

4-Iodoquinoline

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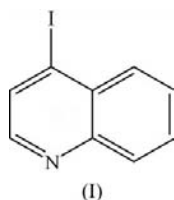
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Nearly planar molecules of the title compound, C₉H₆IN, are packed in inclined stacks along the short crystallographic *b* axis and molecules in adjacent stacks are packed to form antiparallel zigzag chains. Short intermolecular N⋯I contacts [3.131 (3) Å] are observed between molecules in adjacent stacks. A network of C—H⋯π hydrogen bonds [2.821 (5) and 3.083 (3) Å] between molecules in adjacent stacks is also present. These motif-generating interactions, including the weak C—H⋯π interactions, are of relevance in crystal engineering and design.

Comment

Information on the molecular packing of aromatic compounds in crystal structures is of importance for understanding solid-state properties and the influence of molecular structure on molecular packing (Kitaigorodskii, 1973). Halogen–nitrogen interactions have been considered as secondary motif-generating interactions (Desiraju & Harlow, 1989) and could play a useful role in crystal engineering and design. We report here the structure of 4-iodoquinoline, (I), which exhibits the typical herring-bone-type structure known for many planar aromatic hydrocarbons (Desiraju & Gavezzotti, 1989, and references therein) and substituted aromatic compounds, *e.g.* 2,3-diodonaphthalene (Novak, 2007). Short intermolecular N⋯I [3.131 (3) Å] and C—H⋯π [2.821 (5) and 3.083 (3) Å] contacts are present between molecules in adjacent stacks and form a zigzag network of hydrogen bonds.



Compound (I) crystallizes in the monoclinic centrosymmetric space group $P2_1/n$. Fig. 1 shows the asymmetric unit and the atom-numbering scheme. Selected bond lengths and angles are given in Table 1.

Bond lengths and angles for the aromatic rings in (I) are within the ranges reported for substituted quinolines (Harlow *et al.*, 1976; Das *et al.*, 1990; Singh *et al.*, 2008) and those calculated for quinoline (Dewar & Gleicher, 1966). The C—I bond length of 2.110 (4) Å is close to that observed in 4-iodopyridine [2.100 (5) Å; Ahrens & Jones, 1999]. These authors also report a mean value of 2.090 Å for the C—I bond based on entries in the Cambridge Structural Database (CSD, Version of October 1998; Allen & Kennard, 1993) for 39 C—I bonds in substituted benzenes. A comparison of the values of the angles around the ring N atom, namely C1—N—C5, N—C1—C2 and N1—C5—C4 in (I) (117.3, 124.3 and 122.9°, respectively), with those for another 4-substituted quinoline, namely 1,4-bis(4-quinolyl)-1,3-butadiyne (117.04, 124.3 and 123.0°, respectively; Singh *et al.*, 2008), indicates negligible influence of these substituent groups on the bond angles around the ring N atom. Furthermore, it is noteworthy that the two aromatic rings are not entirely coplanar, their ring planes being joined together at the C4—C5 bond edge at an angle of 1.40 (24)°. The I atom is out of the pseudo-molecular plane by about 2.6°. Bond angle values of 117.9 (3) and 122.3 (3)° for C2—C3—I1 and C4—C3—I1, respectively, suggest a significant *peri* interaction between the C—I and C9—H bonds.

Fig. 2 shows the contents of the unit cell, viewed approximately along the crystallographic *c* axis. Molecules of (I) are packed in the centrosymmetric space group in parallel inclined stacks along the crystallographic *b* axis. Planar molecules within a stack are separated by 4.353 Å, indicating weak π–π interactions between adjacent molecules within the stack. Molecules in adjacent stacks are packed to form an anti-

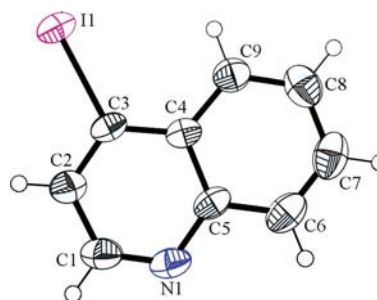


Figure 1

A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

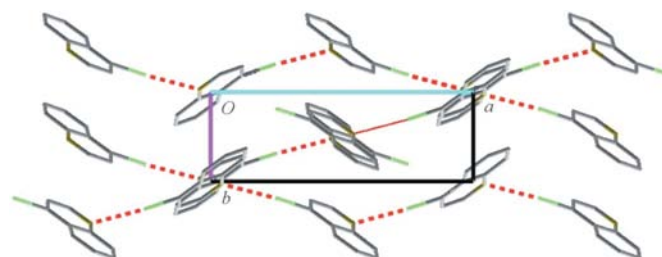


Figure 2

The packing of (I) viewed approximately along the *c* axis. Dashed lines indicate intermolecular N⋯I contacts.

