



Crystal structures of 2,6-bis[(1*H*-1,2,4-triazol-1-yl)-methyl]pyridine and 1,1-[pyridine-2,6-diylbis-(methylene)]bis(4-methyl-1*H*-1,2,4-triazol-4-ium) iodide triiodide

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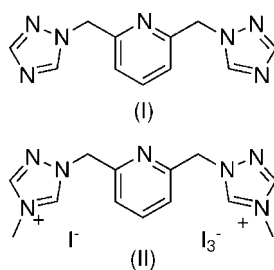
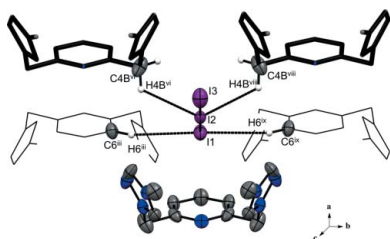
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In the structures of the 2,6-bis(1,2,4-triazol-3-yl)methyl-substituted pyridine compound, C₁₁H₁₁N₇, (I) and the iodide triiodide salt, C₁₃H₁₇N₇²⁺·I⁻·I₃⁻, (II), the dihedral angles between the two triazole rings and the pyridine ring are 66.4 (1) and 74.6 (1)° in (I), and 68.4 (2)° in (II), in which the dication lies across a crystallographic mirror plane. The overall packing structure for (I) is two-dimensional with the layers lying parallel to the (001) plane. In (II), the triiodide anion lies within the mirror plane, occupying the space between the two triazole substituent groups and was found to have minor disorder [occupancy ratio 0.9761 (9):0.0239 (9)]. The overall packing of structure (II) can be described as two-dimensional with the layers stacking parallel to the (001) plane. In the crystal, the predominant intermolecular interactions in (I) and (II) involve the acidic hydrogen atom in the third position of the triazole ring, with either the triazole N-atom acceptor in weak C—H···N hydrogen bonds in (I), or with halide counter-ions through C—H···I interactions, in (II).

1. Chemical context

1,2,4-Triazole analogs first found applications in the pharmaceutical field as antifungal and antibacterial agents over 30 years ago. Recent developments are reviewed by Peng *et al.* (2013). Recently, 1,2,4-triazole rings have been incorporated into ligands used in coordination compounds and polymers (Haasnoot, 2000; Aromí *et al.*, 2011; Ouellette *et al.*, 2011). Related triazolium salts are being used as cations in ionic liquids (Porcar *et al.*, 2013; Meyer & Strassner, 2011; Singh *et al.*, 2006), or as precursors to *N*-heterocyclic carbenes (Lin *et al.*, 2014; Strassner *et al.*, 2013; Huynh & Lee, 2013; Riederer *et al.*, 2011).



To better understand the suitability of the title compounds for use as ligands for the formation of lanthanide complexes, we became interested in the predominant interactions of 1,2,4-triazole rings in the solid state. Herein, we report the struc-

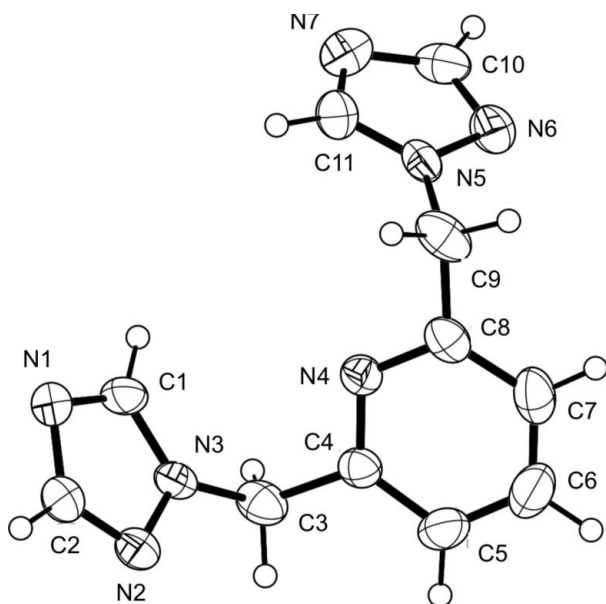


Figure 1
A perspective view of compound (I), showing the atom-numbering scheme. Anisotropic displacement parameters are drawn at the 50% probability level.

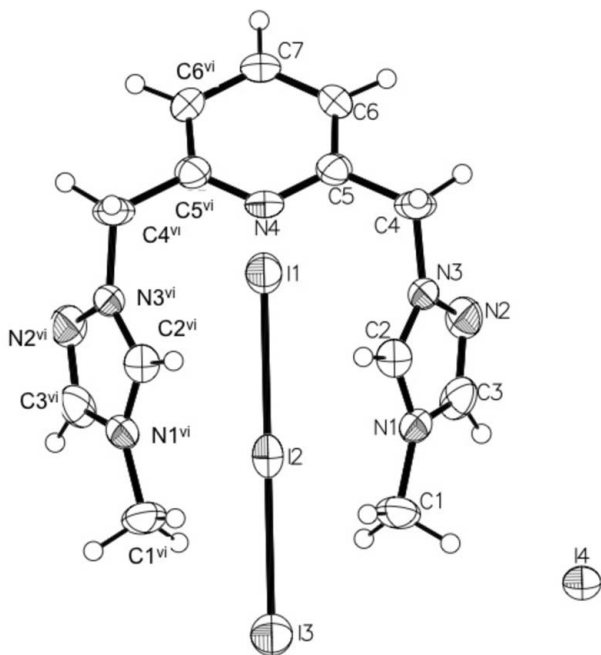


Figure 2
A perspective view of compound (II), showing the atom-numbering scheme, with anisotropic displacement parameters drawn at the 50% probability level. The iodide and triiodide anions lie on crystallographic mirror planes. The minor occupancy component of the disordered triiodide ion is not shown. [Symmetry code: (vi) $x, -y + 1, z$.]

tures of 2,6-bis[(1*H*-1,2,4-triazol-1-yl)methyl]pyridine, (I), and 1,1-[pyridine-2,6-diylbis(methylene)]bis(4-methyl-1*H*-1,2,4-triazol-4-ium) iodide triiodide, (II). The solid-state structures of these compounds by themselves have not been reported, but their structures as ligands in cobalt(II) (Kim *et al.*, 2010) and palladium(II) complexes (Huynh & Lee, 2013) are known.

