

Crystal structure of 3-bromo-2-hydroxybenzonitrile

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The crystal structure of the title compound, C₇H₄BrNO, has been determined, revealing a partial molecular packing disorder such that a 180° rotation of the molecule about the phenol C—O bond results in disorder of the bromine and nitrile groups. The disorder has been parameterized as a disorder of only the bromine and nitrile substituents on a unique phenol ring. An intramolecular O—H...Br contact occurs. In the crystal, O—H...Br/O—H...N_{nitrile} hydrogen bonding is present between the disordered bromine and nitrile substituents and the phenol group, forming a spiral chain about a twofold screw axis extending parallel to the *b*-axis direction. Within this spiral chain, the molecules also interact, forming offset face-to-face π -stacking interactions with plane-to-centroid distance of 3.487 (1) Å.

Keywords: crystal structure; disorder; hydrogen bonding; π -stacking.

CCDC reference: 1408281

1. Related literature

For syntheses of the title compound, see: Anwar & Hansen (2008); Nakai *et al.* (2014); Whiting *et al.* (2015). For its use as a synthetic reagent, see: Li & Chua (2011); Mulzer & Coates (2011). For related crystal structures, see: Beswick *et al.* (1996); Oh & Tanski (2012). For information on π -stacking, see: Hunter & Sanders (1990); Lueckheide *et al.* (2013). For information on the refinement of disordered crystal structures, see: Müller (2009); Thorn *et al.* (2012).

2. Experimental

2.1. Crystal data

C ₇ H ₄ BrNO	<i>V</i> = 677.50 (6) Å ³
<i>M_r</i> = 198.02	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 13.0171 (7) Å	μ = 5.98 mm ⁻¹
<i>b</i> = 3.8488 (2) Å	<i>T</i> = 125 K
<i>c</i> = 13.5989 (7) Å	0.22 × 0.10 × 0.04 mm
β = 96.062 (1)°	

2.2. Data collection

Bruker APEXII CCD diffractometer	9903 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2013)	1777 independent reflections
<i>T</i> _{min} = 0.57, <i>T</i> _{max} = 0.80	1776 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.025

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.049$	$\Delta\rho_{\max} = 0.37 \text{ e \AA}^{-3}$
<i>S</i> = 1.08	$\Delta\rho_{\min} = -0.45 \text{ e \AA}^{-3}$
1977 reflections	
110 parameters	
102 restraints	

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...N1 ⁱ	0.81 (2)	2.04 (2)	2.810 (3)	159 (2)
O1—H1...Br1A	0.81 (2)	2.82 (2)	3.262 (5)	116 (2)
O1—H1...Br1A ⁱ	0.81 (2)	2.62 (2)	3.379 (5)	156 (2)

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

Data collection: APEX2 (Bruker, 2013); cell refinement: SAINT (Bruker, 2013); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2014 (Sheldrick, 2015); molecular graphics: SHELXTL2014; software used to prepare material for publication: SHELXTL2014, OLEX2 (Dolomanov *et al.*, 2009) and Mercury (Macrae *et al.*, 2008).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: LD2134).

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supporting information

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Crystal structure of 3-bromo-2-hydroxybenzotrile

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S1. Structural commentary

The title compound, 3-bromo-2-hydroxybenzotrile, may be prepared by the addition of a cyano group to *o*-bromophenol (Anwar & Hansen, 2008; Nakai *et al.* 2014). It has also recently been synthesized by the one-pot conversion of the salicylaldehyde oxime, (*E*)-3-bromo-2-hydroxybenzaldehyde oxime, directly to 3-bromo-2-hydroxybenzotrile (Whiting *et al.*, 2015). 3-Bromo-2-hydroxybenzotrile is used as a synthetic reagent in the synthesis of 3,4-fused isoquinolin-1(2H)-one analogs (Li & Chua, 2011) and ampakine heterocycles which are a promising as a therapy for neurodegenerative diseases (Mulzer & Coates, 2011). The crystal structure of an isomer of the title compound which differs only in the position of the bromine substituent, 5-bromo-2-hydroxybenzotrile, has previously been published (Oh & Tanski, 2012).

