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Poly[1,4-bis(ammoniomethyl)cyclohexane [di-μ-iodido-diiodidoplumbate(II)]]

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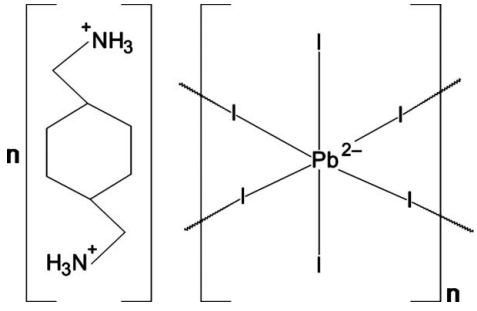
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.010 Å; R factor = 0.033; wR factor = 0.093; data-to-parameter ratio = 32.3.

The title compound, $\{(C_8H_{20}N_2)[PbI_4]\}_n$, is an inorganic–organic hybrid. The structure is composed of alternate layers of two-dimensional corner-sharing PbI_6 octahedra ($\overline{1}$ symmetry) and 1,4-bis(ammoniomethyl)cyclohexane cations ($\overline{1}$ symmetry) extending parallel to the bc plane. The cations interact with the inorganic layer *via* N—H···I hydrogen bonding in the right-angled halogen sub-type of the terminal halide hydrogen-bonding motif.

Related literature

For other examples of inorganic–organic hybrid structures encorporating cyclic ammonium cations, see: Billing & Lemmerer (2006). For hydrogen-bonding nomenclature for inorganic–organic hybrids, see: Mitzi (1999). For the related chloridoplumbate(II), see: Rayner & Billing (2010*a*) and for the isotypic bromidoplumbate(II), see: Rayner & Billing (2010*b*).



Experimental

Crystal data

$(C_8H_{20}N_2)[PbI_4]$
M_r = 859.05
Monoclinic, $P2_1/c$
a = 12.2793 (17) Å
b = 8.7413 (12) Å
c = 8.7829 (13) Å
β = 95.922 (3)°
V = 937.7 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 15.56 mm^{-1}
T = 173 K
0.36 × 0.26 × 0.08 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: integration (*XPREP*; Bruker, 2005)
T_{min} = 0.043, T_{max} = 0.288
5435 measured reflections
2264 independent reflections
2085 reflections with $I > 2\sigma(I)$
R_{int} = 0.080

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.093
S = 1.08
2264 reflections
70 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.76 e Å^{-3}
$\Delta\rho_{min}$ = −2.79 e Å^{-3}

Table 1
Selected bond lengths (Å).

Pb1—I2^{i}	3.1824 (5)	Pb1—I1^{i}	3.2243 (6)
Pb1—I2^{ii}	3.1875 (5)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1D···I1^{i}	0.91	2.88	3.598 (5)	137
N1—H1E···I1^{iii}	0.91	2.84	3.619 (6)	144
N1—H1E···I2^{iv}	0.91	3.12	3.672 (6)	121
N1—H1C···I2	0.91	2.78	3.611 (6)	152

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2340).

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supporting information

Acta Cryst. (2010). E**66**, m660 [https://doi.org/10.1107/S160053681001682X]

Poly[1,4-bis(ammoniomethyl)cyclohexane [di-μ-iodido-diiodidoplumbate(II)]]

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S1. Comment

The title structure (Fig. 1) is one of three 2-dimensional hybrid structures that we have synthesized encorporating this di-ammonium cation. The structures differ in terms of their halogen ligands, which include iodide (presented here), the bromide (Rayner & Billing, 2010*b*) and chloride (Rayner & Billing, 2010*a*). The bromide and iodide hybrids are isotypic and crystallize in the monoclinic system with space group $P2_1/c$ while the chloride hybrid crystallizes in the orthorhombic, *Pnma* system.

In the structure of the title compound the lead atoms in the PbI_6 octahedra occupy inversion centers, giving the octahedra $\bar{1}$ symmetry. The PbI_6 octahedra share corners to form layers extending parallel to the *bc* plane. Octahedra from alternate layers are eclipsed relative to one another (Fig. 2). In all three structures only the *trans* form of the cation has been observed, giving the cation $\bar{1}$ symmetry (Fig. 3). The ammonium cations interact with the inorganic layer via N—H···*X* (*X* = Br, I and Cl) hydrogen bonding in the right-angled halogen subtype of the terminal halide hydrogen bonding motif (Mitzi, 1999). Billing & Lemmerer (2006) reported a series of inorganic-organic hybrids encorpoating cyclic ammonium cations, however no diammonium cations were synthesized.

