hydroxy-5-nitrophenyliminio group and a 4-nitrophenolate group bonded to a methylene C atom with both of the planar six-membered rings nearly in the plane of the molecule [dihedral angle = $1.3(4)^\circ$]. Each of the nitro O atoms is twisted slightly out of the plane of the molecule. The amine group forms an intramolecular hydrogen bond with both nearby O atoms, each of which has partial occupancy of attached H atoms [0.36(3) and 0.64(3)]. An extended π -delocalization throughout the entire molecule exists producing a zwitterionic effect in this region of the molecule. The shortened phenolate C—O bond [1.2749(19) Å], in concert with the slightly longer phenol C—O bond [1.3316(19) Å], provides evidence for this effect. The crystal packing is influenced by extensive strong intermolecular O—H...O hydrogen bonding between the depicted phenolate and hydroxy O atoms and their respective H atoms within the π -delocalized region of the molecule. As a result, molecules are linked into an infinite polymeric chain diagonally along the [110] plane of the unit cell in an alternate inverted pattern. A MOPAC AM1 calculation provides support for these observations.

Related literature

For related structures, see: Butcher *et al.* (2007); Ersanlı *et al.* (2003); Gül *et al.* (2007); Hijji *et al.* (2008); Odabaşoğlu *et al.* (2006); Jasinski *et al.* (2007). For related literature, see: Schmidt & Polik (2007).



Experimental

Crystal data

| | |
|---|---|
| $\text{C}_{13}\text{H}_9\text{N}_3\text{O}_6$ | $V = 1297.11(3) \text{ \AA}^3$ |
| $M_r = 303.23$ | $Z = 4$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation |
| $a = 7.9649(1) \text{ \AA}$ | $\mu = 0.13 \text{ mm}^{-1}$ |
| $b = 8.6110(1) \text{ \AA}$ | $T = 296(2) \text{ K}$ |
| $c = 19.1190(3) \text{ \AA}$ | $0.37 \times 0.27 \times 0.18 \text{ mm}$ |
| $\beta = 98.433(2)^\circ$ | |

Data collection

| | |
|---|--|
| Oxford Diffraction Gemini R diffractometer | 6432 measured reflections |
| Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2007) | 2495 independent reflections |
| $T_{\min} = 0.954$, $T_{\max} = 0.978$ | 1819 reflections with $I > 2\sigma(I)$ |
| | $R_{\text{int}} = 0.023$ |

Refinement

| | |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.041$ | 202 parameters |
| $wR(F^2) = 0.129$ | H-atom parameters constrained |
| $S = 1.05$ | $\Delta\rho_{\max} = 0.22 \text{ e \AA}^{-3}$ |
| 2495 reflections | $\Delta\rho_{\min} = -0.17 \text{ e \AA}^{-3}$ |

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------|-------|-------------|-------------|---------------|
| O1—H1O...O2 ⁱ | 0.82 | 1.77 | 2.5570 (16) | 161 |
| O2—H2O...O1 ⁱⁱ | 0.82 | 1.75 | 2.5570 (16) | 166 |
| N1—H1N...O1 | 0.86 | 1.90 | 2.6001 (19) | 138 |
| C3—H3A...O3 ⁱⁱⁱ | 0.93 | 2.56 | 3.295 (2) | 137 |
| C7—H7A...O4 ^{iv} | 0.93 | 2.67 | 3.289 (2) | 125 |
| C7—H7A...O5 ^v | 0.93 | 2.44 | 3.312 (2) | 156 |
| C10—H10A...O4 ^{vi} | 0.93 | 2.53 | 3.321 (2) | 143 |
| C13—H13A...O4 ^{iv} | 0.93 | 2.64 | 3.195 (2) | 119 |
| C13—H13A...O5 ^v | 0.93 | 2.63 | 3.512 (2) | 160 |

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

Data collection: *CrysAlisPro* (Oxford Diffraction, 2007); cell refinement: *CrysAlisPro*; data reduction: *CrysAlisPro* 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: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2463).