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

<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>
C2—H2···N6 ⁱ	0.95	2.62	3.547 (4)	166
C11—H11···N7 ⁱⁱ	0.95	2.47	3.381 (4)	161
C1—H1···N7 ⁱⁱⁱ	0.95	2.63	3.551 (4)	164
C9—H9B···N4 ^{iv}	0.99	2.57	3.419 (5)	144
C5—H5···N2 ^v	0.95	2.63	3.449 (4)	145

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

2. Structural commentary

Compound (I) crystallizes in the orthorhombic space group, *Pna*2₁, with the entire molecule in the asymmetric unit (Fig. 1). The triazole rings are aromatic with C—C, C—N and N—N bond distances within a range of 1.314 (4) to 1.356 (3) Å. These are twisted above and below the plane of the pyridine ring with dihedral angles between the two triazole rings and the pyridine ring of 66.4 (1) and 74.6 (1)°. The packing structure consists of a stack of triazole molecules with the same handedness translating along the *c*-axis direction. There are no intramolecular interactions due to the inherent steric hindrances within the molecule.

In contrast, compound (II) consists of a dication of 2,6-bis[(1*H*-1,2,4-triazol-1-yl)methyl]pyridine with methyl groups at the fourth nitrogen positions of the triazole rings, with mixed triiodide/iodide anions. This compound crystallizes in the space group *C2/m* with half of the dication, half of a triiodide (I1—I2—I3) and half of one iodide (I4) in the asymmetric unit (Fig. 2). The triiodide counter-ion exhibits positional disorder, which was satisfactorily refined with split positions of 0.9761 (9):0.0239 (9), the minor component being I1'—I2'—I3'. Both disorder positions are on the mirror plane and discussions and illustrations relating to this counter-ion are focused on the major occupancy triiodide atom positions. The bond lengths in the triazolium rings indicate significant aromaticity with C—C, C—N, and N—N bond distances in the narrow range of 1.295 (7) to 1.362 (6) Å. The triazole rings are twisted from the plane of the pyridine ring, forming a dihedral angle of 68.4 (2)°. There are no intramolecular interactions.

3. Supramolecular features

In compound (I), the predominant intermolecular interactions are the C—H···N hydrogen bonds between the acidic hydrogen atoms of the triazole ring and the nitrogen lone pairs of the neighboring triazole molecule (Table 1). For one asymmetric unit, there are a total of six hydrogen bonds with three neighboring molecules (Fig. 3). These hydrogen bonds can be simplified into two categories: *a*) the nitrogen atoms involved are in the fourth position of the triazole ring (C1—H1···N7 and C11—H11···N7), and *b*) the nitrogen atom is in the second position of the ring (C2—H2···N6). Pyridine nitrogen atoms, on the other hand, are involved as acceptors in hydrogen bonds arising from the methylene hydrogen atoms,

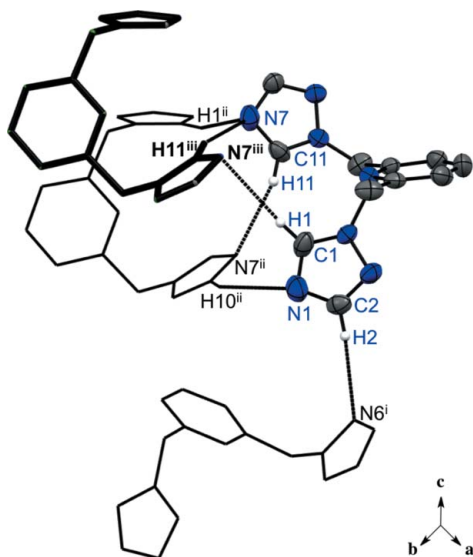


Figure 3
The predominant C–H···N hydrogen bonds between triazole rings in one asymmetric unit of compound (I). H atoms not involved in the hydrogen bonding are not shown. For symmetry codes, see Table 1.

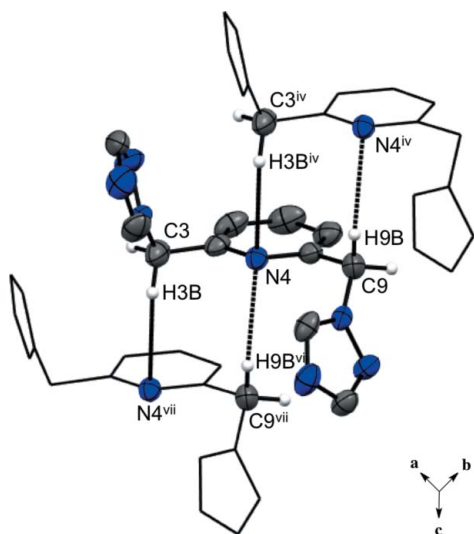


Figure 4
Hydrogen-bond stacking of the pyridine N atoms and the methylene H atoms in compound (I). H atoms not involved in hydrogen bonding are not shown. [Symmetry code: (vii) $x, y, z + 1$; for other symmetry codes, see Table 1.]

forming a stack of one molecule on top of the other (Fig. 4), although no π – π ring interactions are present [minimum ring centroid separation, 4.4323 (3) Å]. Additionally, a non-acidic C–H···N interaction is observed between the triazole nitrogen atom and the *meta*-hydrogen atom of the pyridine ring (C5–H5···N2) (Table 1). The overall packing of structure (I) can be described as layers that lie parallel to (001).

