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Acetylene–ammonia–18-crown-6 (1/2/1)

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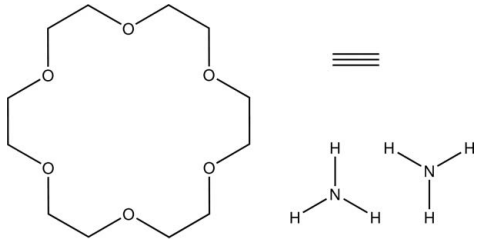
Key indicators: single-crystal X-ray study; T = 123 K; mean σ(C–C) = 0.003 Å; disorder in main residue; R factor = 0.036; wR factor = 0.100; data-to-parameter ratio = 12.1.

The title compound, $C_2H_2\cdot C_{12}H_{24}O_6\cdot 2NH_3$, was formed by co-crystallization of 18-crown-6 and acetylene in liquid ammonia. The 18-crown-6 molecule has threefold rotoinversion symmetry. The acteylene molecule lies on the threefold axis and the whole molecule is generated by an inversion center. The two ammonia molecules are also located on the threefold axis and are related by inversion symmetry. In the crystal, the ammonia molecules are located below and above the crown ether plane and are connected by intermolecular N—H···O hydrogen bonds. The acetylene molecules are additionally linked by weak C—H···N interactions into chains that propagate in the direction of the crystallographic c axis. The 18-crown-6 molecule [occupancy ratio 0.830 (4):0.170 (4)] is disordered and was refined using a split model.

Related literature

For weak intermolecular interactions such as hydrogen bonds and their application in crystal engineering, see: Desiraju (2002, 2007); Boese *et al.* (2003, 2009); Kirchner *et al.* (2004); Steiner (2002)



Experimental

Crystal data

$C_2H_2\cdot C_{12}H_{24}O_6\cdot 2NH_3$ M_r = 324.42
Trigonal, $R\overline{3}$
a = 11.8915 (1) Å
c = 11.5736 (2) Å
V = 1417.33 (3) Å^3
Z = 3
Cu $K\alpha$ radiation
μ = 0.73 mm^{-1}
T = 123 K
0.1 × 0.1 × 0.1 mm

Data collection

Oxford Diffraction SuperNova diffractometer
Absorption correction: analytical [*CrysAlis PRO* (Agilent, 2012), based on expressions derived by Clark & Reid (1995)]
T_{min} = 0.798, T_{max} = 0.841
5835 measured reflections
640 independent reflections
598 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.100
S = 1.11
640 reflections
53 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1	0.88	2.40	3.2709 (12)	171
N1—H1A···O1A	0.88	2.43	3.270 (4)	159
C1—H1···N1	0.95	2.34	3.292 (2)	180

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *olex2.solve* (Bourhis *et al.*, 2012); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, H, 2011); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NC2288).

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supplementary materials

Acta Cryst. (2012). E**68**, o2933 [doi:10.1107/S1600536812038792]

Acetylene–ammonia–18-crown-6 (1/2/1)

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Comment

The crystal structure of the title compound was determined in the course of investigations regarding the reactivity of acetylene in liquid ammonia.

In the crystal structure the acetylene molecule shows moderate hydrogen bonding in axial direction to an ammonia molecule on each side with a H···N distance of 2.3422 (15) Å and a C—H···N angle of 180°. Two ammonia molecules are located below and above the crown ether plane, bound by hydrogen bonds to the oxygen atoms in the ring (Fig. 1 and Fig. 2). Both ammonia molecules are connected to 18-crown-6 *via* three hydrogen bonds each with a H···O distance of 2.40 Å and a N—H···O angle of 171.0° for the crown ether part with a site occupation factor of 0.83 and with a H···O distance of 2.43 Å and a N—H···O angle of 159.4° for the crown ether part with a site occupation factor of 0.17 (Fig. 2 and Table 1).This arrangement leads to one-dimensional strands along the crystallographic *c*-axis, that are packed in a kind of hexagonal closest arrangement (Fig. 3). The formation of hydrogen bonds between acetylene and ammonia molecules as well as the interaction of ammonia molecules with the crown ether is essential to stabilize the fugitive acetylene molecule in the solid state as was shown previously by Boese *et al.* (Boese *et al.*, 2009) in C_2H_2*NH_3. Due to the absence of stronger intermolecular interactions the optimization of hydrogen bonds is the driving force for the axial stacking of the molecules along the crystallographic *c*-axis. This can also be observed in acetylene containing material such as co-crystallized C_2H_2*NH_3 (Boese *et al.*, 2009) and co-crystals of acetylene and acetone/DMSO (Boese *et al.*, 2003) or azacycles (Kirchner *et al.*, 2004).