S2. Experimental

A mixture of 0.050 g (0.11 mmol) PbI_2 and 0.017 g (0.17 mmol) 1,4-bis-(aminomethyl)-cyclohexane (mixture of isomers) was dissolved in 5 ml HI at 383 K and slow cooled at a rate of 0.069 K/min to yield yellow, plate-shaped single crystals suitable for X-ray analysis.

S3. Refinement

The H atoms on the diammonium cation were refined using a riding-model, with C—H = 0.99 Å, N—H = 0.91 Å and with $U_{iso}(H)=1.2U_{eq}(C)$ or $1.5U_{eq}(N)$. The highest residual electron density peak (1.76 e Å-3) was 0.955Å from Pb1.

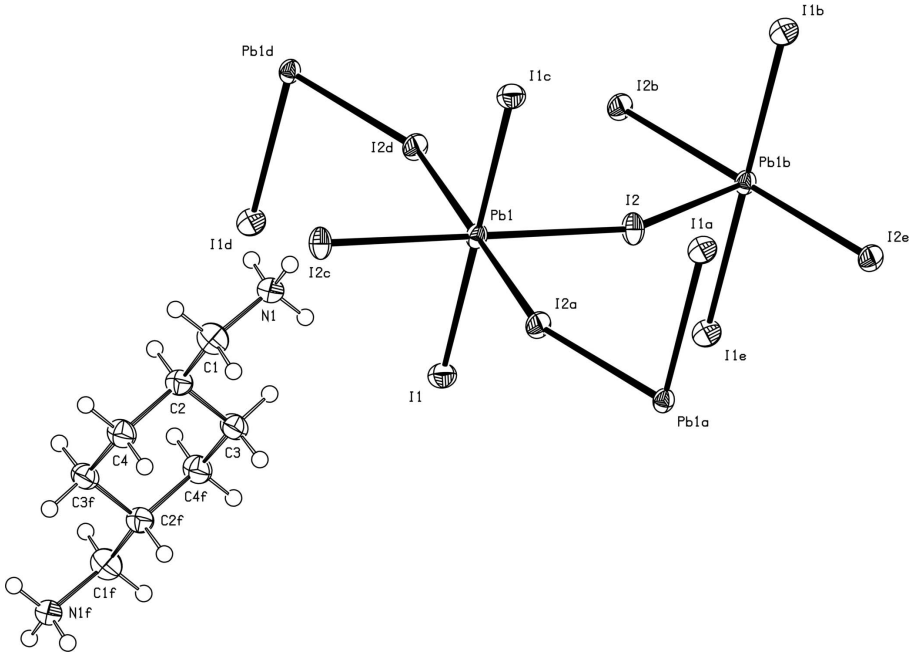

Figure 1

The extended asymmetric unit of the title compound with atom labels. Displacement ellipsoids were drawn at the 50% probability level. Symmetry codes: (a) -x, -1/2+y, 3/2-z (b) -x, 1-y, 1-z (c) x, 3/2-y, -1/2+z (d) 1-x, 1-y, -z.