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(*E*)-2-[(2-Hydroxy-5-nitrophenyl)iminiomethyl]-4-nitrophenolate

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Comment

Schiff bases have a wide range of application in chemistry. The title compound, a Schiff base derivative, was synthesized under microwave conditions and recrystallized from ethanol to give brown crystals. The structural data shows that it exists as an iminio-phenolate zwitterion in the solid state. Typically, keto-amine tautomer behavior has been observed in related derivative compounds (Butcher *et al.* (2007); Jasinski *et al.* (2007); Gül *et al.* (2007); Odabaşoğlu *et al.* (2006)); Ersanlı *et al.* (2003)). Compounds of this type can be used as anion sensors in acetonitrile (Hijji *et al.* (2008)) that tend to exist in the keto-amine form, which is generally favored over the phenol-imine form in the solid state. Introduction of electron deficient groups to the aromatic rings tends to increase the acidity of the phenolic proton.

The title molecule, C₁₃H₉N₃O₆, consists of a 2-hydroxy-5-nitrophenyliminio group and a 4-nitrophenolate group bonded to a methylene carbon atom with both of the planar six-membered rings nearly in the plane of the molecule. The dihedral angle between the mean planes of the phenyl and phenolate rings measures 1.3 (4)°. Each of the nitro oxygen atoms are twisted slightly out of the plane of the molecule [torsion angles = 172.16 (17)° (O3—N2—C4—C5); -7.1 (2)° (O4—N2—C4—C5); -7.6 (3)° (O3—N2—C4—C3); 173.17 (15)° (O4—N2—C4—C3); and 178.63 (16)° (O6—N3—C12—C13); -3.4 (3)° (O5—N3—C12—C13); 174.28 (18)° (O5—N3—C12—C11); -3.7 (3)° (O6—N3—C12—C11)]. The phenolate (O1) and hydroxy (O2) oxygen atoms are essentially in the plane of the molecule [torsion angles = 179.03 (16)° (O1—C1—C6—C5); 0.5 (3)° (O1—C1—C6—C7); 179.31 (18)° (O2—C9—C10—C11); -177.90 (15)° (C13—C8—C9—O2)]. The imino group forms an intramolecular hydrogen bond with each of the nearby oxygen atoms (O1 and O2) which have partial occupancy of hydrogen atoms (H1O [0.36 (3)] and H2O [0.64 (3)], respectively) (see Fig. 1 which shows only the predominant component, H₂O, and Table 2). There appears to be an extended π delocalization effect throughout the entire molecule producing a zwitterionic effect in this region of the molecule. The shortened C1—O1 bond (1.2749 (19) Å in concert with the slightly longer C9—O2 bond (1.3316 (19) Å) provide structural evidence for this effect.

Crystal packing is influenced by extensive strong intermolecular O—H \cdots O hydrogen bonding between the depicted phenolate and hydroxy oxygen atoms (O1 & O2) and their respective hydrogen atoms within the π delocalized region (O1—H1O(0.36) \cdots O2; 2.5570 (16) Å) and O2—H2O(0.64) \cdots O1; 2.5570 (16) Å) of the molecule. Additional weak intermolecular C—H \cdots O hydrogen bond interactions occur involving the methylene carbon (C7) and the phenyl (C10 & C13) and phenolate (C3) groups (Fig. 2), respectively. All of the hydrogen bond interactions are summarized in Table 1. As a result the molecules are linked into an infinite polymeric chain diagonally along the [110] plane of the unit cell in an alternate inverted pattern (Fig. 2). In addition, weak Cg1—Cg1 (3.517 (2) Å; slippage = 1.09 (8)°; -x, 1 - y, -z) and Cg1—Cg2 (3.830 (6) Å; x, y - 1, z) π - π stacking ring interactions also occur where Cg1 = center of gravity of the C1—C6 ring and Cg2 = center of gravity of the C8—C13 ring.

After a MOPAC AMI calculation [Austin Model 1 approximation together with the Hartree-Fock closed-shell (restricted) wavefunction was used and minimizations were terminated at an r.m.s. gradient of less than 0.01 kJ mol⁻¹ Å⁻¹] of the zwitterionic form with *WebMO Pro* (Schmidt, 2007). As a result of this energy minimization, the dihedral angle between

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the phenyl and phenolate rings changes from 1.3 (4)° in the crystal structure to 7.6 (6)°, producing a slightly more twisted molecule than the nearly planar molecule in the crystalline environment. Thus, it is apparent that the extensive hydrogen bonding and π - π stacking intermolecular interactions significantly influence crystal packing with this molecule.

