

# $[\{(H_3C)_3NB(H)_2NC\}_2Au][AuI_2]$ : a linear chain polymer of gold(I) iodide with an unusual isocyanoborane ligand showing aurophilic behaviour

William C. Kaska,<sup>a</sup> Hermann A. Mayer,<sup>b</sup> Mark R. J. Elsegood,<sup>c</sup> Peter N. Horton,<sup>d</sup> Michael B. Hursthouse,<sup>d</sup> Carl Redshaw<sup>e</sup> and Simon M. Humphrey<sup>f\*</sup>

<sup>a</sup>Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106-9510, USA, <sup>b</sup>Universität Tübingen, Institut für Anorganische Chemie, Auf der Morgenstelle 18, D-72076 Tübingen, Germany, <sup>c</sup>Chemistry Department, Loughborough University, Loughborough, Leicestershire LE11 3TU, England, <sup>d</sup>School of Chemistry, University of Southampton, Southampton SO17 1BJ, England, <sup>e</sup>Wolfson Materials and Catalysis Centre, School of Chemical Sciences and Pharmacy, University of East Anglia, Norwich NR4 7TJ, England, and <sup>f</sup>University Chemical Laboratory, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, England

Correspondence e-mail: smh49@cam.ac.uk

## Key indicators

Single-crystal X-ray study

$T = 120$  K

Mean  $\sigma(\text{Au}-\text{I}) = 0.001$  Å

$R$  factor = 0.049

$wR$  factor = 0.125

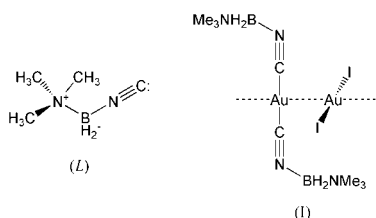
Data-to-parameter ratio = 24.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Treatment of the (isocyanoborane)gold(I) chloride adduct  $[LAuCl]$  [ $L = (H_3C)_3NB(H)_2NC$ ] with KI at room temperature yields the unusual title compound, bis[isocyano(trimethylamino)borane]gold(I) diiodaurate(I),  $[Au(C_4H_{11}BN_2)_2][AuI_2]$ , which forms *via* an *in situ* rearrangement of isocyanoborane and halide ligands. The structure consists of alternating  $[L_2Au]^+$  and  $[AuI_2]^-$  ions, which form an infinite linear one-dimensional chain due to aurophilic  $Au \cdots Au$  interactions. Both Au atoms occupy inversion centres.

## Comment

We have recently been interested in the formation of (isocyanide)gold(I) halide adducts, because of their propensity to interact aurophilically. The term aurophilicity is used to describe observed  $Au \cdots Au$  interactions. These intermolecular contacts have been shown to have bond energies and distances similar to those observed for classical hydrogen-bonding interactions ( $7.5\text{--}12.5$  kcal mol<sup>-1</sup> and  $2.7\text{--}3.5$  Å, respectively) (Schmidbaur, 1990, 2000; Mathieson *et al.*, 2000). Hence, aurophilic behaviour is considered to be a major factor in determining the particular supramolecular motif which a series of monomers is observed to adopt. Our recent synthetic studies have involved the use of an unusual zwitterionic isocyanoborane species ( $L$ ) (Andersen *et al.*, 2001) (see scheme). The substitution reaction of  $[LAuCl]$ , whereby chloride is replaced with iodide, has yielded (I), whose structure shows clear evidence for aurophilic effects directing the appearance of its extended structure.