3-Bromo-2-hydroxybenzotrile, (Fig. 1), crystallizes with a partial molecular packing disorder, where the bromine and nitrile substituents *ortho* to the phenol group are disordered with one another *via* a 180° rotation of the molecule about the carbon-oxygen bond of the phenol moiety. The disorder has been modeled as a disorder of only the bromine and nitrile substituents on a unique phenol ring, where the phenolic hydroxyl itself is not disordered, and the model has been refined with the help of similarity and advanced rigid bond restraints (Thorn *et al.*, 2012). Although the accuracy of the observed metrical parameters for the disordered groups is impacted by the refinement of the disorder, the bond lengths are nevertheless comparable to those found in related structures. The nitrile bond lengths C7—N1 and C7A—N1A of 1.161 (4) and 1.14 (2) Å, respectively, are similar to those seen in the related structures 5-bromo-2-hydroxybenzotrile, with nitrile C≡N distance 1.142 (4) Å (Oh & Tanski, 2012), and the unbrominated analog, *o*-cyanophenol, with C≡N distance 1.136 (2) Å (Beswick *et al.*, 1996). The aromatic bromine bond lengths C1—Br1A and C3—Br1 of 1.988 (5) Å and 1.907 (2) Å, respectively, are also similar to those seen in the related structure 5-bromo-2-hydroxybenzotrile, with C—Br length 1.897 (3) Å (Oh & Tanski, 2012).

The molecules of the title compound pack together in the solid state with intermolecular O—H⋯Br/O—H⋯N_{nitrile} hydrogen bonding (Fig. 2, Table 2). The hydrogen bonding is disordered with respect to the disordered bromine and nitrile substituents, not with respect to the phenol hydroxyl, which is found to have only one orientation. This hydrogen bonding forms a one-dimensional spiral chain extending parallel to the crystallographic *b*-axis, about the two-fold screw axis in P2₁/c with direction [0,1,0] at 1/2, *y*, 1/4. Within the chains, the molecules also interact *via* an offset face-to-face π -stacking interaction. This π -stacking is characterized by a centroid-to-centroid distance of 3.8488 (2) Å, a plane-to-centroid distance of 3.487 (1) Å, and a ring offset or ring-slippage distance of 1.630 (2) Å (Hunter & Saunders, 1990; Lueckheide *et al.*, 2013).

S2. Synthesis and crystallization

3-Bromo-2-hydroxybenzotrile (97%) was purchased from Aldrich Chemical Company, USA, and was recrystallized from acetone.

S3. Refinement

The structure was refined against F^2 using all data with *SHELXL2014* (Sheldrick, 2015), employing established refinement strategies (Müller, 2009). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and refined using a riding model at $C-H = 0.95 \text{ \AA}$ and $U_{iso}(H) = 1.2 \times U_{eq}(C)$ of the aryl C-atoms. Coordinates for the hydrogen atom on oxygen were taken from the difference Fourier synthesis and the hydrogen atom was subsequently refined semi-freely with the help of an O—H distance restraint (target value $0.84(2) \text{ \AA}$) while constraining its U_{iso} to 1.5 times the U_{eq} of the oxygen atom. The extinction parameter refined to zero and was removed from the refinement. The structure exhibits a partial molecular disorder. The disorder was successfully modeled and refined with the help of similarity restraints on 1,2- and 1,3-distances and displacement parameters as well as advanced rigid-bond restraints (Thorn *et al.*, 2012) for anisotropic displacement parameters, and interatomic distance restraints.