Experimental

0.039 g(1.0 mmol) potassium and 0.264 g(1.00 mmol)18-crown-6 were placed under argon atmosphere in a baked-out reaction vessel and 30 ml of dry liquid ammonia were condensed. The mixture was stored at 236 K for one week to ensure that all substances were completely dissolved. Afterwards an excess of acetylene gas was fed into the solution until the colour changed from deep blue to colourless. Colourless crystals of the title compound were obtained after further storage at 236 K for nine month. Well soluble potassium hydrogen acetylide KC_2H remained in solution.

Refinement

The O atom and one C atom of the crown ether are disordered and were refined using a split model with sof of 0.830 (4) and 0.170 (4). The C—H H atoms were positioned with idealized geometry and refined isotropic with U_{iso}(H) = 1.2 U_{eq}(C) using a riding model. The N-H H atom was located in difference map and refined in the riding mode approximation.

Computing details

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO* (Agilent, 2012); data reduction: *CrysAlis PRO* (Agilent, 2012); program(s) used to solve structure: olex2.solve (Bourhis *et al.*, 2012); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, H, 2011); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

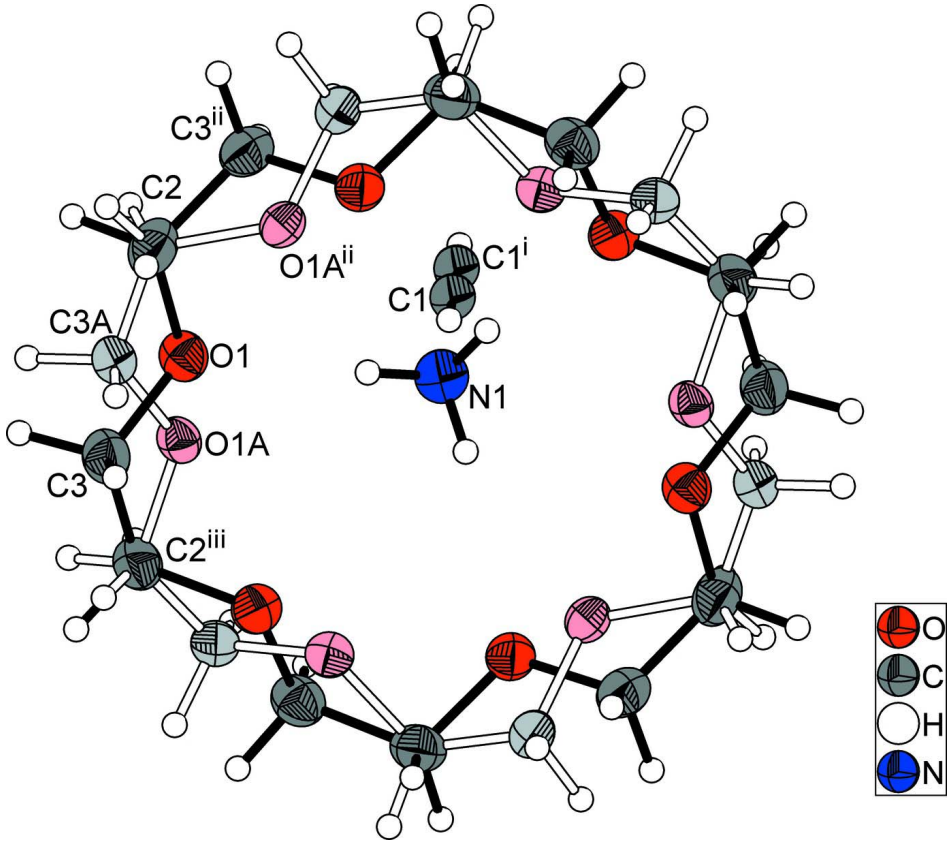

Figure 1

Crystal structure of the title compound with labeling and displacement ellipsoids drawn at the 50% probability level. Disordering is shown as full and open bonds. Symmetry codes: (i) 2/3 - *x*, 4/3 - *y*, 1/3 - *z*; (ii) -1/3 + *y*, 1/3 - *x* + *y*, 4/3 - *z*; (iii) 2/3 + *x*-*y*, 1/3 + *x*, 4/3 - *z*.

