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2,2'-(4-[(*E*)-4-Methoxybenzylidene]-amino}phenylimino)diethanol

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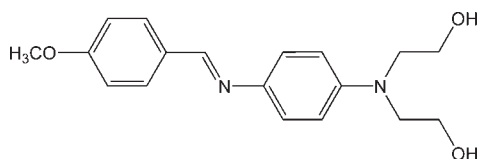
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.038; wR factor = 0.108; data-to-parameter ratio = 6.9.

In the title compound, $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_3$, the dihedral angle between the aromatic rings is 3.9 (2)°. Both H atoms of the hydroxy groups are involved in intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding. In the crystal structure, this hydrogen bonding assembles molecules into chains of 2_1 symmetry extending parallel to the b axis. The almost planar (within 0.09 and 0.06 Å) $4\text{-CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-$ groups are oriented outwards the twofold screw axis.

Related literature

For practical interest in Schiff bases of general type $p\text{-}R'\text{-C}_6\text{H}_4\text{-CH}=\text{N}-\text{C}_6\text{H}_4\text{-}R''\text{-}p$ in various areas, see: von König *et al.* (1982); Haldavanekar *et al.* (2009); Ferlin *et al.* (2004); Lewis *et al.* (2009). For the only two structurally characterized compounds of this type with $R'' = \text{N}(\text{alkyl})_2$, see: Nagao *et al.* (2002); Nakai *et al.* (1976). For 4-[(*E*)-(4-[bis(2-hydroxyethyl)amino]phenyl)imino)methyl]phenol, $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_3$, see: Liu *et al.* (2010). For a description of preparation routines, see: Cho & Park (1997); Ferlin *et al.* (2004); von König *et al.* (1982). For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

$\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_3$
 $M_r = 314.38$
Monoclinic, $P2_1$
 $a = 5.3795$ (9) Å
 $b = 8.0585$ (14) Å

$c = 18.531$ (3) Å
 $\beta = 91.168$ (2)°
 $V = 803.2$ (2) Å³
 $Z = 2$
Mo $K\alpha$ radiation

$\mu = 0.09$ mm⁻¹
 $T = 296$ K

0.24 × 0.13 × 0.07 mm

Data collection

Bruker SMART APEXII
diffractometer
Absorption correction: multi-scan
(TWINABS; Sheldrick, 1996)
 $T_{\min} = 0.979$, $T_{\max} = 0.994$

4036 measured reflections
1541 independent reflections
1225 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.108$
 $S = 1.06$
1541 reflections
222 parameters
1 restraint

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.13$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{O}2-\text{H}2\cdots\text{O}3^i$ | 0.95 (5) | 1.84 (6) | 2.762 (3) | 177 (4) |
| $\text{O}3-\text{H}3\cdots\text{O}2^i$ | 0.82 (4) | 1.95 (4) | 2.757 (4) | 166 (4) |

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

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008) and OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: SHELXTL and OLEX2.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2204).

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supplementary materials

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2,2'-(4-[(*E*)-4-Methoxybenzylidene]amino}phenylimino)diethanol

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Comment

Shiff bases of the general type $p\text{-R}'\text{-C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_4\text{-R}''\text{-}p$ are well-known compounds that find practical application in various areas [photography (for instance, see von König *et al.*, 1982), medicinal and pharmaceutical chemistry (for instance, see Haldavanekar *et al.*, 2009; Ferlin *et al.*, 2004; Lewis *et al.*, 2009)]. Recently, we were interested in preparation of a series of 2-((2-hydroxy-ethyl)-{4-[(benzylidene)-amino]-phenyl}-amino)-ethanols as intermediates for their further conversion into paracyclophanes. This way, 2-((2-hydroxy-ethyl)-{4-[(*E*)-4-methoxy-benzylidene]-amino]-phenyl}-amino)-ethanol, $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_3$, (I), and 4-({(*E*)-4-[bis-(2-hydroxy-ethyl)-amino]-phenylimino}-methyl)-phenol, $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_3$, [II; Liu *et al.* (2010)] were prepared by a condensation reaction between 2-[(4-Amino-phenyl)-(2-hydroxy-ethyl)-amino]-ethanol and 4-methoxy- or 4-hydroxybenzaldehyde, respectively.