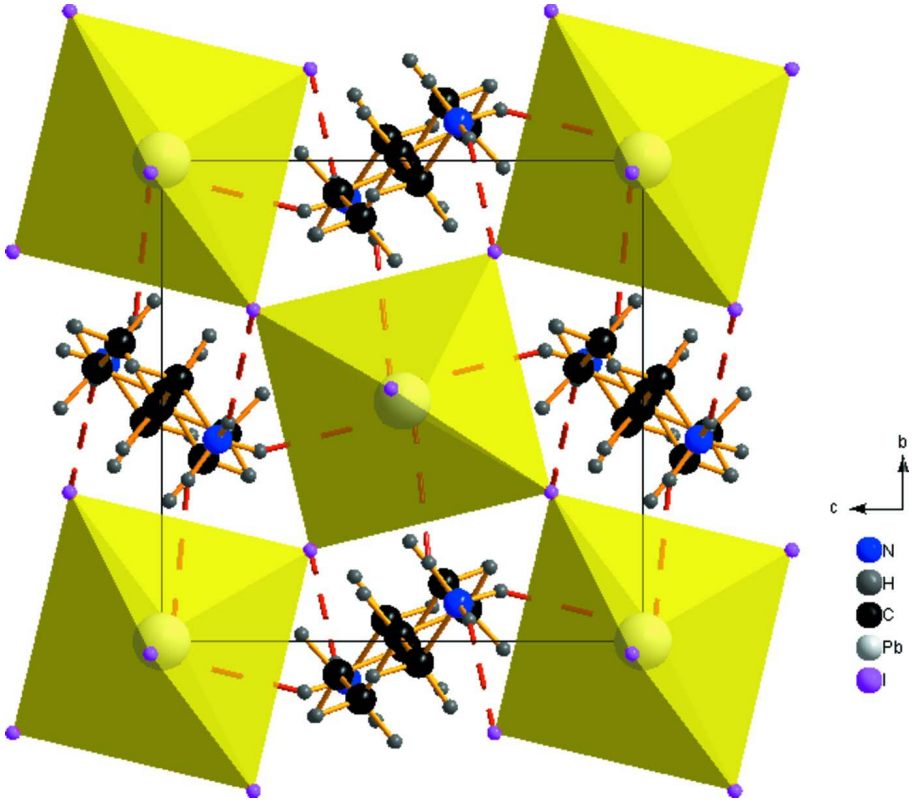

Figure 2

Packing diagram viewed along the *a* axis. Hydrogen bonds are drawn as dashed red lines.

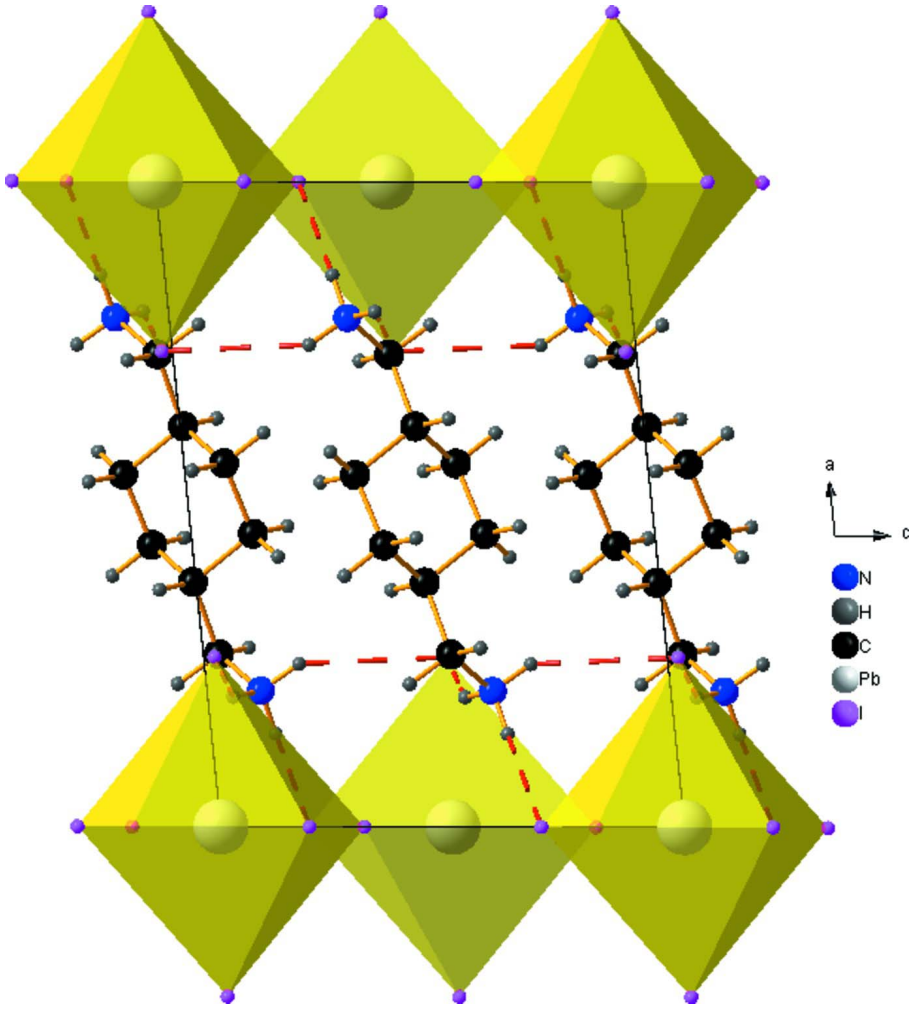

Figure 3

Packing diagram viewed along the *b* axis. Hydrogen bonds are drawn as dashed red lines.