Experimental

The title compound was synthesized as follows: 2-amino-4-nitrophenol (0.15 g, 1 mmol) and 2-hydroxy-5-nitrobenzaldehyde (0.17 g, 1 mmol) were mixed in a loosely capped vial. The reaction mixture was allowed to heat at full power in a conventional microwave for 8 minutes. The compound was recrystallized from ethanol affording a brown solid (0.20 g, 68%). (mp 591–593 K) $^1\text{H-NMR}$ (400 MHz, DMSO-d_6) δ (p.p.m.): 14.64 (s, br, 1H), 11.74 (s, br, 1H) 9.37 (s, 1H), 8.72 (d, $J = 2.87$ Hz, 1 H), 8.41 (d, $J = 3.3$ Hz, 1H), 8..27 (dd, $J = 9.2, 3.1$ Hz, 1H), 8.13 (1H, dd, $J = 9.06, 2.7$ Hz, 1 H), 7.16 (d, $J = 9.1$ Hz, 1H), 7.09 (d, $J = 9.2$ Hz, 1H), $^{13}\text{C-NMR}$ (100 MHz, DMSO-d_6) δ (p.p.m.): 167.90, 162.13, 157.48, 139.89, 138.76, 133.40, 128.95, 128.69, 124.51, 118.78, 118.25, 116.54, 115.24.

Refinement

H1A, H1O and H2O were obtained from a difference Fourier map. The occupancies of H1O and H2O refined to values of 0.36 (3) and 0.64 (3), respectively. The rest of the H atoms were placed in their calculated positions and then refined using the riding model with $\text{C(N,O)}\text{---H} = 0.82$ to 0.93 Å, and with $U_{\text{iso}}(\text{H}) = 1.15\text{--}1.20U_{\text{eq}}(\text{C,N})$.

Figures

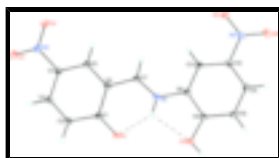


Fig. 1. The molecular structure of $\text{C}_{13}\text{H}_9\text{N}_3\text{O}_6$, showing the atom numbering scheme and 50% probability displacement ellipsoids. H1O (0.36 (3) occupancy) has been omitted from O1 in the diagram and only the predominant component, H2O (0.64 (3) occupancy), has been shown. Dashed lines indicate intramolecular $\text{N-H}\cdots\text{O}$ hydrogen bonds.

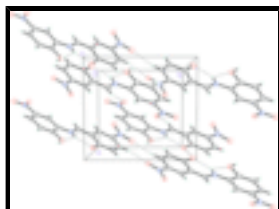


Fig. 2. The molecular packing for $\text{C}_{13}\text{H}_9\text{N}_3\text{O}_6$ viewed down the c axis. Dashed lines indicate intermolecular $\text{O-H}\cdots\text{O}$, $\text{C-H}\cdots\text{O}$ and intramolecular $\text{N-H}\cdots\text{O}$ hydrogen bonds. The predominately occupied (0.64) hydrogen atom (H2O) is shown attached to O2 while H1O at 0.36 occupancy is not depicted.

(E)-2-[(2-Hydroxy-5-nitrophenyl)iminiomethyl]-4-nitrophenolate

Crystal data

$\text{C}_{13}\text{H}_9\text{N}_3\text{O}_6$

$M_r = 303.23$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 7.9649$ (1) Å

$b = 8.6110$ (1) Å

$F_{000} = 624$

$D_x = 1.553$ Mg m^{-3}

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 3209 reflections

$\theta = 3.9\text{--}73.2^\circ$

$\mu = 0.13$ mm^{-1}

$c = 19.1190 (3) \text{ \AA}$
 $\beta = 98.433 (2)^\circ$
 $V = 1297.11 (3) \text{ \AA}^3$
 $Z = 4$

$T = 296 (2) \text{ K}$
 Prism, orange-brown
 $0.37 \times 0.27 \times 0.18 \text{ mm}$

Data collection

Oxford Diffraction Gemini R diffractometer
 Radiation source: fine-focus sealed tube
 Monochromator: graphite
 Detector resolution: $10.5081 \text{ pixels mm}^{-1}$
 $T = 296(2) \text{ K}$
 φ and ω scans
 Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2007)
 $T_{\min} = 0.954, T_{\max} = 0.978$
 6432 measured reflections