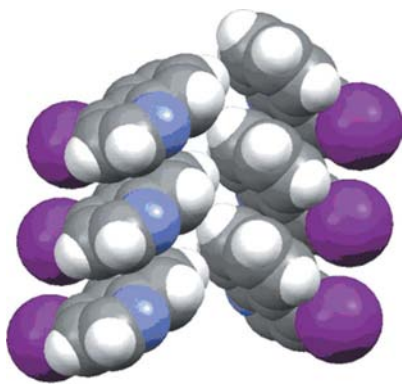


Figure 3
A space-filling representation of the herring-bone packing of (I).

parallel zigzag chain of molecules. The molecular planes in adjacent stacks form an angle of about 69° , forming a herring-bone-type structure, as shown in Fig. 3 and often observed for planar aromatic compounds. The dipolar nature of the layers of the large I atoms seems to cause the molecules to form stacks inclined with the stack axis to reduce atom–atom repulsive interactions, thereby increasing the distance between the planar molecules.

Two types of short intermolecular contacts are present. A short intermolecular $I \cdots N^i$ [symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$] contact of 3.131 (3) Å is observed between the N and I atoms of molecules in adjacent stacks, as shown in Fig. 2. The $C-I \cdots N$ geometry is nearly linear, with an angle of 171.2° . A short $N \cdots I$ contact of 2.988 (5) Å has been observed in 4-iodopyridine (Ahrens & Jones, 1999). Only a limited number of crystal structures with $N \cdots I$ contacts of less than 3.3 Å have been reported to date, as was observed by Ahrens & Jones. An exceptionally short $N \cdots I$ contact of 2.712 (2) Å was reported for a morpholine- β -iodophenylacetylene complex (Batsanov & Howard, 2000). Short $N \cdots I$ contacts have also been observed in the crystal structures of an aggregate of 1-iodoperfluoroheptane and tetramethylenediamine (Fontana *et al.*, 2002), some diiodobenzothiadiazoles (Tomura *et al.*, 2002) and 4,5-diiodo-1,2,5-thiadiazolotetrathiafulvalene (Tomura & Yamashita, 2004). These short contacts could be induced by the weak Lewis acidity of the I atoms due to polarization of the $C-I$ bond. These short $N \cdots I$ contacts lead to the formation of a motif with an antiparallel zigzag arrangement of molecules along the crystallographic a axis, as shown in Fig. 2. Such antiparallel zigzag motifs, as well as parallel linear array motifs, have been observed in the crystal structures of 4-halobenzonitriles (Desiraju & Harlow, 1989). 4-Iodopyridine, in contrast, crystallizes in a polar space group and forms a parallel linear array of molecules along the polar c axis.

The other type of short intermolecular contacts observed in the crystal structure of (I) are weak $C-H \cdots \pi$ hydrogen bonds (Nishio, 2004), which are shown in Fig. 4. Short intermolecular contacts of 2.82 and 3.08 Å are observed for $C7 \cdots H7^{ii}$ and $C6 \cdots H7^{ii}$ [symmetry code: (ii) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$], respectively, between the benzene rings of molecules in

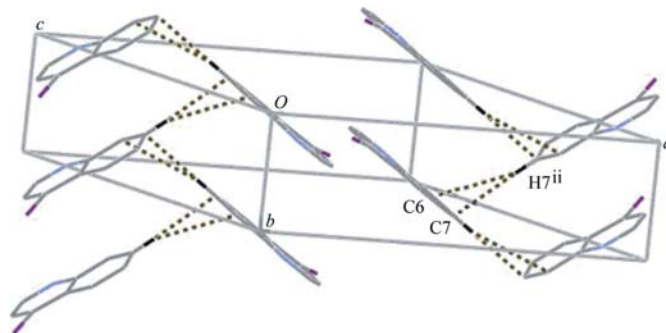


Figure 4
A packing diagram, viewed approximately along the c axis. Dotted lines show the $C-H \cdots \pi$ short contacts for $C7 \cdots H7^{ii}$ (2.82 Å) and $C6 \cdots H7^{ii}$ (3.08 Å). [Symmetry code: (ii) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$.]