Despite of the fact that structurally characterized Shiff bases of general type $p\text{-R}'\text{-C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_4\text{-R}''\text{-}p$ are well presented in the Cambridge Structural Database [CSD; Version 5.27, release February 2009; Allen, 2002; 128 entries, 173 fragments], among them there are only two compounds with $\text{R}'' = N(\text{alkyl})_2$ [namely: $\text{R}' = \text{H}$, $\text{R}'' = \text{NEt}_2$ (Nagao *et al.*, 2002) and $\text{R}' = \text{NO}_2$, $\text{R}'' = \text{NMe}_2$ (Nakai *et al.*, 1976)]. From this viewpoint, X-ray single crystal study of (I) presents a certain descriptive interest.

The asymmetric unit of (I) is shown in Fig. 1. Except of dihedral angle C7-N1-C8-C9 , asymmetric units of (I) and its sister compound [II; Liu *et al.* (2010)] show almost identical geometries (see Supplementary material). Bond lengths and angles as well as the C4-C7-N1-C8 torsion angle match well with the reported average values for $p\text{-R}'\text{-C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_4\text{-R}''\text{-}p$ [analysis of the Cambridge Structural Database (CSD); Version 5.27, release February 2009; Allen, 2002; 128 entries, 173 fragments]. Fragments O1/C1-C7/N1/C18 and C8-C13/N2/C14/C16 are almost planar [within 0.09 and 0.06 Å]. The amino N2 atom is also in a planar environment [sum of the valent angles 359.9 (3)°] which most frequently the case for aryldialkylamines (range from 317.6 to 360.0°, average value 359.0°).

In (I), both hydroxy H-atoms are involved into hydrogen bonding [for the H-bonds lengths and angles values, see the Table]. In (I), molecules along with their equivalents generated by a 2_1 screw axis form a one-dimensional infinite chain stretched along the b -axis. Organic moieties are oriented outwards the corresponding screw axis (see Fig. 2). These one-dimensional assemblies do not interact with their equivalent neighbours by any hydrogen bonds and are just stacked one by another. This results in an evident flattening of the entire $\text{CH}_3\text{O-C}_6\text{H}_4\text{C(H)=NC}_6\text{H}_4$ moieties for the inter-chain repulsion diminishing. Crystal lattice packing of (I) differs markedly from that of (II) (Liu *et al.*, 2010)).

Experimental

1-Chloro-4-nitrobenzene, 4-methoxy-benzaldehyde, 2-(2-hydroxy-ethylamino)-ethanol, ammonium formate, 10% Pd/C catalyst and solvents were purchased from Sinopharm Chemical Reagent and Tianjin Fuyu Chemical companies. 2-[(2-Hydroxy-ethyl)-(4-nitro-phenyl)-amino]-ethanol was prepared as described by Cho & Park (1997) and Ferlin *et al.* (2004).

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Reduction of the nitro-group was carried out as described by Lewis *et al.* (2009). Schiff-base preparation was done by a modification of the procedure reported by von König *et al.* (1982).

Procedure: 1-chloro-4-nitrobenzene (15.76 g, 0.10 mol) was dissolved in 2-(2-hydroxy-ethylamino)-ethanol (50 ml). The reaction mixture was heated to 393 K for 10 h and then cooled down to room temperature. Precipitating crude 2-[(2-Hydroxy-ethyl)-(4-nitro-phenyl)-amino]-ethanol was filtered off, dried in vacuum and recrystallized from a minimal amount of hot ethanol. Yield 11.54 g (51%). 2-[(2-Hydroxy-ethyl)-(4-nitro-phenyl)-amino]-ethanol (8.15 g, 0.036 mol) was then dissolved in MeOH (50 ml). To this solution, HCOONH₄ (0.216 mol) and 10% Pd/C (0.6 g) were added and the slurry was stirred at 293 K for 30 min. On removal of the catalyst by filtration, the filtrate was placed into a N₂-flushed flask containing 1 ml of acetic acid and an equimolar (0.036 mol) amount of 4-methoxybenzaldehyde (0.036 mol) was added dropwise at 333 K during 30 min. The reaction mixture was kept at the same temperature for additional 30 min, cooled down to 273 K and ice-cold water (200 ml) was added. The precipitated yellow solid was collected by filtration, washed with water, dried under reduced pressure and, finally, re-crystallized by a slow evaporation of its methanolic solution in air at 293 K. Yield 95%, m.p. 402 K. ¹H NMR (I) δ : 8.50 (s, 1 H, CH=N), 6.78–7.83 (m, 8 H, C₆H₄), 3.31, 3.72 (both t, 4 H and 4 H, ³J_{HH} = 7.2 Hz, CH₂), 3.86 (s, 3H, CH₃). A single crystal of (I) suitable for X-ray diffraction analysis was picked up directly from the obtained material.