2495 independent reflections
 1819 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 26.2^\circ$
 $\theta_{\text{min}} = 2.6^\circ$
 $h = -9 \rightarrow 9$
 $k = -8 \rightarrow 10$
 $l = -23 \rightarrow 23$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.129$
 $S = 1.05$
 2495 reflections
 202 parameters
 Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0833P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$
 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)

| | | | | |
|-----|-----|-----|----------------------------------|-----------|
| x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|-----|-----|----------------------------------|-----------|

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| | | | | | |
|------|--------------|---------------|--------------|------------|----------|
| O1 | 0.03590 (18) | 0.47993 (15) | 0.16546 (7) | 0.0582 (4) | |
| H1O | 0.0038 | 0.5417 | 0.1934 | 0.070* | 0.36 (3) |
| O2 | 0.11482 (19) | 0.12327 (15) | 0.24445 (7) | 0.0600 (4) | |
| H2O | 0.0821 | 0.0752 | 0.2769 | 0.072* | 0.64 (3) |
| O3 | 0.1437 (2) | 0.91245 (18) | -0.08314 (9) | 0.0810 (5) | |
| O4 | 0.32836 (18) | 0.73565 (16) | -0.09586 (7) | 0.0624 (4) | |
| O5 | 0.57970 (19) | -0.17153 (18) | 0.04796 (7) | 0.0688 (4) | |
| O6 | 0.5900 (2) | -0.35343 (18) | 0.12493 (8) | 0.0745 (5) | |
| N1 | 0.22628 (18) | 0.25045 (16) | 0.13638 (7) | 0.0452 (4) | |
| H1N | 0.1589 | 0.2915 | 0.1624 | 0.054* | |
| N2 | 0.2182 (2) | 0.79148 (18) | -0.06471 (8) | 0.0518 (4) | |
| N3 | 0.54401 (19) | -0.22526 (18) | 0.10334 (8) | 0.0515 (4) | |
| C1 | 0.0787 (2) | 0.5537 (2) | 0.11302 (9) | 0.0448 (4) | |
| C2 | 0.0151 (2) | 0.7055 (2) | 0.09352 (10) | 0.0496 (4) | |
| H2A | -0.0587 | 0.7535 | 0.1202 | 0.060* | |
| C3 | 0.0605 (2) | 0.7798 (2) | 0.03718 (9) | 0.0480 (4) | |
| H3A | 0.0173 | 0.8782 | 0.0253 | 0.058* | |
| C4 | 0.1732 (2) | 0.70949 (19) | -0.00398 (9) | 0.0440 (4) | |
| C5 | 0.2393 (2) | 0.56601 (19) | 0.01239 (9) | 0.0432 (4) | |
| H5A | 0.3139 | 0.5216 | -0.0150 | 0.052* | |
| C6 | 0.1948 (2) | 0.48596 (18) | 0.07028 (8) | 0.0413 (4) | |
| C7 | 0.2629 (2) | 0.3352 (2) | 0.08516 (9) | 0.0451 (4) | |
| H7A | 0.3376 | 0.2956 | 0.0565 | 0.054* | |
| C8 | 0.2832 (2) | 0.09769 (19) | 0.15516 (8) | 0.0423 (4) | |
| C9 | 0.2213 (2) | 0.0350 (2) | 0.21425 (8) | 0.0468 (4) | |
| C10 | 0.2737 (3) | -0.1128 (2) | 0.23769 (9) | 0.0552 (5) | |
| H10A | 0.2348 | -0.1551 | 0.2771 | 0.066* | |
| C11 | 0.3830 (2) | -0.1967 (2) | 0.20269 (9) | 0.0521 (5) | |
| H11A | 0.4196 | -0.2947 | 0.2187 | 0.062* | |
| C12 | 0.4378 (2) | -0.1335 (2) | 0.14340 (8) | 0.0443 (4) | |
| C13 | 0.3896 (2) | 0.01318 (19) | 0.11899 (8) | 0.0434 (4) | |
| H13A | 0.4281 | 0.0539 | 0.0792 | 0.052* | |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|-------------|-------------|-------------|-------------|------------|-------------|
| O1 | 0.0756 (9) | 0.0495 (7) | 0.0590 (8) | 0.0052 (7) | 0.0411 (7) | 0.0022 (6) |
| O2 | 0.0794 (9) | 0.0546 (8) | 0.0554 (8) | 0.0097 (7) | 0.0411 (7) | 0.0059 (6) |
| O3 | 0.1039 (12) | 0.0618 (9) | 0.0839 (11) | 0.0172 (9) | 0.0357 (9) | 0.0286 (8) |
| O4 | 0.0727 (9) | 0.0637 (8) | 0.0571 (8) | -0.0062 (7) | 0.0302 (7) | 0.0013 (7) |
| O5 | 0.0802 (10) | 0.0740 (10) | 0.0606 (8) | 0.0124 (8) | 0.0375 (7) | -0.0015 (7) |
| O6 | 0.0804 (10) | 0.0618 (9) | 0.0859 (11) | 0.0272 (8) | 0.0270 (8) | 0.0051 (8) |
| N1 | 0.0526 (8) | 0.0419 (7) | 0.0464 (8) | 0.0009 (6) | 0.0247 (6) | -0.0008 (6) |
| N2 | 0.0598 (9) | 0.0486 (9) | 0.0496 (8) | -0.0094 (7) | 0.0163 (7) | -0.0001 (7) |
| N3 | 0.0475 (8) | 0.0537 (9) | 0.0547 (9) | 0.0054 (7) | 0.0127 (7) | -0.0049 (7) |
| C1 | 0.0481 (9) | 0.0434 (9) | 0.0467 (9) | -0.0053 (8) | 0.0193 (7) | -0.0017 (7) |
| C2 | 0.0519 (10) | 0.0444 (9) | 0.0572 (10) | 0.0024 (8) | 0.0233 (8) | -0.0053 (8) |
| C3 | 0.0513 (10) | 0.0380 (9) | 0.0566 (10) | 0.0011 (7) | 0.0146 (8) | -0.0003 (8) |