Poly[1,4-bis(ammoniomethyl)cyclohexane [di-μ-iodido-diiodidoplumbate(II)]]

Crystal data

$(C_8H_{20}N_2)[PbI_4]$
$M_r = 859.05$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 12.2793\ (17)$ Å
$b = 8.7413\ (12)$ Å
$c = 8.7829\ (13)$ Å
$\beta = 95.922\ (3)°$
$V = 937.7\ (2)$ Å^3
$Z = 2$
$F(000) = 752$
$D_x = 3.043$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6011 reflections
$\theta = 3.0–28.2°$
$\mu = 15.56$ mm^{-1}
$T = 173$ K
Plate, orange
0.36 × 0.26 × 0.08 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: integration (*XPREP*; Bruker, 2005)
T_{min} = 0.043, T_{max} = 0.288
5435 measured reflections
2264 independent reflections
2085 reflections with $I > 2\sigma(I)$
R_{int} = 0.080
θ_{max} = 28.0°, θ_{min} = 1.7°
h = −16→16
k = −11→10
l = −9→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.093
S = 1.08
2264 reflections
70 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
$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 1.0393P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.009
$\Delta\rho_{max}$ = 1.76 e Å^{-3}
$\Delta\rho_{min}$ = −2.79 e Å^{-3}

Special details

Experimental. Numerical intergration absorption corrections based on indexed crystal faces were applied using the XPREP routine (Bruker, 2005)

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.

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}
C1	0.2676 (6)	0.0434 (9)	−0.4667 (9)	0.0333 (15)
H1A	0.2773	0.1355	−0.4011	0.040*
H1B	0.2216	0.0719	−0.5617	0.040*
C2	0.3794 (6)	−0.0123 (8)	−0.5065 (8)	0.0273 (15)
H2	0.3672	−0.0991	−0.5804	0.033*
C3	0.4366 (6)	0.1194 (9)	−0.5867 (8)	0.0306 (14)
H3A	0.3890	0.1529	−0.6785	0.037*
H3B	0.4475	0.2077	−0.5162	0.037*
C4	0.4542 (6)	−0.0685 (9)	−0.3667 (8)	0.0299 (14)
H4A	0.4654	0.0151	−0.2906	0.036*
H4B	0.4187	−0.1550	−0.3183	0.036*
N1	0.2111 (5)	−0.0797 (7)	−0.3841 (6)	0.0274 (12)
H1C	0.1450	−0.0448	−0.3610	0.041*
H1D	0.2531	−0.1050	−0.2962	0.041*

H1E	0.2012	−0.1637	−0.4451	0.041*
I1	−0.26315 (4)	0.02539 (5)	−0.02301 (5)	0.02714 (13)
I2	0.00031 (4)	0.18981 (5)	−0.30914 (4)	0.02605 (14)
Pb1	0.0000	0.0000	0.0000	0.01915 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.036 (4)	0.026 (3)	0.039 (4)	0.002 (3)	0.005 (3)	0.004 (3)
C2	0.027 (4)	0.027 (4)	0.028 (3)	−0.003 (3)	0.003 (3)	−0.001 (2)
C3	0.028 (3)	0.030 (3)	0.034 (3)	0.000 (3)	0.001 (3)	0.010 (3)
C4	0.023 (3)	0.035 (4)	0.031 (3)	−0.003 (3)	0.002 (3)	0.008 (3)
N1	0.025 (3)	0.031 (3)	0.026 (3)	−0.004 (2)	0.003 (2)	−0.001 (2)
I1	0.0262 (2)	0.0257 (2)	0.0288 (2)	−0.00327 (17)	−0.00048 (18)	−0.00028 (16)
I2	0.0356 (2)	0.0218 (2)	0.0212 (2)	0.00569 (16)	0.00513 (16)	0.00779 (14)
Pb1	0.02537 (19)	0.01599 (17)	0.01602 (16)	0.00087 (11)	0.00182 (12)	0.00032 (10)

