Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

4′-Iodo-2,2′:6′,2″-terpyridine

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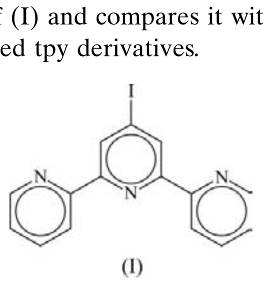
Received 11 April 2008
Accepted 15 April 2008
Online 19 April 2008

In the nearly planar title compound, $C_{15}H_{10}IN_3$, the three pyridine rings exhibit *transoid* conformations about the interannular C—C bonds. Very weak C—H···N and C—H···I interactions link the molecules into ribbons. Significant π–π stacking between molecules from different ribbons completes a three-dimensional framework of intermolecular interactions. Four different packing motifs are observed among the known structures of simple 4′-substituted terpyridines.

Comment

Much effort has been devoted in recent years to the design and synthesis of terpyridines and their metal complexes, which display binding properties conducive to supramolecular chemistry (Hoogenboom & Schubert, 2006). Such materials also have applications in the conversion of solar energy in dye-sensitized solar cells (Kalyanasundaram, 2006). Derivatives of 2,2′:6′,2″-terpyridine (tpy) can be linked together by spacers. Metal-coordinated tpy ligands with spacers at the 4′-position provide a means of influencing directionality and linear communication, meaning that electronic communication can occur along the coordination axis. The functionalization of tpy at this position is thus of particular importance. The title 4′-iodo derivative of tpy, (I), may play a crucial role, since it can be used as a precursor for the preparation of stannyl or boronic acid compounds, which are used in Stille and Suzuki cross-coupling reactions, respectively. This paper describes the crystal structure of (I) and compares it with the structures of related 4′-substituted tpy derivatives.



(I)

In terpyridine derivatives, the three pyridine rings are usually close to being coplanar. For example, the interplanar angles between the terminal rings and the central ring in 4′-ethoxy-5,5″-dimethyl-2,2′:6′,2″-terpyridine are 4.32 (13) and 11.38 (11)° (Fallahpour *et al.*, 1999*b*). In 4′-amino-2,2′:6′,2″-terpyridine, however, the interplanar angles between the two terminal rings and the central ring are 11.24 (15) and 20.71 (11)°, as a result of hydrogen-bond formation (Fallahpour *et al.*, 1999*a*). In contrast, in 2,2′:6′,2″-terpyridine 1,1′-dioxide, the two pyridine *N*-oxide ring planes are almost perpendicular to one another, with an interplanar angle of 87.68 (10)°, while the angle between the plane of the central pyridine *N*-oxide ring and that of the terminal pyridine ring is 38.46 (10)°. The interplanar angle between the terminal pyridine *N*-oxide ring and the terminal pyridine ring is 70.98 (11)° (Fallahpour & Neuburger, 2001).

The molecule of (I) (Fig. 1), with unremarkable bond lengths and angles, has the expected nearly planar *transoid* conformation of the three pyridine rings and pseudo-C_s symmetry, with an r.m.s. fit of the atoms of the two halves of the molecule of 0.16 Å. The angles between the planes of the terminal pyridine rings containing atoms N8 and N14 and the plane of the central ring are 15.1 (2) and 9.4 (2)°, respectively. The angle between the planes of the terminal rings is 12.8 (2)°.

The mean plane of the molecule is nearly parallel to the (100) plane and, in the crystal packing, the molecules are distributed in slightly corrugated layers, which lie parallel to the same plane. There are only two intermolecular distances that are shorter than the sum of the van der Waals radii of any atom pair, although these are only marginally shorter than this limit (<0.06 Å). A very weak intermolecular C—H···N interaction (Table 1) links molecules related by a translation of one unit cell into extended chains, which run parallel to the [001] direction and which can be described by a graph-set motif of *C*(9) (Bernstein *et al.*, 1995). Within the (100) plane, pairs of parallel chains are crosslinked by weak C—H···I interactions to give a ladder-like arrangement, where the C—H···I interactions are the rungs of the ladder and the C—H···N interactions form the ladder uprights (Fig. 2). Within each segment of the ladder structure, an asymmetric ring motif can be discerned, made up of one C—H···N and two C—