Refinement

All non-H atoms were refined anisotropically. H atoms except of H7 and OH were treated as riding atoms with distances of C—H = 0.96 (CH₃), 0.97 (CH₂), 0.93 Å (C_{Ar}H), and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$, 1.2 $U_{\text{eq}}(\text{C})$, and 1.2 $U_{\text{eq}}(\text{C})$, respectively. Atoms H7 and OH hydrogen atoms were found from difference Fourier syntheses and refined isotropically. Despite the fact that an achiral compound (I) crystallizes in a chiral space group $P2_1$, neither the absolute structure determination nor approval of the inversion twinning was possible due to evident reasons (Mo- $K\alpha$ radiation with no atoms heavier than oxygen) and the refinement for (I) was preformed with the Friedel opposites merged (MERC 3 instruction).

Figures

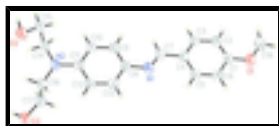


Fig. 1. Asymmetric unit of (I) showing the labelling scheme and thermal ellipsoids at the 50% probability level.

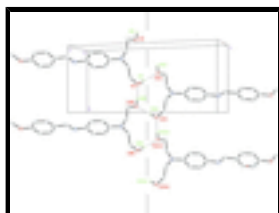


Fig. 2. View of a 2₁-symmetrical chain assembled by molecules of (I) via hydrogen bonds. Hydrogen atoms except of the OH ones are omitted for clarity. Labelling is provided only for atoms involved in H-bonding. H-bonds are depicted as dashed lines. 2-fold screw axis is depicted as a long-dash line.

2,2'-(4-[(*E*)-4-Methoxybenzylidene]amino}phenylimino)diethanol

Crystal data

C₁₈H₂₂N₂O₃

$F(000) = 336$

| | |
|-------------------------------|---|
| $M_r = 314.38$ | $D_x = 1.300 \text{ Mg m}^{-3}$ |
| Monoclinic, $P2_1$ | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| Hall symbol: P 2yb | Cell parameters from 2324 reflections |
| $a = 5.3795 (9) \text{ \AA}$ | $\theta = 2.0\text{--}28.2^\circ$ |
| $b = 8.0585 (14) \text{ \AA}$ | $\mu = 0.09 \text{ mm}^{-1}$ |
| $c = 18.531 (3) \text{ \AA}$ | $T = 296 \text{ K}$ |
| $\beta = 91.168 (2)^\circ$ | Block, yellow |
| $V = 803.2 (2) \text{ \AA}^3$ | $0.24 \times 0.13 \times 0.07 \text{ mm}$ |
| $Z = 2$ | |

Data collection

| | |
|--|--|
| Bruker SMART APEXII diffractometer | 1541 independent reflections |
| Radiation source: fine-focus sealed tube graphite | 1225 reflections with $I > 2\sigma(I)$ |
| Detector resolution: $8.333 \text{ pixels mm}^{-1}$ | $R_{\text{int}} = 0.037$ |
| phi and ω scans | $\theta_{\text{max}} = 25.1^\circ$, $\theta_{\text{min}} = 2.2^\circ$ |
| Absorption correction: multi-scan (TWINABS; Sheldrick, 1996) | $h = -5 \rightarrow 6$ |
| $T_{\text{min}} = 0.979$, $T_{\text{max}} = 0.994$ | $k = -9 \rightarrow 9$ |
| 4036 measured reflections | $l = -22 \rightarrow 20$ |

Refinement

| | |
|--|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.038$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.108$ | $w = 1/[\sigma^2(F_o^2) + (0.0702P)^2]$ |
| $S = 1.06$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 1541 reflections | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 222 parameters | $\Delta\rho_{\text{max}} = 0.17 \text{ e \AA}^{-3}$ |
| 1 restraint | $\Delta\rho_{\text{min}} = -0.13 \text{ e \AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ |
| | Extinction coefficient: 0.028 (7) |

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.