In compound (II), when viewed along the *c*-axis, the triiodide anion lies on the mirror plane in the middle of the dication-iodide units, filling up a pore-like groove within the structure (Fig. 5). There are no C–H···N interactions in compound (II) because the triazole nitrogen atoms are

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

<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>
C3–H3···I4	0.95	3.00	3.844 (5)	149
C2–H2···I4 ⁱ	0.95	2.82	3.744 (5)	164
C4–H4B···I2 ⁱⁱ	0.99	3.18	3.775 (6)	120
C4–H4B···I2 ⁱⁱⁱ	0.99	3.10	3.766 (15)	126
C6–H6···I1 ⁱⁱⁱ	0.95	3.17	4.097 (5)	166
C6–H6···I1 ⁱⁱⁱ	0.95	3.00	3.900 (8)	158
C4–H4A···I1 ⁱⁱⁱ	0.99	2.98	3.94 (2)	166

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

bonded to the methyl groups. The acidic hydrogen atoms in the triazole ring now prefer to interact with the iodide ion. There are four C–H···I(iodide) interactions per iodide: two from C–H donors from the same dication, and two additional interactions from neighboring dication C–H donors (Fig. 6), (C2–H2···I4, C3–H3···I4; Table 2). Meanwhile, the triio-

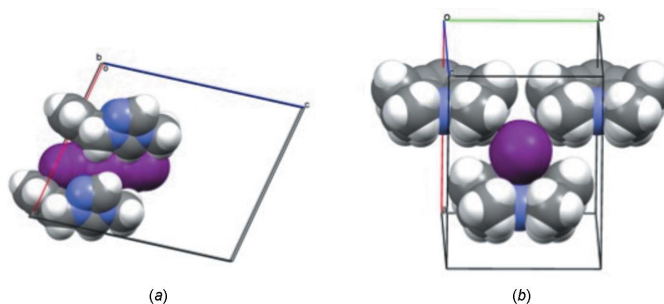


Figure 5
Compound (II) showing the triiodide anion filling up a pore-like groove arrangement built by the triazole dications along (a) the *b* axis and (b) the *c* axis.

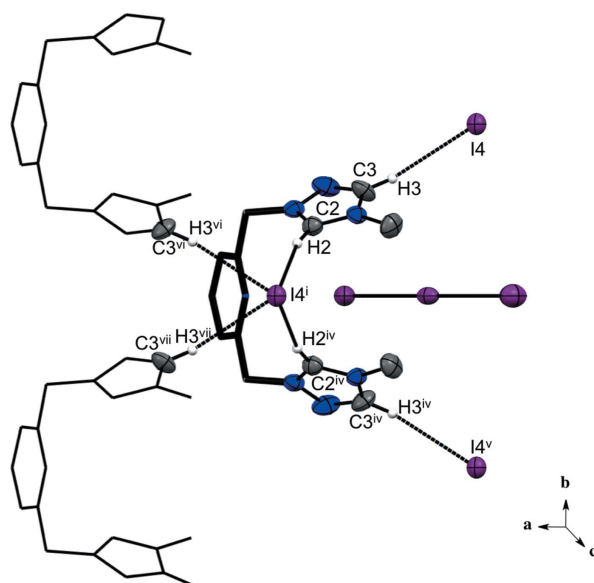


Figure 6
Compound (II) showing the C–H···I(iodide) interactions. H atoms not involved in hydrogen bonding are not shown. [Symmetry codes: (iv) $x, -y + 1, z$; (v) $x, y + 1, z$; (vi) $x + \frac{1}{2}, -y + \frac{1}{2}, z$; (vii) $x + \frac{1}{2}, y + \frac{1}{2}, z$; for other symmetry codes, see Table 2.]

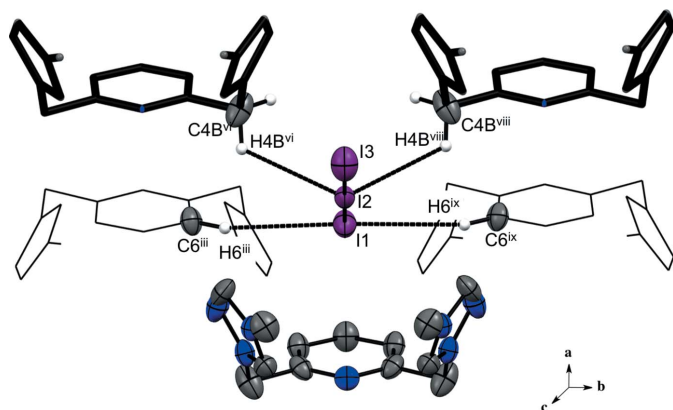


Figure 7

Compound (II) showing the C—H···I(triiodide) interactions. H atoms not involved in the hydrogen-bonding interactions are not shown. [Symmetry codes: (viii) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (ix) $-x + \frac{3}{2}, y + \frac{1}{2}, -z$; for other symmetry codes, see Table 2 and Fig. 6.]

dide anion is involved in two C—H···I(triiodide) interactions with, *a*) the *meta*-hydrogen atoms of the pyridine ring (C6—H6···I1), and *b*) the methylene hydrogen atoms (C4—H4B···I2) (Fig. 7). The minor occupancy triiodide molecule is not shown, but gives similar interactions to those described above for the major component (C6—H6···I1' and C4—H4···I2' as well as C4—H4A···I1'; Table 2). The overall packing of structure (II) can be described as two-dimensional with the layers stacking parallel to the (001) plane.

4. Database survey

(1*H*-Imidazol-1-yl){6-[(1*H*-imidazol-1-yl)methyl]-2-pyridyl}-methane (Meng *et al.*, 2005) is a structure closely related to compound (I). In the solid-state structure, the imidazole nitrogen atoms prefer to form hydrogen bonds with water molecules in the asymmetric unit, not with the hydrogen atoms of the imidazole ring. In another closely related structure, 2,5-bis[(1*H*-1,2,4-triazol-1-yl)methyl]-1*H*-pyrrole (Lin *et al.*, 2014), the acidic triazole hydrogen atom also forms C—H···N hydrogen-bonding interactions similar to those in compound (I).

3-Methyl-1-({6-[(3-methyl-1*H*-imidazol-1-yl)methyl]-2-pyridyl)methyl}-1*H*-imidazole bromide (Nielsen *et al.*, 2002), a structure closely related to compound (II), crystallizes as a monohydrate. An imidazole hydrogen atom also shows C—H···halide(Br) interactions, and at the same time these bromide anions also form hydrogen bonds with the water molecule in the asymmetric unit. Triazolium salt C—H···halide interactions similar to those shown by compound (II) are also observed in ionic liquids utilizing triazolium cations (Porcar *et al.*, 2013).