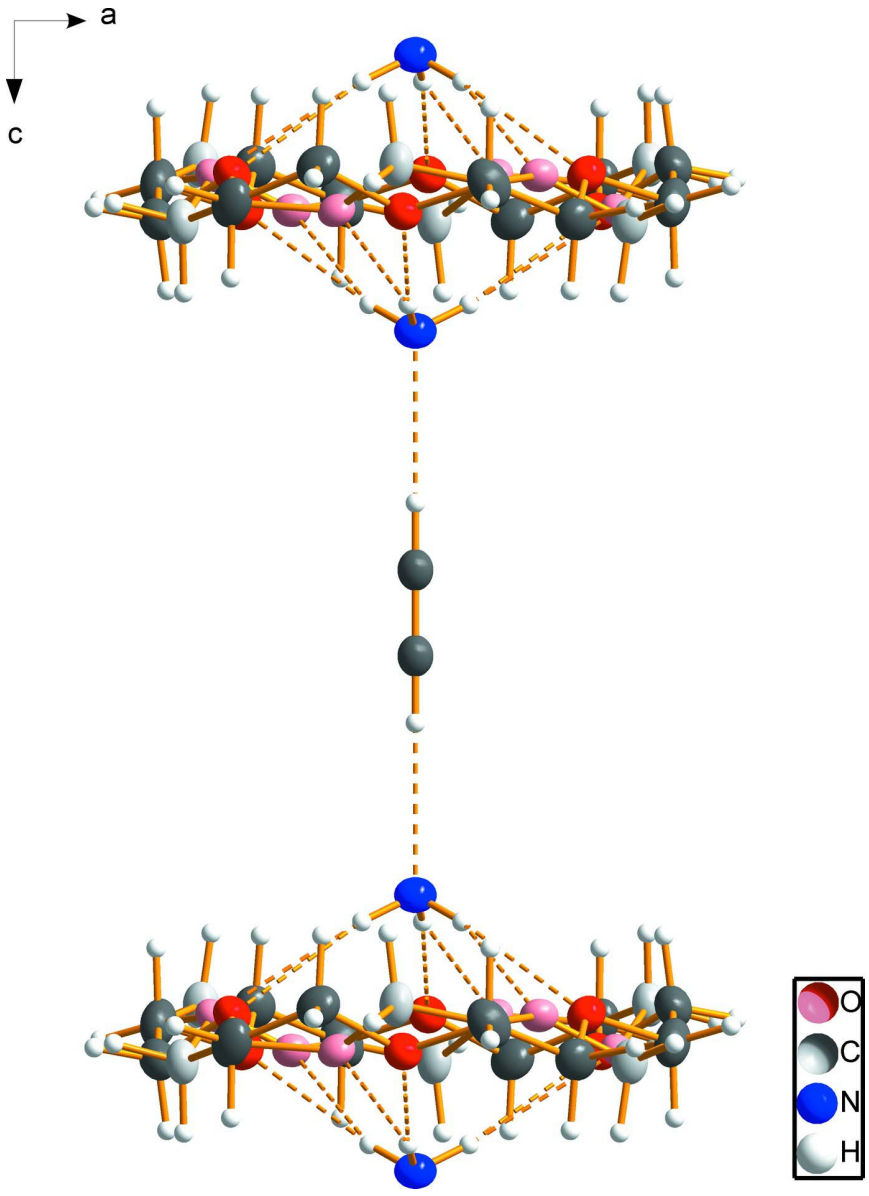

Figure 2

Crystal structure with view along the *b*-axis showing the hydrogen bonding interactions. Displacement ellipsoids are drawn at the 50% probability level and disorder is shown as full and open bonds.