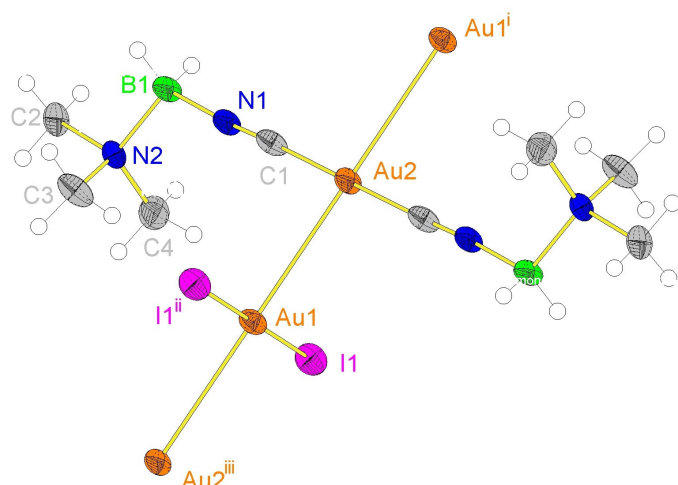


Compound (I) crystallizes in the triclinic space group  $P\bar{1}$  ( $Z = 2$ ). The asymmetric unit comprises one equivalent of the isocyanoborane donor species and a single iodide, each coordinated to crystallographically distinct gold cations Au1 and Au2, both of which are located on inversion centres (Fig. 1). Both Au1 and Au2 exhibit pseudo-square-planar coordination geometry, with bonding angles of  $91.443(11)$  ( $I1-Au1 \cdots Au2$ ) and  $97.1(2)^\circ$  ( $C1-Au2 \cdots Au1^i$ ; symmetry code as in Table 1). Au1 is *trans*-coordinated by two equivalents of iodide; Au2 is also *trans*-coordinated, by isocyanide moieties. The coordination of each gold ion is

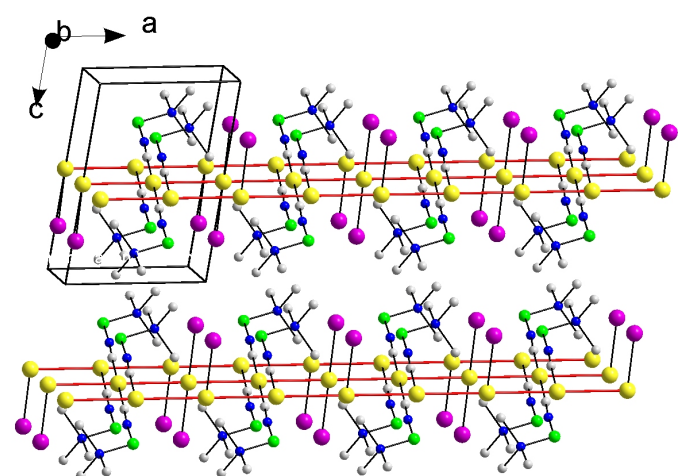
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**Figure 1**

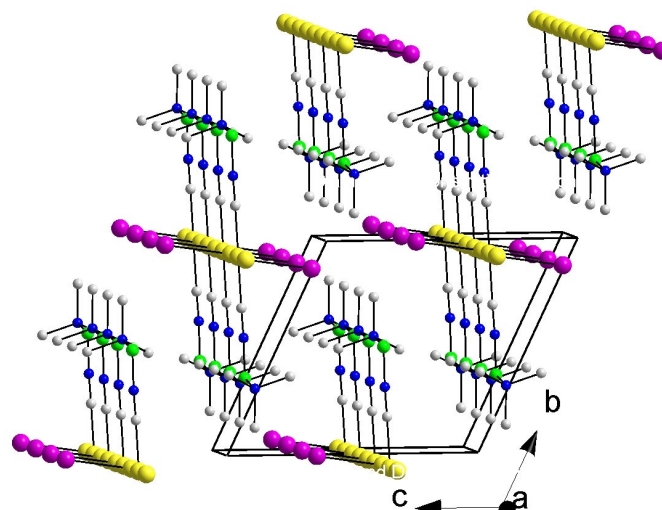
Part of the polymeric structure of (I), showing two asymmetric units and two additional Au atoms, with displacement ellipsoids drawn at the 50% probability level. Coordination environments of all unique atoms are drawn completed. [Symmetry codes: (i)  $-x, -y, 1 - z$ ; (ii)  $1 + x, y, z$ ; (iii)  $-1 - x, -y, 1 - z$ .]


**Figure 2**

View of (I), showing the chains of aurophilically bound gold centres running parallel to the crystallographic  $a$  axis. Aurophilic type bonds are drawn in red.

completed by  $\text{Au} \cdots \text{Au}$  contacts with adjacent Au centres, where  $\text{Au1} \cdots \text{Au2}$  is a mere  $3.0438(7) \text{ \AA}$ , suggesting that significant aurophilic character is present in (I). Literature values for observed  $\text{Au} \cdots \text{Au}$  contact distances suggest an approximate range of  $4.1 \text{ \AA}$  (as often associated with the inter-dimer bonding in chains of dimers) to  $2.9 \text{ \AA}$  for complexes similar in topology to (I).