5. Synthesis and crystallization

For the synthesis of compounds (I) and (II), a procedure similar to that reported by Huynh's group (Huynh & Lee, 2013) was used. In our attempts, we used the microwave

technique for the synthesis of both title compounds but shortened the reaction time for each from 24 hr to roughly 15 min. For (I), 2,6-bis[(1*H*-1,2,4-triazol-1-yl)methyl]pyridine and 1,2,4-triazole (0.0241 mol, 1.665 g) were dissolved in 10–12 mL of acetonitrile by stirring. Once these had completely dissolved, K₂CO₃ (0.0241 mol, 3.331 g) was added and briefly stirred to deprotonate the triazole. 2,6-Bis(bromomethyl)pyridine (0.011 mol, 2.902 g) was then dissolved separately in 5 mL of acetonitrile. The two solutions were then combined in a 10–20 mL microwave vessel and placed in the microwave reactor for 15 min at 403 K, after which the acetonitrile was removed *in vacuo*. Compound (I) was isolated through recrystallization utilizing hot dichloromethane, producing colorless prismatic crystals suitable for single-crystal X-ray diffraction. Yield 83%. ¹H NMR (400MHz, CDCl₃) δ 8.23 (*s*, 2H), 7.98 (*s*, 2H), 7.69 (*t*, 1H), 7.12 (*d*, 2H), 5.44 (*s*, 4H). ¹³C NMR (400 MHz, CDCl₃) δ 152.5, 144.0, 138.6, 121.8, 54.8.

For (II), 1,1'-[pyridine-2,6-diylbis(methylene)]-bis(4-methyl-1*H*-1,2,4-triazol-4-ium) iodide and iodomethane (0.996 mL, 0.016 mol) was added to a 10 mL acetonitrile solution of 2,6-bis[(1*H*-1,2,4-triazol-1-yl)methyl]pyridine (0.947 g, 0.004 mol) in a microwave vial. The mixture was placed in the microwave reactor for 10 min at 413 K, after which the acetonitrile was removed *in vacuo*. Compound (II) was isolated through recrystallization utilizing isopropyl alcohol layered with hexanes, producing brown prismatic crystals suitable for single-crystal X-ray diffraction. Yield 52%. ¹H NMR (400MHz, DMSO-*d*₆) δ 10.15 (*s*, 2H), 9.17 (*s*, 2H), 7.99 (*t*, 1H), 7.51 (*d*, 2H), 5.76 (*s*, 4H), 3.95 (*s*, 6H). ¹³C NMR (400 MHz, DMSO-*d*₆) δ 152.88 (2C), 146.02 (2C), 144.24 (1C), 139.19 (2C), 122.97 (2C), 55.75 (2C), 34.55 (2C), 25.75 (*i*PrOH).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All hydrogen atoms were placed in calculated positions and allowed to ride on their parent atoms at C—H distances of 0.95 Å for the triazole and the pyridine rings, 0.97 Å for the methyl group and 0.99 Å for the methylene group, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. In compound (II), the triiodide counter-ion showed positional disorder, and the positions were allowed to refine using constraints, introducing split positions of 0.9761 (9):0.0239 (9) (the minor component being I1'—I2'—I3'), with satisfactory refinement.

Acknowledgements

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Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	C ₁₁ H ₁₁ N ₇	C ₁₃ H ₁₇ N ₇ ²⁺ ·I ₃ ⁻ ·I ⁻
<i>M_r</i>	241.27	778.94
Crystal system, space group	Orthorhombic, <i>Pna</i> 2 ₁	Monoclinic, <i>C2/m</i>
Temperature (K)	173	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.465 (3), 18.742 (4), 4.3230 (9)	13.784 (3), 10.010 (3), 16.709 (4)
α , β , γ (°)	90, 90, 90	90, 102.648 (7), 90
<i>V</i> (Å ³)	1172.0 (4)	2249.5 (10)
<i>Z</i>	4	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.09	5.55
Crystal size (mm)	0.62 × 0.15 × 0.13	0.34 × 0.14 × 0.09
Data collection		
Diffractometer	Rigaku XtaLAB mini	Rigaku XtaLAB mini
Absorption correction	Multi-scan (<i>REQAB</i> ; Rigaku, 1998)	Multi-scan (<i>REQAB</i> ; Rigaku, 1998)
<i>T</i> _{min} – <i>T</i> _{max}	0.779, 0.988	0.322, 0.607
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	9633, 2381, 1895	11638, 2712, 2303
<i>R</i> _{int}	0.062	0.037
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.625	0.649
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.047, 0.101, 1.05	0.036, 0.080, 1.11
No. of reflections	2381	2712
No. of parameters	163	126
No. of restraints	1	0
H-atom treatment	H-atom parameters constrained <i>w</i> = 1/[$\sigma^2(F_o^2) + (0.042P)^2 + 0.0415P$] where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3	H-atom parameters constrained <i>w</i> = 1/[$\sigma^2(F_o^2) + (0.0241P)^2 + 14.4966P$] where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.13, -0.14	1.09, -1.11

Computer programs: *CrystalClear-SM Expert* (Rigaku, 2011), *SIR2004* (Burla, *et al.*, 2005), *SHELXS97* and *SHELXL2013* (Sheldrick, 2008) and *CrystalStructure* (Rigaku, 2010).