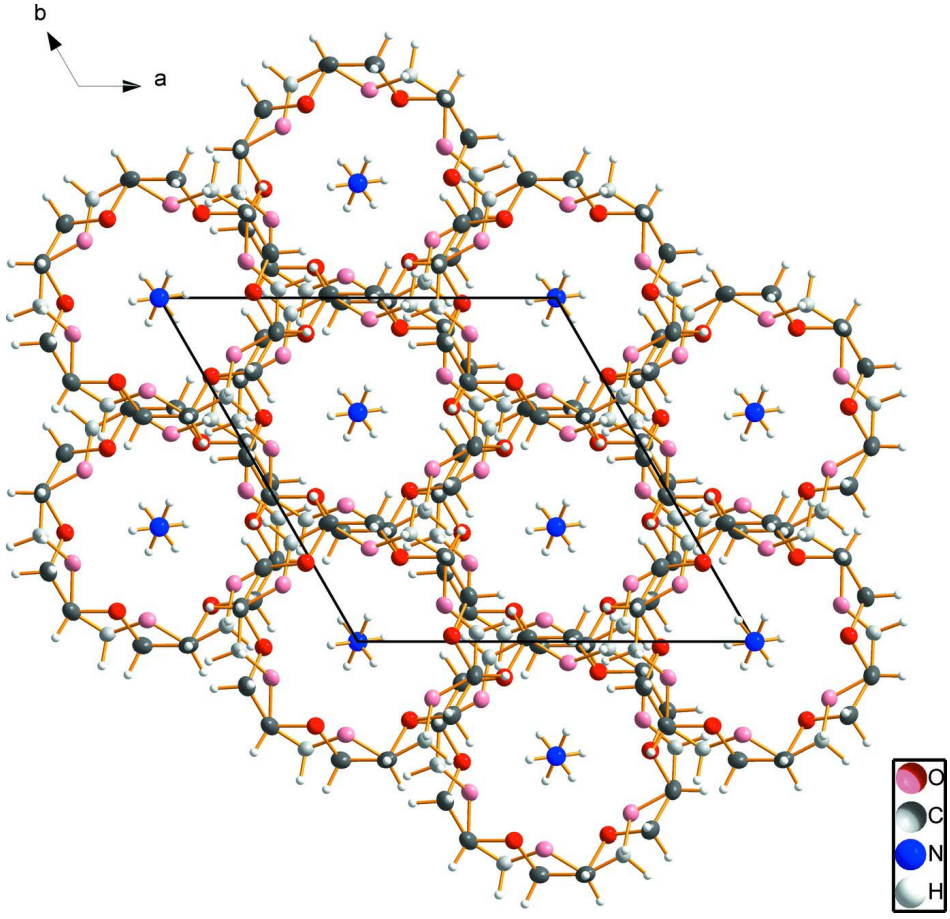

Figure 3

Projection of the unit cell along the crystallographic *c*-axis. Displacement ellipsoids are drawn at the 50% probability level and disorder is shown as full and open bonds

Ethyne–ammonia–1,4,7,10,13,16-hexaoxacyclooctadecane (1/2/1)

Crystal data

$C_2H_2 \cdot C_{12}H_{24}O_6 \cdot 2NH_3$
$M_r = 324.42$
Trigonal, $R\overline{3}$
Hall symbol: -R 3
$a = 11.8915$ (1) Å
$c = 11.5736$ (2) Å
$V = 1417.33$ (3) Å^3
$Z = 3$
$F(000) = 534$
$D_x = 1.140$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 3585 reflections
$\theta = 5.8$–$73.3°$
$\mu = 0.73$ mm^{-1}
$T = 123$ K
Block, clear colourless
0.1 × 0.1 × 0.1 mm

Data collection

Oxford Diffraction SuperNova diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: analytical [*CrysAlis PRO* (Agilent, 2012), based on expressions derived by Clark & Reid (1995)]
$T_{min} = 0.798$, $T_{max} = 0.841$
5835 measured reflections
640 independent reflections

598 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 73.3°$, $\theta_{min} = 5.8°$

$h = -14 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.100$
$S = 1.11$
640 reflections
53 parameters
0 restraints
Primary atom site location: iterative

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 0.8298P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}