| | | | | | | |
|-----|-------------|-------------|------------|-------------|------------|-------------|
| C4 | 0.0470 (9) | 0.0397 (9) | 0.0469 (9) | -0.0046 (7) | 0.0121 (7) | -0.0017 (7) |
| C5 | 0.0442 (9) | 0.0413 (9) | 0.0473 (9) | -0.0035 (7) | 0.0171 (7) | -0.0056 (7) |
| C6 | 0.0436 (9) | 0.0372 (8) | 0.0459 (9) | -0.0030 (7) | 0.0159 (7) | -0.0041 (7) |
| C7 | 0.0480 (9) | 0.0462 (9) | 0.0459 (9) | -0.0011 (8) | 0.0228 (7) | -0.0025 (7) |
| C8 | 0.0490 (9) | 0.0393 (8) | 0.0407 (8) | -0.0009 (7) | 0.0139 (7) | 0.0008 (7) |
| C9 | 0.0552 (10) | 0.0489 (10) | 0.0405 (8) | 0.0009 (8) | 0.0207 (8) | -0.0001 (7) |
| C10 | 0.0739 (13) | 0.0542 (10) | 0.0420 (9) | 0.0033 (9) | 0.0237 (9) | 0.0097 (8) |
| C11 | 0.0639 (12) | 0.0459 (9) | 0.0483 (9) | 0.0081 (8) | 0.0145 (8) | 0.0081 (8) |
| C12 | 0.0437 (9) | 0.0476 (9) | 0.0437 (8) | 0.0022 (7) | 0.0127 (7) | -0.0030 (7) |
| C13 | 0.0475 (9) | 0.0447 (9) | 0.0411 (8) | -0.0049 (7) | 0.0167 (7) | 0.0017 (7) |