References

- Aromí, G., Barrios, L. A., Roubeau, O. & Gamez, P. (2011). *Coord. Chem. Rev.* **255**, 485–546.
- Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
- Haasnoot, J. G. (2000). *Coord. Chem. Rev.* **200–202**, 131–185.
- Huynh, H. V. & Lee, C. (2013). *Dalton Trans.* **42**, 6803–6809.
- Kim, E. Y., Song, Y. J., Koo, H. G., Lee, J. H., Park, H. M., Kim, C., Kwon, T., Huh, S., Kim, Y. & Kim, Y. (2010). *Polyhedron*, **29**, 3335–3341.
- Lin, K., Chile, L., Zhen, S. C., Boyd, P. D. W., Ware, D. C. & Brothers, P. J. (2014). *Inorg. Chim. Acta*, **422**, 95–101.
- Meng, X.-T., Li, Q.-S., Xu, F.-B., Song, H.-B. & Zhang, Z.-Z. (2005). *Acta Cryst. E* **61**, o4338–o4339.
- Meyer, D. & Strassner, T. (2011). *J. Org. Chem.* **76**, 305–308.
- Nielsen, D. J., Cavell, K. J., Skelton, B. W. & White, A. H. (2002). *Inorg. Chim. Acta*, **327**, 116–125.
- Ouellette, W., Jones, S. & Zubietta, J. (2011). *CrystEngComm*, **13**, 4457–4485.
- Peng, X. M., Cai, G. X. & Zhou, C. H. (2013). *Curr. Top. Med. Chem.* **13**, 1963–2010.
- Porcar, R., Ríos-Lombardía, N., Busto, E., Gotor-Fernández, V., Montejo-Bernardo, J., García-Granda, S., Luis, S. V., Gotor, V., Alfonso, I. & García-Verdugo, E. (2013). *Chem. Eur. J.* **19**, 892–904.
- Riederer, S. K., Bechlers, B., Herrmann, W. A. & Kühn, F. E. (2011). *Dalton Trans.* **40**, 41–43.
- Rigaku (1998). *REQAB*. Rigaku Corporation, Tokyo, Japan.
- Rigaku (2010). *CrystalStructure*. Rigaku Corporation, Tokyo, Japan.
- Rigaku (2011). *CrystalClear-SM Expert*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Singh, R. P., Verma, R. D., Meshri, D. T. & Shreeve, J. M. (2006). *Angew. Chem. Int. Ed.* **45**, 3584–3601.
- Strassner, T., Unger, Y., Meyer, D., Molt, O., Münster, I. & Wagenblast, G. (2013). *Inorg. Chem. Commun.* **30**, 39–41.

supporting information

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Crystal structures of 2,6-bis[(1*H*-1,2,4-triazol-1-yl)methyl]pyridine and 1,1-[pyridine-2,6-diylbis(methylene)]bis(4-methyl-1*H*-1,2,4-triazol-4-ium) iodide triiodide

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Computing details

For both compounds, data collection: *CrystalClear-SM Expert* (Rigaku, 2011). Cell refinement: *CrystalClear-SM Expert* (Rigaku, 2011 for (I); *CrystalClear-SM Expert* (Rigaku, 2011) for (II). Data reduction: *CrystalClear-SM Expert* (Rigaku, 2011 for (I); *CrystalClear-SM Expert* (Rigaku, 2011) for (II). Program(s) used to solve structure: *SIR2004* (Burla, *et al.*, 2005) for (I); *SHELXS97* (Sheldrick, 2008) for (II). For both compounds, program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *CrystalStructure* (Rigaku, 2010); software used to prepare material for publication: *CrystalStructure* (Rigaku, 2010).

(I) 2,6-Bis[(1*H*-1,2,4-triazol-1-yl)methyl]pyridine

Crystal data

C₁₁H₁₁N₇

M_r = 241.27

Orthorhombic, *Pna*2₁

a = 14.465 (3) Å

b = 18.742 (4) Å

c = 4.3230 (9) Å

V = 1172.0 (4) Å³

Z = 4

F(000) = 504

D_x = 1.367 Mg m⁻³

Mo *Kα* radiation, λ = 0.71075 Å

Cell parameters from 8485 reflections

θ = 3.0–26.5°

μ = 0.09 mm⁻¹

T = 173 K

Prism, colorless

0.62 × 0.15 × 0.13 mm

Data collection

Rigaku XtaLAB mini

diffractometer

Radiation source: normal-focus sealed tube

Detector resolution: 6.849 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*REQAB*; Rigaku, 1998)

T_{min} = 0.779, *T_{max}* = 0.988

9633 measured reflections

2381 independent reflections

1895 reflections with *I* > 2σ(*I*)

R_{int} = 0.062

θ_{max} = 26.4°, θ_{min} = 3.0°

h = -18→18

k = -23→23

l = -5→5

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.047

wR(*F*²) = 0.101

S = 1.05

2381 reflections

163 parameters

1 restraint

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.042P)^2 + 0.0415P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.13 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.14 \text{ e } \text{Å}^{-3}$

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.74693 (19)	-0.17388 (14)	0.3737 (8)	0.0581 (9)
N2	0.87942 (16)	-0.11410 (13)	0.4504 (8)	0.0471 (7)
N3	0.80940 (15)	-0.08386 (12)	0.6125 (7)	0.0344 (6)
N4	0.75319 (15)	0.06501 (11)	0.4587 (6)	0.0324 (6)
N5	0.58336 (15)	0.13416 (11)	0.2984 (7)	0.0331 (6)
N6	0.54335 (16)	0.19034 (12)	0.4433 (7)	0.0410 (7)
N7	0.46408 (16)	0.08922 (13)	0.5355 (8)	0.0486 (8)
C1	0.7326 (2)	-0.12001 (18)	0.5624 (11)	0.0527 (10)
H1	0.6744	-0.1086	0.6513	0.063*
C2	0.8376 (2)	-0.16807 (16)	0.3142 (9)	0.0466 (8)
H2	0.8693	-0.2005	0.1832	0.056*
C3	0.8238 (2)	-0.02053 (16)	0.7995 (9)	0.0479 (8)
H3A	0.8815	-0.0263	0.9202	0.057*
H3B	0.7720	-0.0158	0.9478	0.057*
C4	0.83028 (19)	0.04624 (15)	0.6106 (8)	0.0370 (7)
C5	0.9105 (2)	0.08642 (18)	0.5924 (10)	0.0503 (9)
H5	0.9649	0.0713	0.6968	0.060*
C6	0.9106 (2)	0.14789 (19)	0.4231 (11)	0.0583 (11)
H6	0.9650	0.1761	0.4103	0.070*
C7	0.8316 (2)	0.16875 (16)	0.2710 (9)	0.0479 (9)
H7	0.8299	0.2116	0.1541	0.057*
C8	0.75449 (19)	0.12512 (14)	0.2939 (8)	0.0344 (7)
C9	0.6670 (2)	0.14229 (16)	0.1146 (9)	0.0439 (8)
H9A	0.6706	0.1920	0.0383	0.053*
H9B	0.6632	0.1105	-0.0677	0.053*
C10	0.47173 (19)	0.16046 (16)	0.5807 (9)	0.0431 (8)
H10	0.4289	0.1868	0.7018	0.052*
C11	0.5357 (2)	0.07513 (15)	0.3578 (9)	0.0429 (9)
H11	0.5512	0.0290	0.2824	0.052*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0518 (18)	0.0445 (15)	0.078 (3)	-0.0075 (13)	0.0027 (18)	0.0032 (18)
N2	0.0368 (14)	0.0460 (16)	0.0585 (19)	0.0077 (12)	0.0104 (15)	-0.0035 (16)
N3	0.0302 (12)	0.0366 (13)	0.0363 (14)	0.0103 (10)	0.0026 (13)	0.0052 (13)