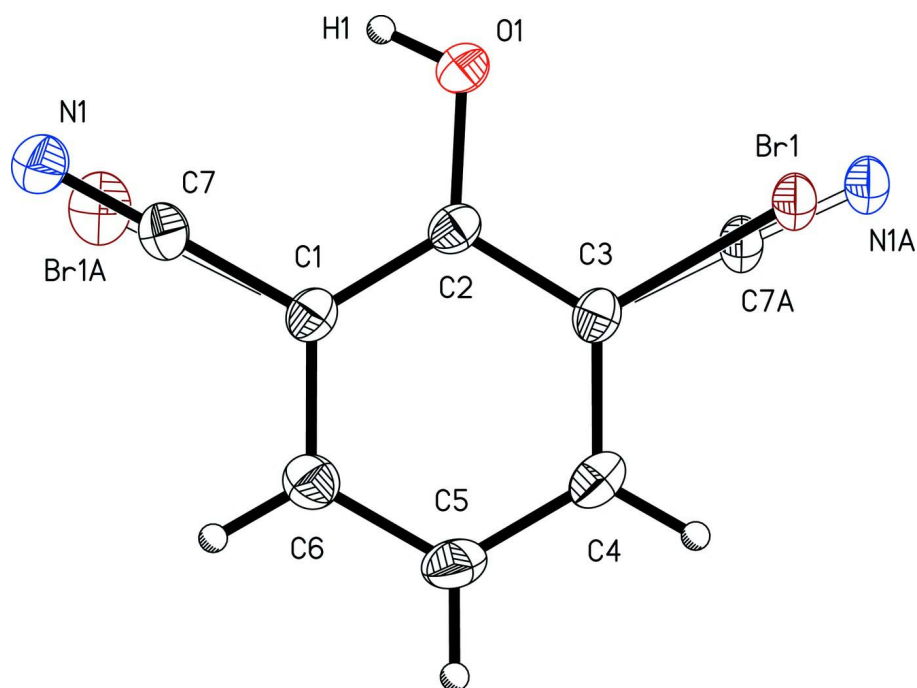


Figure 1

A view of the title compound showing the disordered nitrile and bromine substituents, with displacement ellipsoids shown at the 50% probability level.