Geometric parameters (Å, °)

| | | | |
|-----------|-------------|--------------|-------------|
| O1—C1 | 1.2749 (19) | C3—C4 | 1.414 (2) |
| O1—H1O | 0.8200 | C3—H3A | 0.9300 |
| O2—C9 | 1.3316 (19) | C4—C5 | 1.361 (2) |
| O2—H2O | 0.8200 | C5—C6 | 1.393 (2) |
| O3—N2 | 1.225 (2) | C5—H5A | 0.9300 |
| O4—N2 | 1.2283 (19) | C6—C7 | 1.420 (2) |
| O5—N3 | 1.2264 (19) | C7—H7A | 0.9300 |
| O6—N3 | 1.216 (2) | C8—C13 | 1.378 (2) |
| N1—C7 | 1.288 (2) | C8—C9 | 1.405 (2) |
| N1—C8 | 1.420 (2) | C9—C10 | 1.393 (3) |
| N1—H1N | 0.8600 | C10—C11 | 1.378 (2) |
| N2—C4 | 1.448 (2) | C10—H10A | 0.9300 |
| N3—C12 | 1.455 (2) | C11—C12 | 1.384 (2) |
| C1—C2 | 1.431 (2) | C11—H11A | 0.9300 |
| C1—C6 | 1.444 (2) | C12—C13 | 1.381 (2) |
| C2—C3 | 1.347 (2) | C13—H13A | 0.9300 |
| C2—H2A | 0.9300 | | |
| C1—O1—H1O | 109.5 | C6—C5—H5A | 120.1 |
| C9—O2—H2O | 109.5 | C5—C6—C7 | 118.51 (14) |
| C7—N1—C8 | 128.10 (14) | C5—C6—C1 | 120.56 (15) |
| C7—N1—H1N | 116.0 | C7—C6—C1 | 120.92 (14) |
| C8—N1—H1N | 116.0 | N1—C7—C6 | 123.19 (15) |
| O3—N2—O4 | 122.95 (15) | N1—C7—H7A | 118.4 |
| O3—N2—C4 | 118.60 (15) | C6—C7—H7A | 118.4 |
| O4—N2—C4 | 118.45 (15) | C13—C8—C9 | 121.00 (15) |
| O6—N3—O5 | 122.63 (16) | C13—C8—N1 | 124.02 (14) |
| O6—N3—C12 | 118.91 (15) | C9—C8—N1 | 114.98 (14) |
| O5—N3—C12 | 118.43 (15) | O2—C9—C10 | 124.19 (15) |
| O1—C1—C2 | 122.32 (15) | O2—C9—C8 | 116.76 (15) |
| O1—C1—C6 | 120.74 (15) | C10—C9—C8 | 119.05 (15) |
| C2—C1—C6 | 116.94 (14) | C11—C10—C9 | 120.25 (15) |
| C3—C2—C1 | 121.08 (15) | C11—C10—H10A | 119.9 |
| C3—C2—H2A | 119.5 | C9—C10—H10A | 119.9 |
| C1—C2—H2A | 119.5 | C10—C11—C12 | 119.28 (16) |
| C2—C3—C4 | 120.53 (16) | C10—C11—H11A | 120.4 |
| C2—C3—H3A | 119.7 | C12—C11—H11A | 120.4 |

supplementary materials

| | | | |
|-------------|--------------|-----------------|--------------|
| C4—C3—H3A | 119.7 | C13—C12—C11 | 122.07 (16) |
| C5—C4—C3 | 121.09 (15) | C13—C12—N3 | 118.20 (14) |
| C5—C4—N2 | 119.60 (14) | C11—C12—N3 | 119.68 (16) |
| C3—C4—N2 | 119.31 (15) | C8—C13—C12 | 118.30 (14) |
| C4—C5—C6 | 119.79 (15) | C8—C13—H13A | 120.8 |
| C4—C5—H5A | 120.1 | C12—C13—H13A | 120.8 |
| O1—C1—C2—C3 | -178.96 (18) | C7—N1—C8—C13 | -0.8 (3) |
| C6—C1—C2—C3 | 0.9 (3) | C7—N1—C8—C9 | 179.85 (17) |
| C1—C2—C3—C4 | -0.3 (3) | C13—C8—C9—O2 | -177.90 (15) |
| C2—C3—C4—C5 | -0.4 (3) | N1—C8—C9—O2 | 1.5 (2) |
| C2—C3—C4—N2 | 179.32 (16) | C13—C8—C9—C10 | 2.3 (3) |
| O3—N2—C4—C5 | 172.16 (17) | N1—C8—C9—C10 | -178.38 (16) |
| O4—N2—C4—C5 | -7.1 (2) | O2—C9—C10—C11 | 179.31 (18) |
| O3—N2—C4—C3 | -7.6 (3) | C8—C9—C10—C11 | -0.9 (3) |
| O4—N2—C4—C3 | 173.17 (15) | C9—C10—C11—C12 | -1.0 (3) |
| C3—C4—C5—C6 | 0.5 (3) | C10—C11—C12—C13 | 1.6 (3) |
| N2—C4—C5—C6 | -179.26 (15) | C10—C11—C12—N3 | -175.91 (16) |
| C4—C5—C6—C7 | 178.68 (15) | O6—N3—C12—C13 | 178.63 (16) |
| C4—C5—C6—C1 | 0.2 (3) | O5—N3—C12—C13 | -3.4 (3) |
| O1—C1—C6—C5 | 179.03 (16) | O6—N3—C12—C11 | -3.7 (3) |
| C2—C1—C6—C5 | -0.8 (2) | O5—N3—C12—C11 | 174.28 (18) |
| O1—C1—C6—C7 | 0.5 (3) | C9—C8—C13—C12 | -1.7 (2) |
| C2—C1—C6—C7 | -179.29 (16) | N1—C8—C13—C12 | 179.01 (16) |
| C8—N1—C7—C6 | 178.42 (16) | C11—C12—C13—C8 | -0.3 (3) |
| C5—C6—C7—N1 | -178.28 (16) | N3—C12—C13—C8 | 177.31 (15) |
| C1—C6—C7—N1 | 0.2 (3) | | |