N4	0.0329 (12)	0.0329 (12)	0.0313 (13)	0.0012 (10)	-0.0026 (12)	0.0014 (12)
N5	0.0354 (13)	0.0277 (12)	0.0360 (14)	0.0054 (10)	-0.0040 (13)	0.0027 (13)
N6	0.0381 (14)	0.0332 (13)	0.0517 (17)	0.0066 (11)	0.0028 (14)	-0.0044 (14)
N7	0.0324 (13)	0.0380 (14)	0.075 (2)	0.0003 (11)	-0.0032 (16)	0.0069 (15)
C1	0.0325 (16)	0.0492 (19)	0.076 (3)	0.0049 (15)	0.009 (2)	0.006 (2)
C2	0.060 (2)	0.0330 (16)	0.047 (2)	0.0072 (15)	0.012 (2)	0.0037 (18)
C3	0.059 (2)	0.0491 (19)	0.0351 (18)	0.0175 (16)	-0.0100 (18)	-0.003 (2)
C4	0.0407 (16)	0.0368 (16)	0.0336 (17)	0.0084 (13)	-0.0027 (17)	-0.0110 (16)
C5	0.0336 (16)	0.054 (2)	0.063 (2)	0.0063 (15)	-0.0096 (19)	-0.022 (2)
C6	0.0388 (18)	0.053 (2)	0.084 (3)	-0.0119 (16)	0.010 (2)	-0.017 (2)
C7	0.0506 (19)	0.0322 (16)	0.061 (2)	-0.0024 (14)	0.015 (2)	-0.0041 (19)
C8	0.0358 (15)	0.0317 (15)	0.0358 (16)	0.0037 (12)	0.0070 (16)	-0.0025 (15)
C9	0.0487 (18)	0.0433 (18)	0.0397 (18)	0.0095 (14)	0.0042 (18)	0.0100 (17)
C10	0.0341 (15)	0.0393 (17)	0.056 (2)	0.0056 (13)	0.0041 (18)	-0.0016 (18)
C11	0.0430 (18)	0.0278 (15)	0.058 (3)	0.0016 (13)	-0.0109 (18)	-0.0060 (16)

Geometric parameters (Å, °)

N1—C1	1.314 (4)	C3—C4	1.497 (4)
N1—C2	1.340 (4)	C3—H3A	0.9900
N2—C2	1.318 (4)	C3—H3B	0.9900
N2—N3	1.356 (3)	C4—C5	1.386 (4)
N3—C1	1.319 (4)	C5—C6	1.365 (5)
N3—C3	1.451 (4)	C5—H5	0.9500
N4—C8	1.333 (4)	C6—C7	1.375 (5)
N4—C4	1.341 (4)	C6—H6	0.9500
N5—C11	1.329 (3)	C7—C8	1.386 (4)
N5—N6	1.355 (3)	C7—H7	0.9500
N5—C9	1.455 (4)	C8—C9	1.519 (4)
N6—C10	1.319 (4)	C9—H9A	0.9900
N7—C11	1.317 (4)	C9—H9B	0.9900
N7—C10	1.354 (4)	C10—H10	0.9500
C1—H1	0.9500	C11—H11	0.9500
C2—H2	0.9500		
C1—N1—C2	102.2 (3)	C5—C4—C3	122.5 (3)
C2—N2—N3	102.0 (2)	C6—C5—C4	119.3 (3)
C1—N3—N2	109.3 (3)	C6—C5—H5	120.3
C1—N3—C3	129.2 (3)	C4—C5—H5	120.3
N2—N3—C3	121.5 (2)	C5—C6—C7	119.7 (3)
C8—N4—C4	118.1 (2)	C5—C6—H6	120.1
C11—N5—N6	109.6 (3)	C7—C6—H6	120.1
C11—N5—C9	128.6 (3)	C6—C7—C8	117.8 (3)
N6—N5—C9	121.7 (2)	C6—C7—H7	121.1
C10—N6—N5	102.3 (2)	C8—C7—H7	121.1
C11—N7—C10	102.6 (2)	N4—C8—C7	123.2 (3)
N1—C1—N3	111.3 (3)	N4—C8—C9	116.1 (2)
N1—C1—H1	124.4	C7—C8—C9	120.6 (3)

N3—C1—H1	124.4	N5—C9—C8	113.1 (3)
N2—C2—N1	115.2 (3)	N5—C9—H9A	109.0
N2—C2—H2	122.4	C8—C9—H9A	109.0
N1—C2—H2	122.4	N5—C9—H9B	109.0
N3—C3—C4	112.9 (3)	C8—C9—H9B	109.0
N3—C3—H3A	109.0	H9A—C9—H9B	107.8
C4—C3—H3A	109.0	N6—C10—N7	114.7 (3)
N3—C3—H3B	109.0	N6—C10—H10	122.6
C4—C3—H3B	109.0	N7—C10—H10	122.6
H3A—C3—H3B	107.8	N7—C11—N5	110.7 (3)
N4—C4—C5	121.8 (3)	N7—C11—H11	124.6
N4—C4—C3	115.7 (3)	N5—C11—H11	124.6
C2—N2—N3—C1	-0.6 (4)	C3—C4—C5—C6	-178.0 (3)
C2—N2—N3—C3	-179.3 (3)	C4—C5—C6—C7	-0.6 (6)
C11—N5—N6—C10	-0.7 (3)	C5—C6—C7—C8	-0.8 (5)
C9—N5—N6—C10	-179.7 (3)	C4—N4—C8—C7	0.3 (5)
C2—N1—C1—N3	0.3 (4)	C4—N4—C8—C9	177.3 (3)
N2—N3—C1—N1	0.2 (4)	C6—C7—C8—N4	1.0 (5)
C3—N3—C1—N1	178.8 (3)	C6—C7—C8—C9	-175.9 (3)
N3—N2—C2—N1	0.8 (4)	C11—N5—C9—C8	-83.0 (4)
C1—N1—C2—N2	-0.7 (4)	N6—N5—C9—C8	95.8 (3)
C1—N3—C3—C4	-101.9 (4)	N4—C8—C9—N5	46.9 (4)
N2—N3—C3—C4	76.6 (3)	C7—C8—C9—N5	-136.0 (3)
C8—N4—C4—C5	-1.8 (4)	N5—N6—C10—N7	0.6 (4)
C8—N4—C4—C3	178.2 (3)	C11—N7—C10—N6	-0.3 (4)
N3—C3—C4—N4	65.3 (3)	C10—N7—C11—N5	-0.2 (4)
N3—C3—C4—C5	-114.7 (3)	N6—N5—C11—N7	0.6 (4)
N4—C4—C5—C6	2.0 (5)	C9—N5—C11—N7	179.5 (3)