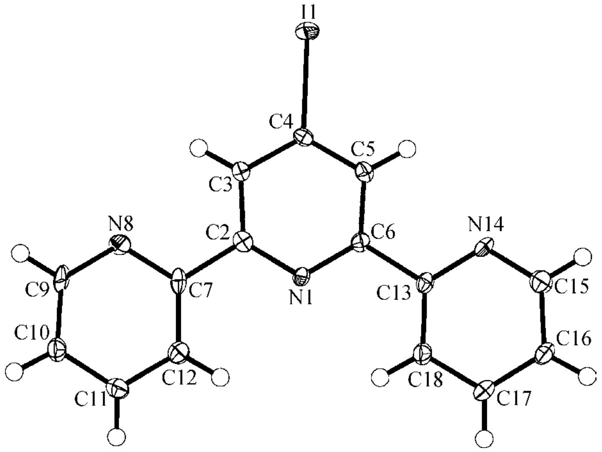


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

doi:10.1107/S0108270108010354

H···I interactions. This ring motif can be described by a binary graph set of $R_3^3(19)$. Essentially, one terminal pyridine ring acts as a single acceptor, the other terminal ring acts as a donor for both types of interaction and the central ring is involved in one acceptor interaction *via* the I atom. There are no significant intermolecular interactions between adjacent ladders in the same plane.

The molecules are stacked perpendicular to the (100) plane such that the planes of overlapping rings are almost parallel, but adjacent molecules in the stack appear as if they are rotated alternately about an axis almost perpendicular to the plane of the central pyridine ring by approximately 120° with respect to one another [Fig. 3; in reality this is a glide operation, which yields a reflection in a plane parallel to (010)]. This means that the central pyridine rings stack with potential π–π interactions, the centroid–centroid distance being 3.813 (3) Å, while one of the terminal pyridine rings in each molecule also partakes in weak π–π stacking, with a centroid–centroid distance of 3.972 (3) Å, although adjacent ring planes are inclined at an angle of about 21°. In contrast, the other terminal pyridine ring stacks in an alternating fashion with the I atom of the molecule below it, to give centroid–iodine distances of 3.738 (2) and 3.754 (2) Å. The combination of the ladder-generating C—H···X (X = N or I) interactions with the π–π and I···π interactions generates a three-dimensional framework, because adjacent ladders in the π–π stacks are offset from one another, thereby creating a brickwork stacking pattern of ladders.

The crystal structures of the 4′-bromo and 4′-chloro analogues of (I) are known (Clegg & Scott, 2005; Beves *et al.*, 2006). The molecules are slightly flatter than that of (I), the angles between the terminal pyridine ring planes and that of the central pyridine ring being 8.0 (1) and 5.4 (1)° for the chloro derivative, and 5.1 (1) and 5.6 (1)° for the bromo derivative. These two structures are isomorphous, but although the structure of (I) has the same space group, the unit-cell dimensions differ markedly. Thus, (I) is not isomorphous with the chloro and bromo analogues, which is manifested in the quite different packing arrangements of the molecules. Unlike in (I), the molecules of the chloro and bromo analogues stack exactly on top of one another without a 120° rotation, as they are related by one unit-cell translation along the short *b* axis. According to Beves *et al.* (2006), the molecules are π-stacked, although the planes of the molecules are tilted somewhat with respect to the stacking axis direction. In addition, these two analogues do not exhibit any C—H···X (X = N or halogen) or halogen–π interactions, so the intermolecular interactions only form one-dimensional motifs. The lack of isomorphism between the structure of (I) and those of the other 4′-halo tpy derivatives must be related to the influence of the bulkier I atom on the packing efficiency of the molecules.

The stacking motifs of adjacent molecules in (I) and related derivatives show four main patterns. Infinite stacks with an alternating 120° rotation of adjacent molecules within the stack are formed in (I) and 4′-azido-2,2′:6′,2″-terpyridine (Fallahpour *et al.*, 1999*c*). Infinite stacks with exact superposition of the molecules are present in the 4′-bromo and 4′-chloro analogues of (I), as described above, as well as in the orthorhombic polymorph of unsubstituted 2,2′:6′,2″-terpyridine itself (Bessel *et al.*, 1992). The third motif involves just pairs of molecules, perfectly superimposed but not propagating beyond the pair. This motif is seen in the monoclinic polymorph of unsubstituted 2,2′:6′,2″-terpyridine (Boves *et al.*, 2005). The fourth motif also involves just pairs of molecules, but this time they are related by a centre of inversion,