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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)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|-------------|-------------|---------------|----------------------------------|
| O1 | 0.5558 (4) | 0.2396 (3) | -0.24985 (10) | 0.0589 (6) |
| O2 | -0.3959 (5) | -0.0877 (3) | 0.43576 (14) | 0.0712 (8) |
| O3 | -0.4849 (5) | 0.5749 (3) | 0.43870 (13) | 0.0628 (7) |
| N1 | 0.1089 (5) | 0.2496 (3) | 0.06704 (12) | 0.0469 (6) |
| N2 | -0.1774 (5) | 0.2079 (3) | 0.35822 (11) | 0.0515 (7) |
| C1 | 0.5101 (5) | 0.2264 (4) | -0.17743 (13) | 0.0424 (7) |
| C2 | 0.6533 (6) | 0.1361 (4) | -0.12960 (15) | 0.0485 (7) |
| H2A | 0.7947 | 0.0811 | -0.1450 | 0.058* |
| C3 | 0.5840 (6) | 0.1278 (4) | -0.05799 (15) | 0.0476 (7) |
| H3A | 0.6830 | 0.0680 | -0.0255 | 0.057* |
| C4 | 0.3737 (6) | 0.2052 (4) | -0.03335 (14) | 0.0427 (7) |
| C5 | 0.2341 (5) | 0.3012 (4) | -0.08283 (14) | 0.0466 (7) |
| H5 | 0.0939 | 0.3577 | -0.0675 | 0.056* |
| C6 | 0.3029 (6) | 0.3123 (4) | -0.15342 (15) | 0.0487 (8) |
| H6 | 0.2106 | 0.3776 | -0.1855 | 0.058* |
| C7 | 0.3019 (6) | 0.1862 (4) | 0.04166 (16) | 0.0494 (8) |
| C8 | 0.0474 (5) | 0.2305 (4) | 0.14073 (14) | 0.0416 (7) |
| C9 | 0.1730 (6) | 0.1309 (4) | 0.19122 (15) | 0.0471 (7) |
| H9 | 0.3095 | 0.0692 | 0.1769 | 0.057* |
| C10 | 0.0986 (5) | 0.1223 (4) | 0.26191 (15) | 0.0434 (7) |
| H10 | 0.1849 | 0.0537 | 0.2940 | 0.052* |
| C11 | -0.1033 (5) | 0.2140 (3) | 0.28648 (14) | 0.0405 (7) |
| C12 | -0.2278 (5) | 0.3138 (4) | 0.23556 (14) | 0.0474 (7) |
| H12 | -0.3625 | 0.3774 | 0.2498 | 0.057* |
| C13 | -0.1543 (5) | 0.3197 (4) | 0.16480 (14) | 0.0478 (7) |
| H13 | -0.2432 | 0.3857 | 0.1322 | 0.057* |
| C14 | -0.0579 (6) | 0.0964 (4) | 0.40875 (15) | 0.0508 (8) |
| H14B | -0.0800 | 0.1388 | 0.4572 | 0.061* |
| H14A | 0.1190 | 0.0952 | 0.3997 | 0.061* |
| C15 | -0.1541 (6) | -0.0790 (4) | 0.40534 (16) | 0.0562 (8) |
| H15A | -0.1624 | -0.1158 | 0.3555 | 0.067* |
| H15B | -0.0413 | -0.1519 | 0.4318 | 0.067* |
| C16 | -0.3805 (6) | 0.3088 (4) | 0.38402 (15) | 0.0488 (8) |
| H16B | -0.4516 | 0.2560 | 0.4259 | 0.059* |
| H16A | -0.5092 | 0.3158 | 0.3467 | 0.059* |
| C17 | -0.2951 (6) | 0.4822 (4) | 0.40415 (17) | 0.0547 (8) |
| H17B | -0.1508 | 0.4747 | 0.4362 | 0.066* |
| H17A | -0.2457 | 0.5403 | 0.3609 | 0.066* |
| C18 | 0.7676 (6) | 0.1549 (5) | -0.27577 (17) | 0.0647 (10) |
| H18C | 0.7739 | 0.1667 | -0.3273 | 0.097* |