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>
C2—H2...N6 ⁱ	0.95	2.62	3.547 (4)	166
C11—H11...N7 ⁱⁱ	0.95	2.47	3.381 (4)	161
C1—H1...N7 ⁱⁱⁱ	0.95	2.63	3.551 (4)	164
C9—H9B...N4 ^{iv}	0.99	2.57	3.419 (5)	144
C5—H5...N2 ^v	0.95	2.63	3.449 (4)	145

Symmetry codes: (i) $-x+3/2, y-1/2, z-1/2$; (ii) $-x+1, -y, z-1/2$; (iii) $-x+1, -y, z+1/2$; (iv) $x, y, z-1$; (v) $-x+2, -y, z+1/2$.(II) 1,1-[Pyridine-2,6-diylbis(methylene)]bis(4-methyl-1*H*-1,2,4-triazol-4-ium) iodide triiodide

Crystal data

C₁₃H₁₇N₇²⁺·I₃⁻·I⁻*M_r* = 778.94Monoclinic, *C*2/*m**a* = 13.784 (3) Å*b* = 10.010 (3) Å*c* = 16.709 (4) Å β = 102.648 (7)°*V* = 2249.5 (10) Å³*Z* = 4*F*(000) = 1424

$D_x = 2.300 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71075 \text{ \AA}$
 Cell parameters from 10090 reflections
 $\theta = 3.0\text{--}27.5^\circ$

$\mu = 5.55 \text{ mm}^{-1}$
 $T = 173 \text{ K}$
 Prism, brown
 $0.34 \times 0.14 \times 0.09 \text{ mm}$

Data collection

Rigaku XtaLAB mini
 diffractometer
 Radiation source: normal-focus sealed tube
 Detector resolution: $6.849 \text{ pixels mm}^{-1}$
 ω scans
 Absorption correction: multi-scan
 (REQAB; Rigaku, 1998)
 $T_{\min} = 0.322$, $T_{\max} = 0.607$

11638 measured reflections
 2712 independent reflections
 2303 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.0^\circ$
 $h = -17 \rightarrow 17$
 $k = -12 \rightarrow 12$
 $l = -21 \rightarrow 21$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.080$
 $S = 1.11$
 2712 reflections
 126 parameters
 0 restraints

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0241P)^2 + 14.4966P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.09 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.11 \text{ e \AA}^{-3}$

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.

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)
I1	0.64670 (4)	0.5000	0.08917 (4)	0.04623 (16)	0.9761 (9)
I2	0.60699 (4)	0.5000	0.25579 (3)	0.03549 (14)	0.9761 (9)
I3	0.55437 (5)	0.5000	0.41333 (4)	0.05505 (18)	0.9761 (9)
I1'	0.6681 (18)	0.5000	0.0437 (17)	0.04623 (16)	0.0239 (9)
I2'	0.6331 (15)	0.5000	0.2138 (16)	0.03549 (14)	0.0239 (9)
I3'	0.577 (2)	0.5000	0.3681 (17)	0.05505 (18)	0.0239 (9)
I4	0.62747 (3)	0.0000	0.39551 (3)	0.03401 (13)	
N1	0.8485 (3)	0.2640 (4)	0.3182 (2)	0.0330 (9)	
N2	0.7994 (4)	0.1816 (5)	0.1944 (3)	0.0497 (12)	
N3	0.8876 (3)	0.2471 (4)	0.2021 (2)	0.0338 (9)	
N4	0.9323 (4)	0.5000	0.1270 (3)	0.0324 (12)	
C1	0.8505 (4)	0.2959 (7)	0.4053 (3)	0.0487 (14)	
H1A	0.8496	0.2128	0.4362	0.058*	
H1B	0.7921	0.3498	0.4086	0.058*	
H1C	0.9110	0.3461	0.4288	0.058*	
C2	0.9165 (4)	0.2969 (5)	0.2765 (3)	0.0360 (11)	
H2	0.9752	0.3472	0.2965	0.043*	