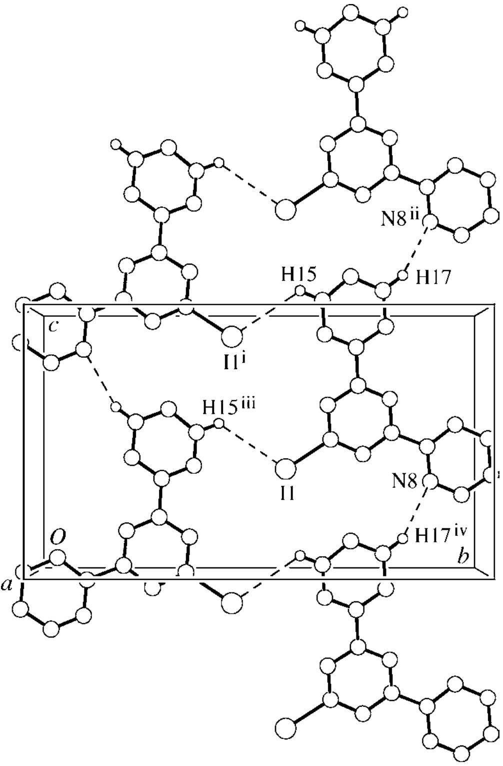


Figure 2
A plane of molecules of (I), viewed down the *a* axis, showing the ladder-like structure formed by the shortest intermolecular C—H···N and C—H···I distances (dashed lines). [Symmetry codes: (i) $-x + 1, -y + 1, z + \frac{1}{2}$; (ii) $x, y, z + 1$; (iii) $-x + 1, -y + 1, z - \frac{1}{2}$; (iv) $x, y, z - 1$.]

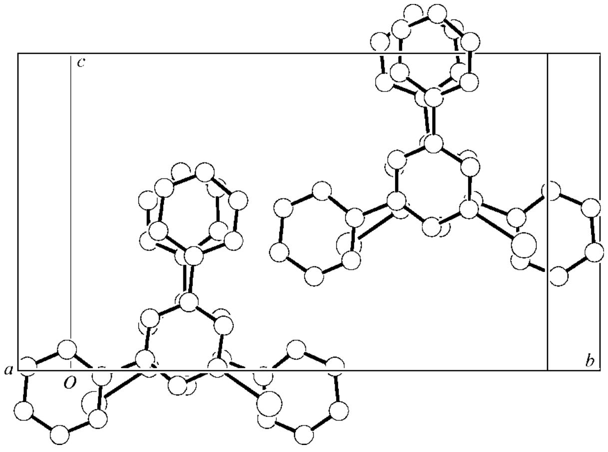


Figure 3
The stacking of molecules of (I) along the *a* direction, showing the alternating positions of atom I1 and the consequent stacking of the pyridine rings.

so that all pyridine rings are sufficiently offset so as to preclude any possibility of π–π interactions. This is much like superimposing a 'Y' on an upside-down 'Y'. This motif is displayed by 4′-amino-2,2′:6′,2′′-terpyridine (Fallahpour *et al.*, 1999*a*) and 4′-dimethylamino-2,2′:6′,2′′-terpyridine (Constable *et al.*, 1992).

Experimental

The title compound was prepared from 4′-amino-2,2′:6′,2′′-terpyridine (Fallahpour *et al.*, 1999*a*) according to the standard procedure of Coudret (1996) (yield 70%, m.p. 399–400 K). The spectroscopic data have been reported by Sauer *et al.* (1999). Crystals of (I) were grown by slow evaporation of a warm dichloromethane solution of the compound.

Crystal data

$C_{15}H_{10}IN_3$
$M_r = 359.17$
Orthorhombic, $Pna2_1$
$a = 7.4518$ (2) Å
$b = 17.2432$ (3) Å
$c = 10.0691$ (2) Å
$V = 1293.81$ (5) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.46$ mm^{-1}
$T = 160$ (1) K
$0.30 \times 0.28 \times 0.25$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.448$, $T_{\max} = 0.544$
19500 measured reflections
3713 independent reflections
3524 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.054$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.096$
$S = 1.05$
3712 reflections
172 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{\max} = 0.79$ e Å^{-3}
$\Delta\rho_{\min} = -1.87$ e Å^{-3}
Absolute structure: Flack & Bernardinelli (1999, 2000), 1738 Friedel pairs
Flack parameter: 0.03 (3)

Table 1
Geometry of the intermolecular contacts (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C15—H15$\cdots$I1$^{\rm i}$	0.95	3.17	3.793 (5)	125
C17—H17$\cdots$N8$^{\rm ii}$	0.95	2.69	3.526 (6)	147

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

H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms [C—H = 0.95 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C)].

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

HetCat, Switzerland, is thanked for providing a sample of the title compound (http://www.hetcat.com).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3224). Services for accessing these data are described at the back of the journal.

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