

2,6-Dibromo-3,5-dimethylpyridine and 2,6-diiodo-3,5-dimethylpyridine

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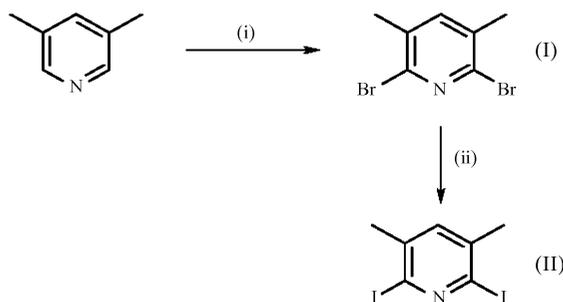
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The title compounds 2,6-dibromo-3,5-dimethylpyridine, $C_7H_7Br_2N$, (I), and 2,6-diiodo-3,5-dimethylpyridine, $C_7H_7I_2N$, (II), constitute the first structurally characterized examples of 2,6-dihalo-3,5-dimethylpyridines. Compound (I) crystallizes as a racemic twin with two symmetry-independent molecules in the asymmetric unit, while (II) is non-planar with the pyridine ring slightly deformed into a saddle shape, and exhibits crystallographically imposed twofold symmetry. Both (I) and (II) exhibit aromatic face-to-face π -stacking in the solid state, although there are no other long-range interactions. In (I), alternate molecules are oriented at 90° , resulting in X-shaped columns, while in (II), molecules pack in a parallel fashion, leading to a zigzag array.

Comment

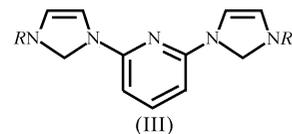
To date, 2,6-dihalo-3,5-dimethylpyridine compounds have not been structurally characterized. Indeed, the only known crystal structure of a 2,6-dihalo-3,5-dialkylpyridine was reported by Kasturi *et al.* (1992), although as part of a larger structure. Although several methods exist for synthesizing 2,6-dichloro-3,5-dimethylpyridine (Crouch & Lochte, 1943; Meerpoel *et al.*, 1991; Gros *et al.*, 2002), only one route to the dibromide (I) has been disclosed (Dunn & Guillermic, 1988), and neither the difluoride nor the diiodide is known.

Conditions: (i) Oleum, Br_2 , 433 K

(ii) NaI, cat. CuI, DMEDA, dioxane, 383 K

2,6-Dibromopyridine is commonly used in the synthesis of (CNC) 'pincer' ligands containing N-heterocyclic carbene groups. It has been used to form (CNC) 'pincer' ligands (III)

by quaternization with the appropriately substituted imidazole at high temperature, followed by deprotonation of the resulting imidazolium salt with a base (Danopoulos *et al.*, 2002).



C–H activation at the 3- and 5-positions of the pyridine ring was seen with Fe and Ir complexes of (III) (R is 2,6-diisopropylphenyl). To counter this, a 'pincer' ligand with blocking groups in the 3- and 5-positions on the pyridine ring was desired, which led to the use of (I) as a starting material. Despite the use of very high temperatures (> 473 K) and lengthy reaction times (14 days), the reaction did not afford the doubly quaternized product. In order to overcome this obstacle, compound (II) with its weaker carbon–halogen bond was synthesized.

The asymmetric unit of (I) (Fig. 1) contains two independent molecules with similar geometric parameters (Table 1) and an overall Z of 8. The cell dimensions are close to tetragonal $P4_22_1$, but the data do not merge; instead, the structure was refined in the orthorhombic space group $P2_12_1$. The molecular dimensions are unremarkable, but the structure is a racemic twin with a Flack (1983) parameter of 0.471 (17). The molecule is planar, and the $Br1A-C1A-C2A-C6A$ and $N1A-C1A-C2A-C3A$ torsion angles (Table 1) do not indicate any significant steric interactions between the Br atoms and the methyl groups.

The molecule of compound (II) (Fig. 2) is slightly deformed into a saddle shape due to steric repulsion between the I atoms

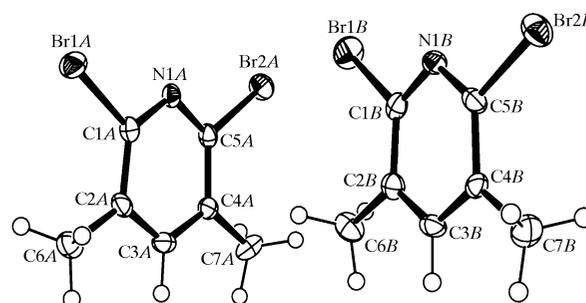


Figure 1

The two independent molecules of (I) in the asymmetric unit, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

