$S = 1.032$
2584 reflections
166 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2 + 0.5211P]$ where $P = (F_o^2 + 2F_c^2)/3$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.025 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C1—O1	1.220 (3)	C22—C221	1.493 (3)
C1—C11	1.485 (3)	C221—O221	1.238 (3)
C1—C21	1.525 (3)	C221—O222	1.299 (3)
O1—C1—C11	122.6 (2)	O221—C221—O222	123.9 (2)
O1—C1—C21	118.6 (2)	O221—C221—C22	121.2 (2)
C11—C1—C21	118.5 (2)	O222—C221—C22	114.9 (2)
O1—C1—C11—C12	−164.3 (2)	O1—C1—C21—C22	80.3 (3)
O1—C1—C11—C16	16.3 (4)	C21—C22—C221—O221	5.1 (4)
O1—C1—C21—C26	−94.0 (3)	C23—C22—C221—O222	4.7 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O222—H222···O221^{i}	0.84	1.79	2.628 (2)	172
C141—H14*C*···O1^{ii}	0.98	2.57	3.512 (3)	160
C23—H23···O1^{iii}	0.95	2.64	3.326 (3)	130
C141—H14*A*···O1^{iv}	0.98	2.83	3.712 (3)	150

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

All H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [$U(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$, $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $U(\text{H}) = 1.2U_{\text{eq}}(\text{O})$] using a riding model with C—H(methyl) = 0.98, C—H(aromatic) = 0.95 or O—H = 0.84 Å. The methyl group attached to the aromatic ring was allowed to rotate about its local threefold axis, and the torsion angle about the C—O bond of the hydroxyl group was also refined.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1357). Services for accessing these data are described at the back of the journal.

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4-Iodopyridine, a structure with very short nitrogen–iodine contacts

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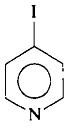
Abstract

The title compound, C_5H_4IN, crystallizes in the polar space group *Fdd*2 with imposed twofold symmetry (through the N atom and the C—I group). The C—I bond length is 2.100 (5) Å (2.106 Å after libration correction). The molecules are arranged in chains parallel to the polar z axis, with very short intermolecular N···I contacts of 2.988 (5) Å.

Comment

We are interested in secondary bonding in halogenopyridines (Jones & Freytag, 1999). We report here the crystal structure of a 4-iodopyridine, (I). As far as we are aware, this is the first reported structure of 4-iodo-substituted pyridine or of any simple (monosubstituted) iodopyridine.



(I)

The title compound crystallizes in the polar space group *Fdd*2 with half a molecule in the asymmetric unit (Fig. 1); atoms I, N and C3 lie on a twofold axis. The bond lengths within the molecule [C—N 1.337 (5), C—C 1.387 Å (mean value)] display no significant differences from those in pyridine [C—N 1.336, C—C 1.379 Å (mean values)] (Mootz & Wussow, 1981). A rigid body libration correction (Schomaker & Trueblood,

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1968; $R_{\rm lib}$ 0.086), led to corrected bond lengths of 1.344 (N—C) and 1.392 Å (C—C, mean), also consistent with those in pyridine (1.347, 1.391 Å, respectively). The C—I bond length of 2.100 (5) Å (2.106 Å after correction for libration) is similar to the C—I bond length of 2.093 (3) Å in 4-iodobenzonitrile (Desiraju & Harlow, 1989); a search of the Cambridge Structural Database (Allen & Kennard, 1993; version of October 1998) revealed a mean value of 2.090 Å for 39 C—I bonds (at any ring position) in substituted benzenes. The bond angles in 4-iodopyridine differ slightly from those in pyridine, but display the same tendency: the C—N—C angle is the smallest, the N—C—C angle the widest [115.2 (5), 125.3 (4)° in 4-iodopyridine, *cf.* 116.6, 123.7° (mean values) in pyridine]. The C—C—C angles are not significantly affected by coordination of iodine, with mean values of 118.5 (4-iodopyridine) and 118.7° (pyridine).

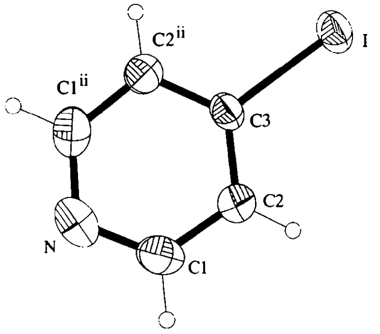

Fig. 1. The molecular structure of (I). Displacement ellipsoids are shown with 50% probability and H atoms are of arbitrary radii. [Symmetry code: (ii) $-x$, $-y$, z.]