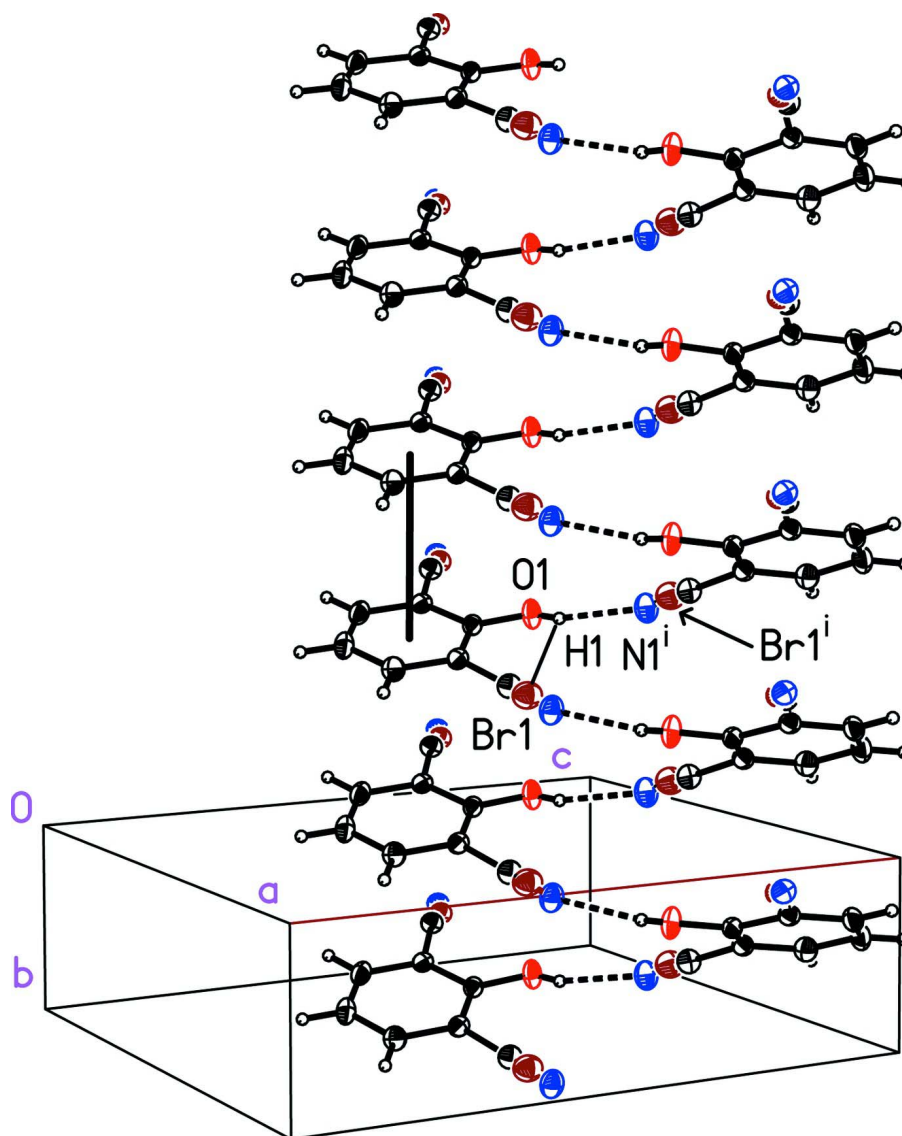


Figure 2

A view of the intermolecular $O-H\cdots Br/O-H\cdots N_{\text{nitrile}}$ hydrogen bonding interactions (dashed lines) forming a helical one-dimensional chain, with displacement ellipsoids shown at the 50% probability level. See Table 1 for symmetry code (i). A thin solid line indicates an intramolecular $O-H\cdots Br$ hydrogen bond, and a thick solid line indicates a π -stacking centroid-to-centroid interaction.

3-Bromo-2-hydroxybenzoinitrile

Crystal data

C_7H_4BrNO

$M_r = 198.02$

Monoclinic, $P2_1/c$

$a = 13.0171(7) \text{ \AA}$

$b = 3.8488(2) \text{ \AA}$

$c = 13.5989(7) \text{ \AA}$

$\beta = 96.062(1)^\circ$

$V = 677.50(6) \text{ \AA}^3$

$Z = 4$

$F(000) = 384$

$D_x = 1.941 \text{ Mg m}^{-3}$

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

Cell parameters from 6401 reflections

$\theta = 3.0\text{--}30.5^\circ$

$\mu = 5.98 \text{ mm}^{-1}$
 $T = 125 \text{ K}$

Needle, colourless
 $0.22 \times 0.10 \times 0.04 \text{ mm}$

Data collection

Bruker APEXII CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 Detector resolution: $8.3333 \text{ pixels mm}^{-1}$
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2013)
 $T_{\min} = 0.57, T_{\max} = 0.80$

9903 measured reflections
 1977 independent reflections
 1776 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\max} = 30.0^\circ, \theta_{\min} = 3.0^\circ$
 $h = -18 \rightarrow 18$
 $k = -5 \rightarrow 5$
 $l = -19 \rightarrow 19$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.049$
 $S = 1.08$
 1977 reflections
 110 parameters
 102 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0241P)^2 + 0.2328P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.45 \text{ e } \text{\AA}^{-3}$

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.70927 (9)	0.4093 (4)	0.76425 (9)	0.0264 (3)	
H1	0.6483 (13)	0.420 (6)	0.7450 (18)	0.04*	
C1	0.66122 (12)	0.6091 (4)	0.92251 (12)	0.0195 (3)	
C7	0.5648 (2)	0.7338 (8)	0.8786 (2)	0.0225 (6)	0.9272 (13)
N1	0.4862 (2)	0.8421 (7)	0.84343 (18)	0.0281 (5)	0.9272 (13)
Br1A	0.5216 (4)	0.7707 (10)	0.8684 (3)	0.0332 (13)	0.0728 (13)
C2	0.73013 (11)	0.4575 (4)	0.86256 (11)	0.0185 (3)	
C3	0.82692 (11)	0.3564 (4)	0.90818 (11)	0.0186 (3)	
Br1	0.92397 (2)	0.15982 (5)	0.82834 (2)	0.02008 (6)	0.9272 (13)
C7A	0.8979 (14)	0.192 (6)	0.8577 (15)	0.02008 (6)	0.0728 (13)
N1A	0.9658 (13)	0.131 (5)	0.8138 (13)	0.02008 (6)	0.0728 (13)
C4	0.85334 (13)	0.3982 (4)	1.00854 (12)	0.0234 (3)	
H4	0.9194	0.3259	1.0376	0.028*	