Special details

Experimental. Absorption correction: Crysalis Pro, Agilent Technologies, Version 1.171.35.21, Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R. C. Clark & J. S. Reid (1995).
Crystal mounting in perfluorether
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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.34988 (11)	0.43774 (10)	0.64475 (7)	0.0298 (4)	0.830 (4)
C2	0.23519 (11)	0.32279 (10)	0.67833 (11)	0.0387 (4)	
H2AA	0.2314	0.3164	0.7637	0.046*	0.830 (4)
H2AB	0.2375	0.2463	0.6476	0.046*	0.830 (4)
H2BC	0.1912	0.2473	0.7309	0.046*	0.170 (4)
H2BD	0.2225	0.2880	0.5987	0.046*	0.170 (4)
C3	0.46325 (13)	0.45185 (13)	0.69816 (12)	0.0344 (4)	0.830 (4)
H3B	0.4711	0.3743	0.6819	0.041*	0.830 (4)
H3A	0.4568	0.4586	0.7829	0.041*	0.830 (4)
O1A	0.4390 (5)	0.5013 (5)	0.6463 (3)	0.0254 (17)	0.170 (4)
C3A	0.3587 (6)	0.3803 (6)	0.7006 (6)	0.0312 (12)	0.17
H3AB	0.3905	0.3206	0.6786	0.037*	0.170 (4)
H3AA	0.3700	0.3934	0.7852	0.037*	0.170 (4)
N1	0.3333	0.6667	0.50242 (13)	0.0330 (4)	
H1A	0.3430	0.6046	0.5340	0.040*	
C1	0.3333	0.6667	0.21796 (16)	0.0289 (4)	
H1	0.3333	0.6667	0.3000	0.035*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0306 (8)	0.0310 (6)	0.0287 (5)	0.0160 (5)	0.0010 (4)	0.0042 (4)
C2	0.0397 (7)	0.0276 (6)	0.0487 (7)	0.0168 (5)	0.0111 (5)	0.0046 (4)
C3	0.0379 (8)	0.0347 (7)	0.0359 (8)	0.0220 (7)	−0.0045 (5)	−0.0002 (5)
O1A	0.027 (3)	0.029 (3)	0.022 (2)	0.016 (2)	−0.0035 (16)	0.0004 (17)
C3A	0.027 (3)	0.029 (3)	0.040 (3)	0.016 (3)	−0.002 (2)	0.000 (3)
N1	0.0363 (6)	0.0363 (6)	0.0263 (7)	0.0182 (3)	0.000	0.000
C1	0.0257 (5)	0.0257 (5)	0.0351 (8)	0.0129 (3)	0.000	0.000

Geometric parameters (Å, º)

O1—C2	1.4196 (15)	C3—H3B	0.9900
O1—C3	1.4148 (18)	C3—H3A	0.9900
C2—H2AA	0.9900	O1A—C2^{ii}	1.446 (5)
C2—H2AB	0.9900	O1A—C3A	1.416 (8)
C2—H2BC	0.9900	C3A—H3AB	0.9900
C2—H2BD	0.9900	C3A—H3AA	0.9900
C2—C3^{i}	1.4698 (18)	N1—H1A	0.8810
C2—O1A^{i}	1.446 (5)	C1—C1^{iii}	1.187 (4)
C2—C3A	1.298 (6)	C1—H1	0.9500
C3—C2^{ii}	1.4698 (18)		
C3—O1—C2	113.22 (10)	C3A—C2—H2BC	107.5
O1—C2—H2AA	109.4	C3A—C2—H2BD	107.5
O1—C2—H2AB	109.4	C3A—C2—C3^{i}	152.4 (3)
O1—C2—H2BC	149.2	C3A—C2—O1A^{i}	119.3 (3)
O1—C2—H2BD	91.2	O1—C3—C2^{ii}	110.55 (11)
O1—C2—C3^{i}	111.27 (10)	O1—C3—H3B	109.5
O1—C2—O1A^{i}	89.71 (18)	O1—C3—H3A	109.5
H2AA—C2—H2AB	108.0	C2^{ii}—C3—H3B	109.5
H2BC—C2—H2BD	107.0	C2^{ii}—C3—H3A	109.5
C3^{i}—C2—H2AA	109.4	H3B—C3—H3A	108.1
C3^{i}—C2—H2AB	109.4	C3A—O1A—C2^{ii}	122.5 (4)
C3^{i}—C2—H2BC	97.7	C2—C3A—O1A	117.3 (5)
C3^{i}—C2—H2BD	74.6	C2—C3A—H3AB	108.0
O1A^{i}—C2—H2AA	87.6	C2—C3A—H3AA	108.0
O1A^{i}—C2—H2AB	148.6	O1A—C3A—H3AB	108.0
O1A^{i}—C2—H2BC	107.5	O1A—C3A—H3AA	108.0
O1A^{i}—C2—H2BD	107.5	H3AB—C3A—H3AA	107.2
C3A—C2—H2AA	80.7	C1^{iii}—C1—H1	180.0
C3A—C2—H2AB	90.6		

Symmetry codes: (i) *y*−1/3, −*x*+*y*+1/3, −*z*+4/3; (ii) *x*−*y*+2/3, *x*+1/3, −*z*+4/3; (iii) −*x*+2/3, −*y*+4/3, −*z*+1/3.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O1	0.88	2.40	3.2709 (12)	171

N1—H1*A*···O1*A*	0.88	2.43	3.270 (4)	159
C1—H1···N1	0.95	2.34	3.292 (2)	180