A perfectly linear infinite chain of gold atoms is thus formed, aligned parallel to the crystallographic  $a$  axis (Fig. 2). It can be seen that adjacent chains are displaced from each other along the  $b$  axis, thus forming a two-dimensional grid-like array of sheets. The  $\text{B1-N1-C1}$  angle is  $175.7(7)^\circ$ , this portion of the coordinated isocyanoborane being almost linear. Adjacent iodide and isocyanide substituents are aligned approximately orthogonally to one another (Fig. 3). A


**Figure 3**

Projection of (I) on the  $bc$  plane, detailing the approximately orthogonal arrangement of the iodide and isocyanoborane substituents.

network of classical (van der Waals) intermolecular interactions is formed primarily between methyl H atoms and adjacent  $\text{I}^-$  atoms (Fig. 3).

## Experimental

A solution of  $[\text{LAuCl}]$  (42 mg, 0.202 mmol) in dichloromethane (10 ml) was stirred vigorously with KI (51 mg, 0.307 mmol) in  $\text{H}_2\text{O}$  (10 ml) over a period of 18 h. After removal of all solvent, the yellow-green residual solid was dissolved in dichloromethane (5 ml). Small light green shard-like crystals of (I) were grown from the solution by layering with heptane (1:1) and allowing slow evaporation of the solvent. For full experimental details and characterization data, see Humphrey *et al.* (2004).

### Crystal data

$[\text{Au}(\text{C}_4\text{H}_{11}\text{BN}_2)_2][\text{AuI}_2]$   
 $M_r = 421.82$   
 Triclinic,  $P\bar{1}$   
 $a = 6.0875(1) \text{ \AA}$   
 $b = 9.3080(2) \text{ \AA}$   
 $c = 9.6876(2) \text{ \AA}$   
 $\alpha = 115.970(1)^\circ$   
 $\beta = 91.039(1)^\circ$   
 $\gamma = 102.127(2)^\circ$   
 $V = 478.680(16) \text{ \AA}^3$

$Z = 2$   
 $D_x = 2.927 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 2009 reflections  
 $\theta = 2.9\text{--}27.5^\circ$   
 $\mu = 18.52 \text{ mm}^{-1}$   
 $T = 120(2) \text{ K}$   
 Shard, light green  
 $0.10 \times 0.06 \times 0.02 \text{ mm}$

### Data collection

Nonius KappaCCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)  
 $T_{\min} = 0.267, T_{\max} = 0.689$   
 7106 measured reflections

2174 independent reflections  
 2033 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.066$   
 $\theta_{\max} = 27.5^\circ$   
 $h = -7 \rightarrow 7$   
 $k = -12 \rightarrow 12$   
 $l = -12 \rightarrow 12$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.125$   
 $S = 1.06$   
 2174 reflections  
 88 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0926P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 6.24 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -4.28 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Au1–I1	2.5604 (5)	C1–N1	1.156 (10)
Au1···Au2	3.0438 (1)	N1–B1	1.550 (9)
Au2–C1	1.977 (8)		
I1–Au1–I1 <sup>i</sup>	180	C1–Au2···Au1	82.9 (2)
I1–Au1···Au2	91.443 (11)	C1 <sup>iii</sup> –Au2···Au1	97.1 (2)
I1 <sup>i</sup> –Au1···Au2	88.557 (11)	N1–C1–Au2	178.1 (7)
Au2···Au1···Au2 <sup>ii</sup>	180	C1–N1–B1	175.7 (7)
C1–Au2–C1 <sup>iii</sup>	180	N1–B1–N2	108.2 (6)

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

Methyl H (C–H distance = 0.98 Å) and BH<sub>2</sub> (B–H distance = 0.99 Å) atoms were placed in calculated positions using a riding model.  $U_{\text{iso}}$  values were set to  $1.2U_{\text{eq}}$  of the parent atom for BH ( $1.5U_{\text{eq}}$  for methyl H). The maximum and minimum difference map features were located 0.94 Å from Au1 and 0.81 Å from Au2, respectively.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL* (Sheldrick, 1997); molecular

graphics: *DIAMOND* (Crystal Impact, 2001); software used to prepare material for publication: *PLATON* (Spek, 2003).