C5	0.78350 (14)	0.5460 (5)	1.06728 (12)	0.0267 (3)
H5	0.8017	0.5739	1.1363	0.032*
C6	0.68739 (13)	0.6519 (4)	1.02446 (12)	0.0237 (3)
H6	0.6394	0.7532	1.064	0.028*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0175 (5)	0.0414 (7)	0.0194 (5)	0.0021 (5)	-0.0026 (4)	-0.0046 (5)
C1	0.0174 (7)	0.0191 (7)	0.0216 (7)	-0.0012 (5)	0.0008 (6)	0.0021 (6)
C7	0.0186 (12)	0.0255 (11)	0.0237 (10)	0.0015 (11)	0.0044 (11)	-0.0002 (7)
N1	0.0217 (12)	0.0369 (13)	0.0253 (11)	0.0038 (9)	0.0012 (8)	0.0005 (9)
Br1A	0.029 (3)	0.031 (2)	0.040 (2)	0.001 (2)	0.003 (2)	-0.0004 (15)
C2	0.0173 (7)	0.0186 (7)	0.0190 (7)	-0.0024 (6)	-0.0007 (5)	0.0016 (6)
C3	0.0161 (6)	0.0173 (7)	0.0224 (7)	-0.0009 (6)	0.0012 (5)	0.0015 (6)
Br1	0.01502 (9)	0.02106 (9)	0.02437 (10)	0.00176 (7)	0.00305 (6)	-0.00176 (7)
C7A	0.01502 (9)	0.02106 (9)	0.02437 (10)	0.00176 (7)	0.00305 (6)	-0.00176 (7)
N1A	0.01502 (9)	0.02106 (9)	0.02437 (10)	0.00176 (7)	0.00305 (6)	-0.00176 (7)
C4	0.0198 (7)	0.0252 (8)	0.0241 (8)	-0.0006 (6)	-0.0037 (6)	0.0047 (6)
C5	0.0290 (8)	0.0325 (9)	0.0176 (7)	-0.0004 (7)	-0.0023 (6)	0.0027 (7)
C6	0.0236 (8)	0.0265 (8)	0.0215 (7)	-0.0004 (6)	0.0043 (6)	0.0003 (7)

Geometric parameters (Å, °)

O1—C2	1.3487 (19)	C3—C4	1.381 (2)
O1—H1	0.810 (16)	C3—Br1	1.9071 (16)
C1—C2	1.401 (2)	C7A—N1A	1.143 (16)
C1—C6	1.402 (2)	C4—C5	1.393 (2)
C1—C7	1.416 (3)	C4—H4	0.95
C1—Br1A	1.988 (5)	C5—C6	1.384 (2)
C7—N1	1.161 (4)	C5—H5	0.95
C2—C3	1.400 (2)	C6—H6	0.95
C3—C7A	1.363 (14)		
C2—O1—H1	113.7 (18)	C4—C3—Br1	119.86 (12)
C2—C1—C6	121.38 (14)	C2—C3—Br1	118.52 (11)
C2—C1—C7	119.29 (17)	N1A—C7A—C3	164 (3)
C6—C1—C7	119.28 (17)	C3—C4—C5	120.30 (15)
C2—C1—Br1A	122.09 (17)	C3—C4—H4	119.9
C6—C1—Br1A	116.52 (16)	C5—C4—H4	119.9
N1—C7—C1	178.7 (4)	C6—C5—C4	119.63 (15)
O1—C2—C3	118.60 (14)	C6—C5—H5	120.2
O1—C2—C1	124.04 (14)	C4—C5—H5	120.2
C3—C2—C1	117.35 (14)	C5—C6—C1	119.71 (16)
C7A—C3—C4	116.1 (9)	C5—C6—H6	120.1
C7A—C3—C2	122.2 (9)	C1—C6—H6	120.1
C4—C3—C2	121.62 (15)		

C6—C1—C2—O1	179.94 (15)	C1—C2—C3—Br1	-178.46 (11)
C7—C1—C2—O1	-2.6 (3)	C4—C3—C7A—N1A	-88 (8)
Br1A—C1—C2—O1	0.4 (3)	C2—C3—C7A—N1A	96 (8)
C6—C1—C2—C3	-1.2 (2)	C7A—C3—C4—C5	-176.5 (12)
C7—C1—C2—C3	176.33 (18)	C2—C3—C4—C5	-0.4 (2)
Br1A—C1—C2—C3	179.33 (18)	Br1—C3—C4—C5	179.11 (13)
O1—C2—C3—C7A	-4.1 (13)	C3—C4—C5—C6	-0.2 (3)
C1—C2—C3—C7A	176.9 (13)	C4—C5—C6—C1	0.1 (3)
O1—C2—C3—C4	-179.97 (15)	C2—C1—C6—C5	0.6 (2)
C1—C2—C3—C4	1.1 (2)	C7—C1—C6—C5	-176.89 (19)
O1—C2—C3—Br1	0.5 (2)	Br1A—C1—C6—C5	-179.86 (18)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...N1 ⁱ	0.81 (2)	2.04 (2)	2.810 (3)	159 (2)
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