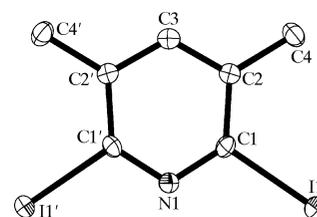


Figure 2

A representation of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted. Atoms marked with a prime (') are at the equivalent position $(1 - x, y, \frac{3}{2} - z)$.

and the respective *ortho* methyl groups. The extent of the distortion of the atoms bonded to the pyridine ring is indicated by the I1–C1–C2–C4 torsion angle (Table 2), where atom I1 and the methyl group (C4) are located on either side of the ring. Substituents *trans* to each other are distorted in the same direction above or below the ring, resulting in a saddle-shaped molecule. The saddle point can be found in the middle of the pyridine ring; this can be seen from the torsion angle for the atoms in the pyridine ring (N1–C1–C2–C3) being smaller than that for the atoms on the outside of the ring. The distortion of the ring can also be noted by the deviation out of the mean plane of all atoms in the ring, atom C2 lying 0.021 (2) Å out of the plane.

The molecular dimensions of (II) are unremarkable. Although only three structurally characterized compounds with 2-iodopyridine groups exist, the C1–I1 bond lengths are similar, as are the C1–N1 bond lengths (Table 2; Holmes *et al.*, 2002; Saha *et al.*, 2005).

A packing diagram of (I) is shown in Fig. 3. The only supramolecular interaction is face–face π -stacking, with no face–edge π -stacking. The molecules are arranged in alternating columns, resulting in an 'X' shape when viewed down the *b* axis. The dihedral angle between planes of the pyridine rings in successive molecules in a column is 72.69 (10)°.

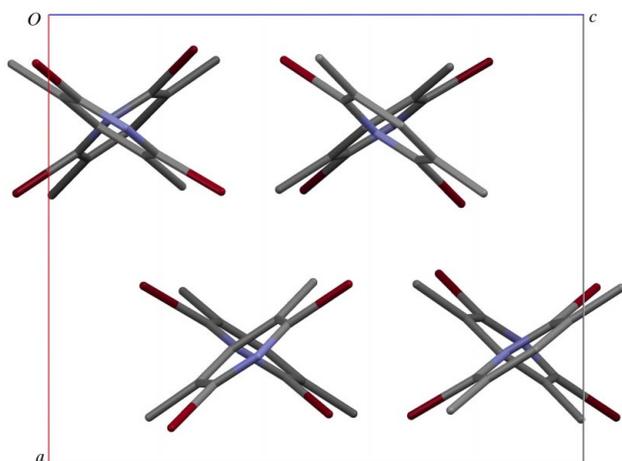


Figure 3
The packing of (I).

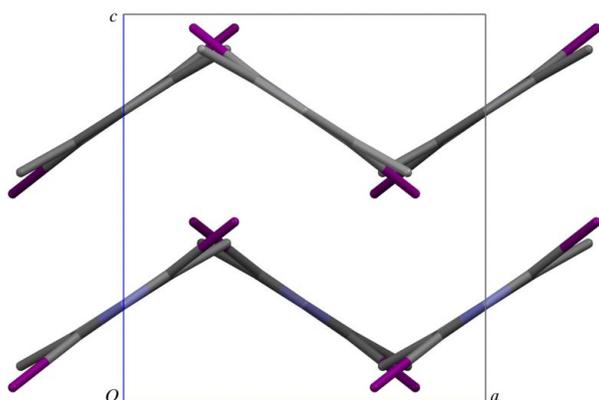


Figure 4
The packing of (II).

Compound (II) exhibits the same supramolecular interactions as (I), with face–face π -stacking the only supramolecular interaction. However, the molecules pack in a slightly different way, with alternating slanted columns of molecules resulting in a zigzag arrangement when viewed down the *b* axis (Fig. 4). Although 2,6-diiodopyridine exhibits both weak hydrogen-bonding interactions and weak halogen–halogen interactions (Holmes *et al.*, 2002), neither is present in (II); the intermolecular I···I distance of 4.233 Å is greater than the sum of the van der Waals radii, estimated as 4.00 Å by Rowland & Taylor (1996).