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## supporting information

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**[[ $(\text{H}_3\text{C})_3\text{NB}(\text{H})_2\text{NC}$ ] $_2\text{Au}$ ][ $\text{AuI}_2$ ]: a linear chain polymer of gold(I) iodide with an unusual isocyanoborane ligand showing aurophilic behaviour**

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(I)

*Crystal data*

[ $\text{Au}(\text{C}_4\text{H}_{11}\text{BN}_2)_2$ ][ $\text{AuI}_2$ ]

$M_r = 421.82$

Triclinic,  $P\bar{1}$

Hall symbol: -P 1

$a = 6.0875$  (1) Å

$b = 9.3080$  (2) Å

$c = 9.6876$  (2) Å

$\alpha = 115.970$  (1)°

$\beta = 91.039$  (1)°

$\gamma = 102.127$  (2)°

$V = 478.68$  (2) Å<sup>3</sup>

$Z = 2$

$F(000) = 372$

$D_x = 2.927$  Mg m<sup>-3</sup>

Melting point: 417–419 K

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 2009 reflections

$\theta = 2.9$ – $27.5$ °

$\mu = 18.52$  mm<sup>-1</sup>

$T = 120$  K

Shard, light green

$0.10 \times 0.06 \times 0.02$  mm

*Data collection*

Nonius KappaCCD area-detector  
diffractometer

Radiation source: Nonius FR591 rotating anode

Graphite monochromator

Detector resolution: 9.091 pixels mm<sup>-1</sup>

$\varphi$  and  $\omega$  scans to fill Ewald Sphere

Absorption correction: multi-scan  
(SORTAV; Blessing, 1997)

$T_{\min} = 0.267$ ,  $T_{\max} = 0.689$

7106 measured reflections

2174 independent reflections

2033 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.066$

$\theta_{\max} = 27.5$ °,  $\theta_{\min} = 3.5$ °

$h = -7 \rightarrow 7$

$k = -12 \rightarrow 12$

$l = -12 \rightarrow 12$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.125$

$S = 1.06$

2174 reflections

88 parameters

0 restraints

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

$w = 1/[\sigma^2(F_o^2) + (0.0926P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 6.24$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -4.28$  e Å<sup>-3</sup>

*Special details*

**Experimental.** PLEASE NOTE cell\_measurement\_fields are not relevant to area detector data, the entire data set is used to refine the cell, which is indexed from all observed reflections in a 10 degree phi range.

**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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Au1	0.0000	0.0000	0.5000	0.02402 (17)
Au2	-0.5000	0.0000	0.5000	0.02413 (17)
I1	-0.01262 (8)	-0.04700 (6)	0.21874 (5)	0.03220 (19)
N2	-0.3642 (10)	-0.6158 (7)	0.1986 (7)	0.0241 (12)
C1	-0.5406 (12)	-0.2415 (10)	0.3899 (9)	0.0281 (15)
C4	-0.4108 (14)	-0.8005 (9)	0.1236 (10)	0.0313 (16)
H4A	-0.2715	-0.8344	0.0892	0.047*
H4B	-0.5274	-0.8471	0.0343	0.047*
H4C	-0.4638	-0.8403	0.1984	0.047*
C2	-0.1955 (14)	-0.5474 (12)	0.3387 (10)	0.0372 (18)
H2A	-0.0579	-0.5864	0.3091	0.056*
H2B	-0.2595	-0.5840	0.4133	0.056*
H2C	-0.1581	-0.4268	0.3858	0.056*
C3	-0.2679 (15)	-0.5580 (11)	0.0871 (10)	0.0359 (18)
H3A	-0.2440	-0.4381	0.1321	0.054*
H3B	-0.3732	-0.6101	-0.0087	0.054*
H3C	-0.1229	-0.5876	0.0641	0.054*
N1	-0.5586 (10)	-0.3820 (7)	0.3243 (7)	0.0245 (12)
B1	-0.5989 (14)	-0.5722 (9)	0.2423 (10)	0.0257 (16)
H1A	-0.7086	-0.6197	0.1477	0.031*
H1B	-0.6613	-0.6184	0.3119	0.031*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Au1	0.0190 (3)	0.0229 (3)	0.0262 (3)	0.00771 (17)	0.00457 (17)	0.00637 (19)
Au2	0.0205 (3)	0.0164 (2)	0.0295 (3)	0.00851 (17)	0.00569 (17)	0.00314 (18)
I1	0.0319 (3)	0.0359 (3)	0.0273 (3)	0.0120 (2)	0.0062 (2)	0.0113 (2)
N2	0.022 (3)	0.024 (3)	0.028 (3)	0.013 (2)	0.008 (2)	0.010 (2)
C1	0.018 (3)	0.034 (4)	0.029 (4)	0.010 (3)	0.006 (3)	0.010 (3)
C4	0.036 (4)	0.018 (3)	0.039 (4)	0.017 (3)	0.011 (3)	0.007 (3)
C2	0.025 (4)	0.047 (5)	0.034 (4)	0.016 (3)	0.005 (3)	0.010 (3)
C3	0.040 (5)	0.037 (4)	0.038 (4)	0.019 (4)	0.016 (4)	0.019 (4)
N1	0.019 (3)	0.019 (3)	0.029 (3)	0.009 (2)	0.007 (2)	0.003 (2)