Geometric parameters (Å, º)

C1—N1	1.507 (9)	C4—H4B	0.9900
C1—C2	1.530 (10)	N1—H1C	0.9100
C1—H1A	0.9900	N1—H1D	0.9100
C1—H1B	0.9900	N1—H1E	0.9100
C2—C4	1.536 (10)	I1—Pb1	3.2243 (6)
C2—C3	1.554 (9)	I2—Pb1	3.1824 (5)
C2—H2	1.0000	I2—Pb1^{ii}	3.1875 (5)
C3—C4^{i}	1.510 (10)	Pb1—I2^{iii}	3.1824 (5)
C3—H3A	0.9900	Pb1—I2^{iv}	3.1875 (5)
C3—H3B	0.9900	Pb1—I2^{v}	3.1875 (5)
C4—C3^{i}	1.510 (10)	Pb1—I1^{iii}	3.2243 (6)
C4—H4A	0.9900		

N1—C1—C2	110.5 (6)	H4A—C4—H4B	108.1
N1—C1—H1A	109.5	C1—N1—H1C	109.5
C2—C1—H1A	109.5	C1—N1—H1D	109.5
N1—C1—H1B	109.5	H1C—N1—H1D	109.5
C2—C1—H1B	109.5	C1—N1—H1E	109.5
H1A—C1—H1B	108.1	H1C—N1—H1E	109.5
C4—C2—C1	113.3 (6)	H1D—N1—H1E	109.5
C4—C2—C3	109.8 (6)	Pb1—I2—Pb1^{ii}	153.144 (15)
C1—C2—C3	109.0 (6)	I2—Pb1—I2^{iii}	180.00 (2)
C4—C2—H2	108.2	I2—Pb1—I2^{iv}	90.294 (11)
C1—C2—H2	108.2	I2^{iii}—Pb1—I2^{iv}	89.706 (11)
C3—C2—H2	108.2	I2—Pb1—I2^{v}	89.706 (11)
C4^{i}—C3—C2	111.1 (6)	I2^{iii}—Pb1—I2^{v}	90.294 (11)
C4^{i}—C3—H3A	109.4	I2^{iv}—Pb1—I2^{v}	180.0
C2—C3—H3A	109.4	I2—Pb1—I1^{iii}	89.999 (12)
C4^{i}—C3—H3B	109.4	I2^{iii}—Pb1—I1^{iii}	90.001 (12)

C2—C3—H3B	109.4	I2^{iv}—Pb1—I1^{iii}	94.518 (12)
H3A—C3—H3B	108.0	I2^{v}—Pb1—I1^{iii}	85.482 (12)
C3^{i}—C4—C2	110.6 (6)	I2—Pb1—I1	90.001 (12)
C3^{i}—C4—H4A	109.5	I2^{iii}—Pb1—I1	89.999 (12)
C2—C4—H4A	109.5	I2^{iv}—Pb1—I1	85.482 (12)
C3^{i}—C4—H4B	109.5	I2^{v}—Pb1—I1	94.518 (12)
C2—C4—H4B	109.5	I1^{iii}—Pb1—I1	180.0
N1—C1—C2—C4	−55.7 (8)	C3—C2—C4—C3^{i}	−57.0 (9)
N1—C1—C2—C3	−178.2 (6)	Pb1^{ii}—I2—Pb1—I2^{iv}	−0.35 (4)
C4—C2—C3—C4^{i}	57.3 (8)	Pb1^{ii}—I2—Pb1—I2^{v}	179.65 (4)
C1—C2—C3—C4^{i}	−178.1 (6)	Pb1^{ii}—I2—Pb1—I1^{iii}	−94.87 (4)
C1—C2—C4—C3^{i}	−179.1 (6)	Pb1^{ii}—I2—Pb1—I1	85.13 (4)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*D*···I1^{iii}	0.91	2.88	3.598 (5)	137
N1—H1*E*···I1^{v}	0.91	2.84	3.619 (6)	144
N1—H1*E*···I2^{vi}	0.91	3.12	3.672 (6)	121
N1—H1*C*···I2	0.91	2.78	3.611 (6)	152

Symmetry codes: (iii) −*x*, −*y*, −*z*; (v) −*x*, *y*−1/2, −*z*−1/2; (vi) −*x*, −*y*, −*z*−1.