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|-------|-------------|-------------|---------------|
| O1—H10 \cdots O2 ⁱ | 0.82 | 1.77 | 2.5570 (16) | 161 |
| O2—H20 \cdots O1 ⁱⁱ | 0.82 | 1.75 | 2.5570 (16) | 166 |
| N1—H1N \cdots O1 | 0.86 | 1.90 | 2.6001 (19) | 138 |
| C3—H3A \cdots O3 ⁱⁱⁱ | 0.93 | 2.56 | 3.295 (2) | 137 |
| C7—H7A \cdots O4 ^{iv} | 0.93 | 2.67 | 3.289 (2) | 125 |
| C7—H7A \cdots O5 ^v | 0.93 | 2.44 | 3.312 (2) | 156 |
| C10—H10A \cdots O4 ^{vi} | 0.93 | 2.53 | 3.321 (2) | 143 |
| C13—H13A \cdots O4 ^{iv} | 0.93 | 2.64 | 3.195 (2) | 119 |
| C13—H13A \cdots O5 ^v | 0.93 | 2.63 | 3.512 (2) | 160 |

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

Fig. 1

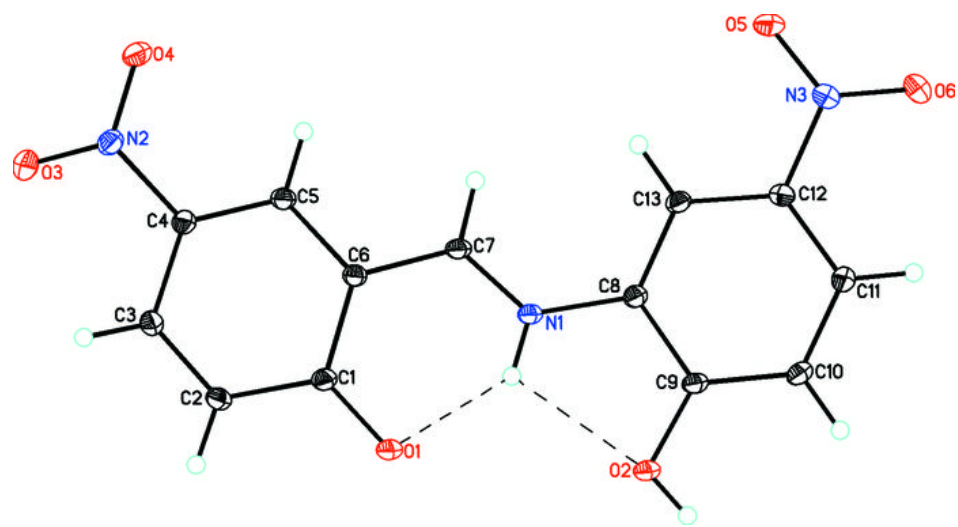


Fig. 2