Experimental

Compound (I) was synthesized according to the method of Dunn & Guillermic (1988) in 64% yield and was crystallized from ethanol. Compound (II) was synthesized *via* an aromatic Finkelstein reaction from the reaction of (I) (15.00 g, 56.6 mmol), anhydrous NaI (34.13 g, 227.7 mmol), CuI (1.08 g, 5.7 mmol) and *N,N*-dimethylethylenediamine (DMEDA; 1.20 ml, 11.3 mmol) in refluxing 1,4-dioxane (250 ml) for 40 h under an inert atmosphere. After cooling, water (100 ml) was added, and the product was extracted into CH₂Cl₂, dried over MgSO₄, filtered and concentrated *in vacuo*. The resulting pale-orange solid was recrystallized from ethanol, affording colourless crystals in 83% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.20 (1H, *s*, Ar), 2.30 (6H, *s*, Me); ¹³C NMR (100.6 MHz, CDCl₃): δ 138.69 (C, C2/6), 137.49 (CH, C4), 119.38 (C, C3/5), 25.20 (CH₃, Me).

Compound (I)

Crystal data

C₇H₇Br₂N
M_r = 264.96
 Orthorhombic, *P*2₁2₁2₁
a = 10.5429 (3) Å
b = 12.4821 (4) Å
c = 12.6458 (3) Å
V = 1664.16 (8) Å³

Z = 8
D_x = 2.115 Mg m^{−3}
 Mo *K*α radiation
 μ = 9.66 mm^{−1}
T = 120 (2) K
 Fragment, colourless
 0.10 × 0.10 × 0.02 mm

Data collection

Bruker–Nonius KappaCCD
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2003)
*T*_{min} = 0.397, *T*_{max} = 0.826

14709 measured reflections
 2175 independent reflections
 1984 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.043
 θ _{max} = 27.5°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.026
wR (*F*²) = 0.049
S = 1.08
 2175 reflections
 186 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0144P)^2 + 1.0475P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.022
 $\Delta\rho$ _{max} = 0.46 e Å^{−3}
 $\Delta\rho$ _{min} = −0.50 e Å^{−3}
 Absolute structure: Flack (1983),
 1623 Friedel pairs
 Flack parameter: 0.471 (17)

Table 1

Selected geometric parameters (Å, °) for (I).

C1A–N1A	1.323 (5)	C1B–N1B	1.317 (5)
C1A–Br1A	1.904 (4)	C1B–Br1B	1.906 (4)
C5A–N1A	1.323 (5)	C5B–N1B	1.327 (5)
C5A–Br2A	1.905 (4)	C5B–Br2B	1.898 (4)
N1A–C1A–C2A–C3A	1.1 (6)	Br1A–C1A–C2A–C6A	0.6 (6)

Compound (II)

Crystal data

C₇H₇I₂N
M_r = 358.94
 Orthorhombic, *Pbcn*
a = 7.6194 (3) Å
b = 14.6296 (6) Å
c = 8.1057 (2) Å
V = 903.53 (6) Å³
Z = 4
D_x = 2.639 Mg m⁻³
 Mo *K*α radiation
 μ = 6.89 mm⁻¹
T = 120 (2) K
 Blade, colourless
 0.36 × 0.04 × 0.01 mm

Data collection

Bruker–Nonius KappaCCD
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2003)
T_{min} = 0.191, *T_{max}* = 0.934
 7765 measured reflections
 1049 independent reflections
 933 reflections with *I* > 2σ(*I*)
R_{int} = 0.035
θ_{max} = 27.7°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.021
wR(*F*²) = 0.047
S = 1.12
 1049 reflections
 48 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0083P)^2 + 2.3067P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.037
 Δρ_{max} = 0.60 e Å⁻³
 Δρ_{min} = -1.23 e Å⁻³

Table 2

Selected geometric parameters (Å, °) for (II).

C1–N1	1.330 (4)	C1–I1	2.116 (3)
N1–C1–C2–C3	3.9 (4)	I1–C1–C2–C4	6.8 (4)

The unit cell of (I) is close to being metrically primitive tetragonal, but the data do not merge in this setting (*R_{merge}* = 0.587). Compound (I) was refined as a racemic twin using the TWIN and BASF instructions; the final value of the BASF parameter was 0.471 (17). 1623 Friedel pairs were merged in the final cycle of refinement. For both (I) and (II), H atoms were placed in geometrically assigned positions, with fixed bond lengths of 0.95 (CH) and 0.98 Å (CH₃), and refined using a riding model, with *U_{iso}*(H) values of 1.2*U_{eq}*(CH) or 1.5*U_{eq}*(CH₃) of the parent atom.

For both compounds, data collection: COLLECT (Hooft, 1998); cell refinement: DENZO (Otwinowski & Minor, 1997) and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994) for (I) and

SHELXS97 (Sheldrick, 1997) for (II); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: PLATON (Spek, 2003), WinGX (Farrugia, 1999) and enCIFer (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3034). Services for accessing these data are described at the back of the journal.

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