B1	0.020 (4)	0.016 (3)	0.032 (4)	0.008 (3)	0.009 (3)	0.002 (3)
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*Geometric parameters (Å, °)*

Au1—I1	2.5604 (5)	C4—H4A	0.9800
Au1—I1 <sup>i</sup>	2.5604 (5)	C4—H4B	0.9800
Au1—Au2	3.0438 (1)	C4—H4C	0.9800
Au1—Au2 <sup>ii</sup>	3.0438 (1)	C2—H2A	0.9800
Au2—C1	1.977 (8)	C2—H2B	0.9800
Au2—C1 <sup>iii</sup>	1.977 (8)	C2—H2C	0.9800
Au2—Au1 <sup>iv</sup>	3.0438 (1)	C3—H3A	0.9800
N2—C3	1.484 (10)	C3—H3B	0.9800
N2—C2	1.490 (10)	C3—H3C	0.9800
N2—C4	1.502 (9)	N1—B1	1.550 (9)
N2—B1	1.581 (9)	B1—H1A	0.9900
C1—N1	1.156 (10)	B1—H1B	0.9900
I1—Au1—I1 <sup>i</sup>	180	N2—C4—H4C	109.5
I1—Au1—Au2	91.443 (11)	H4A—C4—H4C	109.5
I1 <sup>i</sup> —Au1—Au2	88.557 (11)	H4B—C4—H4C	109.5
I1—Au1—Au2 <sup>ii</sup>	88.557 (11)	N2—C2—H2A	109.5
I1 <sup>i</sup> —Au1—Au2 <sup>ii</sup>	91.443 (11)	N2—C2—H2B	109.5
Au2—Au1—Au2 <sup>ii</sup>	180	H2A—C2—H2B	109.5
C1—Au2—C1 <sup>iii</sup>	180	N2—C2—H2C	109.5
C1—Au2—Au1	82.9 (2)	H2A—C2—H2C	109.5
C1 <sup>iii</sup> —Au2—Au1	97.1 (2)	H2B—C2—H2C	109.5
C1—Au2—Au1 <sup>iv</sup>	97.1 (2)	N2—C3—H3A	109.5
C1 <sup>iii</sup> —Au2—Au1 <sup>iv</sup>	82.9 (2)	N2—C3—H3B	109.5
Au1—Au2—Au1 <sup>iv</sup>	180	H3A—C3—H3B	109.5
C3—N2—C2	109.3 (7)	N2—C3—H3C	109.5
C3—N2—C4	108.4 (6)	H3A—C3—H3C	109.5
C2—N2—C4	108.7 (6)	H3B—C3—H3C	109.5
C3—N2—B1	112.7 (6)	C1—N1—B1	175.7 (7)
C2—N2—B1	111.5 (6)	N1—B1—N2	108.2 (6)
C4—N2—B1	106.2 (6)	N1—B1—H1A	110.1
N1—C1—Au2	178.1 (7)	N2—B1—H1A	110.1
N2—C4—H4A	109.5	N1—B1—H1B	110.1
N2—C4—H4B	109.5	N2—B1—H1B	110.1
H4A—C4—H4B	109.5	H1A—B1—H1B	108.4

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