| | | | | |
|------|------------|------------|-----------|-------------|
| H18A | 0.7567 | 0.0394 | -0.2636 | 0.097* |
| H18B | 0.9154 | 0.2013 | -0.2540 | 0.097* |
| H2 | -0.428 (9) | -0.200 (7) | 0.438 (2) | 0.116 (18)* |
| H3 | -0.542 (8) | 0.522 (6) | 0.473 (2) | 0.094 (16)* |
| H7 | 0.417 (7) | 0.122 (5) | 0.072 (2) | 0.070 (10)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| O1 | 0.0670 (15) | 0.0725 (15) | 0.0376 (10) | 0.0002 (13) | 0.0076 (10) | 0.0024 (11) |
| O2 | 0.0969 (19) | 0.0440 (14) | 0.0745 (16) | -0.0085 (13) | 0.0465 (14) | -0.0068 (12) |
| O3 | 0.1009 (19) | 0.0386 (12) | 0.0500 (13) | 0.0089 (12) | 0.0287 (12) | 0.0006 (11) |
| N1 | 0.0500 (15) | 0.0515 (15) | 0.0395 (12) | 0.0011 (13) | 0.0089 (11) | -0.0011 (12) |
| N2 | 0.0741 (18) | 0.0424 (14) | 0.0388 (13) | 0.0072 (14) | 0.0176 (12) | 0.0014 (11) |
| C1 | 0.0462 (17) | 0.0451 (16) | 0.0362 (14) | -0.0077 (15) | 0.0069 (12) | -0.0046 (14) |
| C2 | 0.0472 (17) | 0.0520 (18) | 0.0469 (16) | 0.0042 (15) | 0.0118 (13) | -0.0010 (15) |
| C3 | 0.0505 (17) | 0.0494 (18) | 0.0431 (16) | 0.0040 (15) | 0.0041 (13) | 0.0035 (14) |
| C4 | 0.0463 (17) | 0.0440 (18) | 0.0380 (14) | -0.0032 (14) | 0.0044 (12) | -0.0022 (13) |
| C5 | 0.0446 (16) | 0.0497 (18) | 0.0454 (16) | 0.0039 (15) | 0.0030 (13) | -0.0061 (14) |
| C6 | 0.0501 (17) | 0.0525 (18) | 0.0431 (15) | 0.0013 (16) | -0.0041 (13) | 0.0026 (15) |
| C7 | 0.055 (2) | 0.053 (2) | 0.0408 (16) | 0.0006 (17) | 0.0054 (15) | -0.0003 (14) |
| C8 | 0.0459 (16) | 0.0408 (16) | 0.0384 (14) | -0.0046 (14) | 0.0062 (12) | -0.0015 (14) |
| C9 | 0.0505 (17) | 0.0436 (17) | 0.0477 (16) | 0.0027 (15) | 0.0124 (13) | -0.0021 (14) |
| C10 | 0.0499 (17) | 0.0405 (16) | 0.0400 (15) | 0.0022 (14) | 0.0063 (13) | 0.0026 (13) |
| C11 | 0.0524 (18) | 0.0319 (15) | 0.0375 (14) | -0.0050 (13) | 0.0077 (12) | -0.0007 (12) |
| C12 | 0.0472 (17) | 0.0478 (17) | 0.0477 (16) | 0.0060 (15) | 0.0129 (13) | -0.0021 (15) |
| C13 | 0.0499 (18) | 0.0497 (17) | 0.0439 (16) | 0.0055 (16) | 0.0029 (13) | 0.0042 (15) |
| C14 | 0.0660 (19) | 0.0506 (19) | 0.0360 (14) | -0.0014 (16) | 0.0083 (13) | 0.0003 (14) |
| C15 | 0.074 (2) | 0.0450 (18) | 0.0506 (17) | 0.0049 (17) | 0.0215 (15) | 0.0067 (15) |
| C16 | 0.064 (2) | 0.0413 (17) | 0.0423 (15) | -0.0047 (15) | 0.0172 (14) | -0.0018 (14) |
| C17 | 0.074 (2) | 0.0420 (17) | 0.0483 (16) | -0.0061 (16) | 0.0156 (15) | -0.0042 (14) |
| C18 | 0.063 (2) | 0.084 (3) | 0.0475 (18) | -0.010 (2) | 0.0156 (16) | -0.0099 (18) |