adjacent stacks. These hydrogen bonds are almost linear, with respective $C7-H7 \cdots C7^{ii}$ and $C7-H7 \cdots C6^{ii}$ angles of 171° and 161° . This results in a zigzag network of hydrogen bonds in the crystallographic b -axis direction. The hydrogen-bond network and the $N \cdots I$ network are quite isolated from each other and generate independent packing motifs.

Experimental

4-Iodoquinoline was prepared from 4-chloroquinoline hydrochloride by treatment with sodium iodide (Wolf *et al.*, 2003). Suitable X-ray-quality rectangular crystals of (I) were grown by crystallization from an ethyl acetate–hexane solvent system by interfacial diffusion (m.p. 362–363 K).

Crystal data

| | |
|--------------------------------|---|
| C_9H_6IN | $V = 832.01 (15) \text{ \AA}^3$ |
| $M_r = 255.05$ | $Z = 4$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation |
| $a = 14.1973 (17) \text{ \AA}$ | $\mu = 3.78 \text{ mm}^{-1}$ |
| $b = 4.3526 (4) \text{ \AA}$ | $T = 293 (2) \text{ K}$ |
| $c = 14.9151 (14) \text{ \AA}$ | $0.35 \times 0.30 \times 0.30 \text{ mm}$ |
| $\beta = 115.484 (8)^\circ$ | |

Data collection

| | |
|---|--|
| Enraf–Nonius MACH3 diffractometer | 1465 independent reflections |
| Absorption correction: ψ scan (North <i>et al.</i> , 1968) | 1267 reflections with $I > 2\sigma(I)$ |
| $T_{\min} = 0.351, T_{\max} = 0.397$ (expected range = 0.285–0.322) | $R_{\text{int}} = 0.025$ |
| 1528 measured reflections | 3 standard reflections |
| | frequency: 3600 min |
| | intensity decay: <3% |

Table 1

Selected geometric parameters (Å, °).

| | | | |
|----------|-----------|----------|-----------|
| I1–C3 | 2.110 (4) | C1–C2 | 1.405 (7) |
| N1–C1 | 1.307 (6) | C2–C3 | 1.358 (6) |
| N1–C5 | 1.371 (5) | C4–C5 | 1.419 (5) |
| C1–N1–C5 | 117.3 (3) | C3–C4–C9 | 125.2 (3) |
| N1–C1–C2 | 124.3 (4) | C3–C4–C5 | 116.7 (3) |
| C3–C2–C1 | 119.0 (4) | C9–C4–C5 | 118.2 (4) |
| C2–C3–C4 | 119.8 (4) | N1–C5–C6 | 117.5 (4) |
| C2–C3–I1 | 117.9 (3) | N1–C5–C4 | 122.9 (4) |
| C4–C3–I1 | 122.3 (3) | | |

Table 2

Intermolecular atomic contacts (Å, °).

| Contact | Distance | Angle at central atom |
|---|-----------|-----------------------|
| C3—N1...N1 ⁱ | 3.131 (3) | 171.2 |
| C7...H7 ⁱⁱ —C7 ⁱⁱ | 2.82 | 171 |
| C6...H7 ⁱⁱ ...C7 ⁱⁱ | 3.08 | 161 |

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

Refinement

| | |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.030$ | 101 parameters |
| $wR(F^2) = 0.075$ | H-atom parameters constrained |
| $S = 1.11$ | $\Delta\rho_{\max} = 1.06 \text{ e } \text{Å}^{-3}$ |
| 1465 reflections | $\Delta\rho_{\min} = -1.08 \text{ e } \text{Å}^{-3}$ |

All H atoms were positioned geometrically and treated using a riding model, with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *ARGUS* (Nonius, 1997); cell refinement: *ARGUS*; data reduction: *maXus* (Mackay *et al.*, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLUTO* (Motherwell & Clegg, 1978) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3071). Services for accessing these data are described at the back of the journal.

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