The extended structure consists of chains of molecules parallel to the (polar) z axis (Fig. 2). These chains arise from short N···I contacts of 2.988 (5) Å. A search of the Cambridge Structural Database (Allen & Kennard, 1993) revealed a mean value for N···I contacts of 4.015 Å (maximum 4.53 Å). Only a few contacts less than 3.3 Å were observed, namely in *p*-iodobenzonitrile (Schlemper & Britton, 1965; Desiraju & Harlow, 1989), iodo(cyano)acetylene (Borgen *et al.*, 1962), pyrazine diiodine (Bailey *et al.*, 1992) [N···I 3.127 (4), 2.93, 2.817 (1) Å, respectively]. The chains within the title compound are parallel to each other, consistent with the polar space group, and there is no indication of disorder. It is possible that other crystalline modifications could involve chain inversion. The structures of various forms of the *para*-halobenzonitriles (Desiraju & Harlow, 1989) displayed either parallel or antiparallel chains; variable alignment of the chains was shown to lead to disorder phenomena. Hulliger & Langley (1998, and references therein) have discussed defect-forming mechanisms in similar chain-like structures.

Intermolecular contacts of the form C—H(···I)$_2$ (three-centre) and C—H···N are long; the latter displays a very narrow angle at H (Table 2). They represent at best very weak hydrogen bonds.

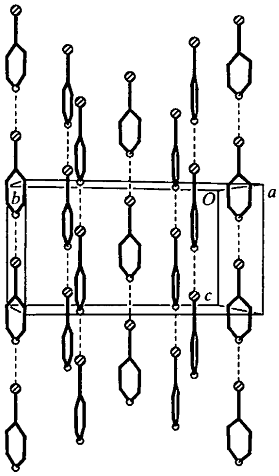

Fig. 2. Packing diagram, viewed approximately perpendicular to the yz plane. Atoms have an arbitrary radius. H atoms are omitted for clarity. Dashed lines represent N···I contacts.

Experimental

4-Iodopyridine was prepared by the method of Gergely & Iredale (1953), although the yield was poor. A more efficient synthesis has been published recently (Coudret, 1996). Single crystals were obtained by sublimation.

Crystal data

C_5H_4IN
M_r = 204.99
Orthorhombic
*Fdd*2
a = 10.390 (2) Å
b = 14.394 (3) Å
c = 7.884 (2) Å
V = 1179.0 (4) Å^3
Z = 8
D_x = 2.310 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 64 reflections
θ = 10.0–11.5°
μ = 5.299 mm^{-1}
T = 143 (2) K
Square prism
0.42 × 0.23 × 0.19 mm
Colourless

Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: ψ scan (*XEMP*; Siemens, 1994*a*)
$T_{\rm min}$ = 0.247, $T_{\rm max}$ = 0.365
1375 measured reflections
370 independent reflections (plus 321 Friedel-related reflections)
636 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.025
$\theta_{\rm max}$ = 27.49°
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 18$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.015$
$wR(F^2) = 0.034$
$S = 1.127$
691 reflections
34 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0115P)^2 + 0.1774P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.00 (5)

Table 1. *Selected geometric parameters (Å, °)*

I—C3	2.100 (5)	C1—C2	1.387 (4)
N—C1	1.337 (5)	C2—C3	1.386 (4)
N···I^{i}	2.988 (5)		
C1^{ii}—N—C1	115.2 (5)	C3—C2—C1	117.2 (4)
C1—N—I^{i}	122.4 (2)	C2—C3—C2^{ii}	119.8 (4)
N—C1—C2	125.3 (4)	C2—C3—I	120.1 (2)

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

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···I^{i}	0.95	3.26	3.951 (4)	130.9
C1—H1···I^{ii}	0.95	3.51	4.165 (4)	127.9
C2—H2···N^{iii}	0.95	3.01	3.499 (4)	113.6

Symmetry codes: (i) $\frac{1}{4} + x, -\frac{1}{4} - y, \frac{3}{4} + z$; (ii) $\frac{1}{2} + x, y, \frac{1}{2} + z$; (iii) $\frac{1}{4} + x, -\frac{1}{4} - y, z - \frac{1}{4}$.

H atoms were included at calculated positions and refined using a riding model.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* (Siemens, 1994*b*). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1321). Services for accessing these data are described at the back of the journal.

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Colletoketol

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Abstract

The configuration of the title compound (6*R*,12*R*,14*R*)-(3*E*,9*E*)-12-hydroxy-6,14-dimethyl-1,7-dioxacyclotetradeca-3,9-diene-2,8,11-trione, $C_{14}H_{18}O_6$, at the two double bonds and three asymmetric centres has been confirmed. The α,β-unsaturated carbonyl functions depart significantly from planarity. The molecules are connected into layers parallel to the *xy* plane by one conventional and four C—H···O hydrogen bonds.

Comment

Research into new and biologically active natural products from marine sources also involves micro-organisms such as marine fungi. We recently isolated more than 1000 fungal strains from marine sponges and algae. One of the isolates was the obligate marine mitosporic fungus *Varicosporina ramulosa*, obtained from an unidentified alga of the genus *Cytoseira*, collected off Tenerife, Spain. Investigations of its culture extract yielded the five macrodiolides grahamimycin A_1, (1) (Ronald & Gurusiddaiah, 1980; Seidel & Seebach, 1982), colletoketol, (2) (MacMillan & Simpson, 1973), colletodiol, (3) (Grove *et al.*, 1966; MacMillan &

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