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

| | | | |
|--------|-----------|----------|-----------|
| O1—C1 | 1.373 (3) | C8—C13 | 1.383 (4) |
| O1—C18 | 1.420 (4) | C8—C9 | 1.396 (4) |
| O2—C15 | 1.430 (4) | C9—C10 | 1.379 (4) |
| O2—H2 | 0.92 (5) | C9—H9 | 0.9300 |
| O3—C17 | 1.427 (4) | C10—C11 | 1.398 (4) |
| O3—H3 | 0.82 (5) | C10—H10 | 0.9300 |
| N1—C7 | 1.257 (4) | C11—C12 | 1.400 (4) |
| N1—C8 | 1.420 (3) | C12—C13 | 1.378 (4) |
| N2—C11 | 1.397 (3) | C12—H12 | 0.9300 |
| N2—C14 | 1.440 (4) | C13—H13 | 0.9300 |
| N2—C16 | 1.451 (4) | C14—C15 | 1.506 (5) |
| C1—C2 | 1.372 (4) | C14—H14B | 0.9700 |
| C1—C6 | 1.393 (4) | C14—H14A | 0.9700 |
| C2—C3 | 1.387 (4) | C15—H15A | 0.9700 |

supplementary materials

| | | | |
|--------------|-----------|---------------|-----------|
| C2—H2A | 0.9300 | C15—H15B | 0.9700 |
| C3—C4 | 1.378 (4) | C16—C17 | 1.515 (4) |
| C3—H3A | 0.9300 | C16—H16B | 0.9700 |
| C4—C5 | 1.405 (4) | C16—H16A | 0.9700 |
| C4—C7 | 1.458 (4) | C17—H17B | 0.9700 |
| C5—C6 | 1.369 (4) | C17—H17A | 0.9700 |
| C5—H5 | 0.9300 | C18—H18C | 0.9600 |
| C6—H6 | 0.9300 | C18—H18A | 0.9600 |
| C7—H7 | 0.98 (4) | C18—H18B | 0.9600 |
| C1—O1—C18 | 117.0 (2) | N2—C11—C12 | 121.3 (2) |
| C15—O2—H2 | 104 (3) | C10—C11—C12 | 116.6 (2) |
| C17—O3—H3 | 111 (3) | C13—C12—C11 | 121.2 (3) |
| C7—N1—C8 | 121.7 (3) | C13—C12—H12 | 119.4 |
| C11—N2—C14 | 120.6 (2) | C11—C12—H12 | 119.4 |
| C11—N2—C16 | 121.7 (2) | C12—C13—C8 | 122.1 (3) |
| C14—N2—C16 | 117.7 (2) | C12—C13—H13 | 119.0 |
| C2—C1—O1 | 124.3 (3) | C8—C13—H13 | 119.0 |
| C2—C1—C6 | 120.0 (2) | N2—C14—C15 | 114.2 (3) |
| O1—C1—C6 | 115.7 (2) | N2—C14—H14B | 108.7 |
| C1—C2—C3 | 119.0 (3) | C15—C14—H14B | 108.7 |
| C1—C2—H2A | 120.5 | N2—C14—H14A | 108.7 |
| C3—C2—H2A | 120.5 | C15—C14—H14A | 108.7 |
| C4—C3—C2 | 122.2 (3) | H14B—C14—H14A | 107.6 |
| C4—C3—H3A | 118.9 | O2—C15—C14 | 110.1 (3) |
| C2—C3—H3A | 118.9 | O2—C15—H15A | 109.6 |
| C3—C4—C5 | 117.7 (2) | C14—C15—H15A | 109.6 |
| C3—C4—C7 | 120.2 (3) | O2—C15—H15B | 109.6 |
| C5—C4—C7 | 122.1 (3) | C14—C15—H15B | 109.6 |
| C6—C5—C4 | 120.5 (3) | H15A—C15—H15B | 108.1 |
| C6—C5—H5 | 119.7 | N2—C16—C17 | 111.8 (3) |
| C4—C5—H5 | 119.7 | N2—C16—H16B | 109.3 |
| C5—C6—C1 | 120.4 (3) | C17—C16—H16B | 109.3 |
| C5—C6—H6 | 119.8 | N2—C16—H16A | 109.3 |
| C1—C6—H6 | 119.8 | C17—C16—H16A | 109.3 |
| N1—C7—C4 | 123.4 (3) | H16B—C16—H16A | 107.9 |
| N1—C7—H7 | 121 (2) | O3—C17—C16 | 112.2 (3) |
| C4—C7—H7 | 115 (2) | O3—C17—H17B | 109.2 |
| C13—C8—C9 | 117.0 (2) | C16—C17—H17B | 109.2 |
| C13—C8—N1 | 117.0 (3) | O3—C17—H17A | 109.2 |
| C9—C8—N1 | 126.0 (3) | C16—C17—H17A | 109.2 |
| C10—C9—C8 | 121.3 (3) | H17B—C17—H17A | 107.9 |
| C10—C9—H9 | 119.4 | O1—C18—H18C | 109.5 |
| C8—C9—H9 | 119.4 | O1—C18—H18A | 109.5 |
| C9—C10—C11 | 121.7 (3) | H18C—C18—H18A | 109.5 |
| C9—C10—H10 | 119.2 | O1—C18—H18B | 109.5 |
| C11—C10—H10 | 119.2 | H18C—C18—H18B | 109.5 |
| N2—C11—C10 | 122.0 (3) | H18A—C18—H18B | 109.5 |
| C18—O1—C1—C2 | -0.8 (4) | C8—C9—C10—C11 | -0.8 (5) |