C3	0.7785 (4)	0.1942 (6)	0.2659 (3)	0.0443 (13)
H3	0.7205	0.1583	0.2798	0.053*
C4	0.9370 (5)	0.2575 (6)	0.1327 (3)	0.0510 (15)
H4A	0.9171	0.1807	0.0953	0.061*
H4B	1.0099	0.2534	0.1535	0.061*
C5	0.9101 (4)	0.3866 (5)	0.0855 (3)	0.0366 (11)
C6	0.8671 (4)	0.3811 (5)	0.0021 (3)	0.0391 (12)
H6	0.8522	0.2978	-0.0251	0.047*
C7	0.8468 (6)	0.5000	-0.0403 (4)	0.0421 (18)
H7	0.8192	0.5000	-0.0976	0.051*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0523 (3)	0.0345 (3)	0.0584 (4)	0.000	0.0263 (3)	0.000
I2	0.0342 (3)	0.0255 (2)	0.0439 (3)	0.000	0.0023 (2)	0.000
I3	0.0775 (4)	0.0464 (3)	0.0400 (3)	0.000	0.0100 (3)	0.000
I1'	0.0523 (3)	0.0345 (3)	0.0584 (4)	0.000	0.0263 (3)	0.000
I2'	0.0342 (3)	0.0255 (2)	0.0439 (3)	0.000	0.0023 (2)	0.000
I3'	0.0775 (4)	0.0464 (3)	0.0400 (3)	0.000	0.0100 (3)	0.000
I4	0.0302 (2)	0.0402 (3)	0.0309 (2)	0.000	0.00506 (17)	0.000
N1	0.040 (2)	0.029 (2)	0.030 (2)	-0.0001 (17)	0.0069 (17)	0.0043 (17)
N2	0.067 (3)	0.038 (3)	0.038 (2)	-0.017 (2)	-0.001 (2)	-0.006 (2)
N3	0.048 (2)	0.027 (2)	0.0266 (19)	0.0058 (19)	0.0082 (17)	0.0040 (17)
N4	0.038 (3)	0.039 (3)	0.022 (3)	0.000	0.010 (2)	0.000
C1	0.063 (4)	0.055 (4)	0.028 (3)	0.007 (3)	0.012 (3)	-0.003 (2)
C2	0.035 (2)	0.034 (3)	0.038 (3)	0.001 (2)	0.006 (2)	0.000 (2)
C3	0.047 (3)	0.040 (3)	0.043 (3)	-0.019 (3)	0.004 (2)	0.002 (2)
C4	0.079 (4)	0.049 (3)	0.032 (3)	0.023 (3)	0.028 (3)	0.011 (3)
C5	0.041 (3)	0.037 (3)	0.036 (3)	0.011 (2)	0.018 (2)	0.005 (2)
C6	0.053 (3)	0.032 (3)	0.035 (3)	0.004 (2)	0.016 (2)	-0.005 (2)
C7	0.059 (5)	0.043 (4)	0.025 (3)	0.000	0.012 (3)	0.000

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

I1—I2	2.9524 (10)	C1—H1A	0.9800
I2—I3	2.8796 (10)	C1—H1B	0.9800
I1'—I2'	2.98 (3)	C1—H1C	0.9800
I2'—I3'	2.85 (4)	C2—H2	0.9500
N1—C2	1.326 (6)	C3—H3	0.9500
N1—C3	1.347 (6)	C4—C5	1.517 (7)
N1—C1	1.485 (6)	C4—H4A	0.9900
N2—C3	1.295 (7)	C4—H4B	0.9900
N2—N3	1.362 (6)	C5—C6	1.391 (7)
N3—C2	1.317 (6)	C6—C7	1.381 (6)
N3—C4	1.471 (6)	C6—H6	0.9500
N4—C5 ⁱ	1.331 (6)	C7—C6 ⁱ	1.381 (6)
N4—C5	1.331 (6)	C7—H7	0.9500

I3—I2—I1	176.19 (2)	N2—C3—N1	112.1 (5)
I3'—I2'—I1'	173.8 (10)	N2—C3—H3	123.9
C2—N1—C3	106.0 (4)	N1—C3—H3	123.9
C2—N1—C1	126.8 (4)	N3—C4—C5	111.6 (4)
C3—N1—C1	127.2 (4)	N3—C4—H4A	109.3
C3—N2—N3	103.9 (4)	C5—C4—H4A	109.3
C2—N3—N2	110.5 (4)	N3—C4—H4B	109.3
C2—N3—C4	128.4 (5)	C5—C4—H4B	109.3
N2—N3—C4	121.1 (4)	H4A—C4—H4B	108.0
C5 ⁱ —N4—C5	117.2 (6)	N4—C5—C6	123.7 (5)
N1—C1—H1A	109.5	N4—C5—C4	117.0 (5)
N1—C1—H1B	109.5	C6—C5—C4	119.3 (5)
H1A—C1—H1B	109.5	C7—C6—C5	118.3 (5)
N1—C1—H1C	109.5	C7—C6—H6	120.9
H1A—C1—H1C	109.5	C5—C6—H6	120.9
H1B—C1—H1C	109.5	C6 ⁱ —C7—C6	118.9 (7)
N3—C2—N1	107.5 (4)	C6 ⁱ —C7—H7	120.5
N3—C2—H2	126.3	C6—C7—H7	120.5
N1—C2—H2	126.3		
C3—N2—N3—C2	-0.3 (6)	C2—N3—C4—C5	-84.4 (7)
C3—N2—N3—C4	-179.2 (5)	N2—N3—C4—C5	94.3 (6)
N2—N3—C2—N1	0.5 (6)	C5 ⁱ —N4—C5—C6	1.0 (10)
C4—N3—C2—N1	179.3 (5)	C5 ⁱ —N4—C5—C4	179.1 (4)
C3—N1—C2—N3	-0.4 (6)	N3—C4—C5—N4	59.2 (7)
C1—N1—C2—N3	178.6 (5)	N3—C4—C5—C6	-122.7 (5)
N3—N2—C3—N1	0.0 (6)	N4—C5—C6—C7	0.4 (9)
C2—N1—C3—N2	0.3 (6)	C4—C5—C6—C7	-177.6 (6)
C1—N1—C3—N2	-178.8 (5)	C5—C6—C7—C6 ⁱ	-1.8 (11)

Symmetry code: (i) $x, -y+1, z$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3 \cdots I4	0.95	3.00	3.844 (5)	149
C2—H2 \cdots I4 ⁱⁱ	0.95	2.82	3.744 (5)	164
C4—H4B \cdots I2 ⁱⁱⁱ	0.99	3.18	3.775 (6)	120
C4—H4B \cdots I2 ⁱⁱⁱ	0.99	3.10	3.766 (15)	126
C6—H6 \cdots I1 ^{iv}	0.95	3.17	4.097 (5)	166
C6—H6 \cdots I1 ^{iv}	0.95	3.00	3.900 (8)	158
C4—H4A \cdots I1 ^{iv}	0.99	2.98	3.94 (2)	166

Symmetry codes: (ii) $x+1/2, y+1/2, z$; (iii) $x+1/2, y-1/2, z$; (iv) $-x+3/2, -y+1/2, -z$.