| | | | |
|---------------|------------|-----------------|------------|
| C18—O1—C1—C6 | 179.3 (3) | C14—N2—C11—C10 | -4.5 (4) |
| O1—C1—C2—C3 | -178.0 (3) | C16—N2—C11—C10 | 177.3 (3) |
| C6—C1—C2—C3 | 1.9 (5) | C14—N2—C11—C12 | 175.9 (3) |
| C1—C2—C3—C4 | 1.1 (5) | C16—N2—C11—C12 | -2.3 (4) |
| C2—C3—C4—C5 | -3.0 (5) | C9—C10—C11—N2 | -179.0 (3) |
| C2—C3—C4—C7 | 177.0 (3) | C9—C10—C11—C12 | 0.6 (4) |
| C3—C4—C5—C6 | 1.9 (4) | N2—C11—C12—C13 | -180.0 (3) |
| C7—C4—C5—C6 | -178.0 (3) | C10—C11—C12—C13 | 0.4 (4) |
| C4—C5—C6—C1 | 1.0 (4) | C11—C12—C13—C8 | -1.2 (5) |
| C2—C1—C6—C5 | -3.0 (5) | C9—C8—C13—C12 | 1.0 (4) |
| O1—C1—C6—C5 | 177.0 (3) | N1—C8—C13—C12 | -178.5 (3) |
| C8—N1—C7—C4 | -179.0 (3) | C11—N2—C14—C15 | -81.9 (3) |
| C3—C4—C7—N1 | -178.0 (3) | C16—N2—C14—C15 | 96.3 (3) |
| C5—C4—C7—N1 | 1.9 (5) | N2—C14—C15—O2 | -72.9 (3) |
| C7—N1—C8—C13 | 173.3 (3) | C11—N2—C16—C17 | -83.9 (3) |
| C7—N1—C8—C9 | -6.2 (5) | C14—N2—C16—C17 | 97.9 (3) |
| C13—C8—C9—C10 | 0.0 (4) | N2—C16—C17—O3 | -172.0 (2) |
| N1—C8—C9—C10 | 179.5 (3) | | |

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------------------|----------|-------------|-------------|---------------|
| O2—H2 \cdots O3 ⁱ | 0.95 (5) | 1.84 (6) | 2.762 (3) | 177 (4) |
| O3—H3 \cdots O2 ⁱⁱ | 0.82 (4) | 1.95 (4) | 2.757 (4) | 166 (4) |

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

Fig. 1

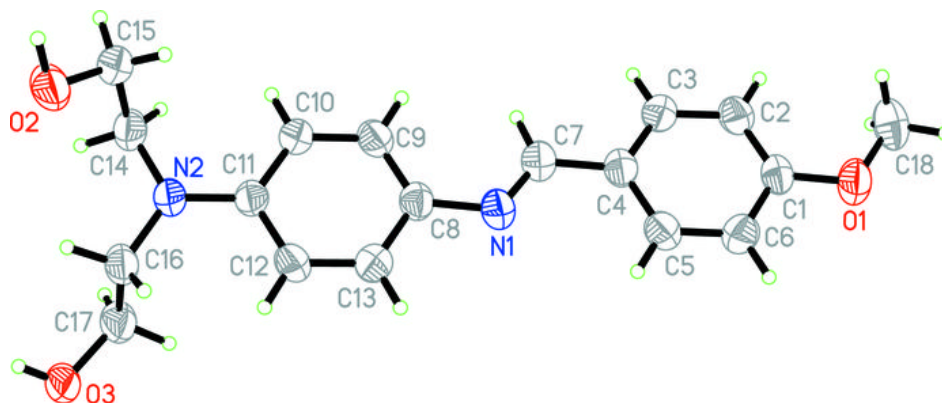


Fig. 2

