4-Iodo-1H-pyrrole-2-carbaldehyde

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4-Iodo-1*H*-pyrrole-2-carbaldehyde

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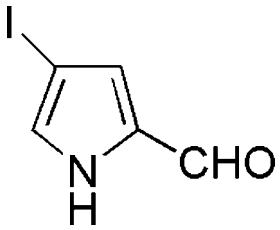
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.006 Å; R factor = 0.026; wR factor = 0.068; data-to-parameter ratio = 20.3.

The title compound, C_5H_4INO, was synthesized during research aimed at producing suitable halogenated pyrrole building blocks for Suzuki–Miyaura coupling reactions. In the crystal structure, the molecules are planar and exhibit N—H···O bonding to form centrosymmetric dimers.

Related literature

For related literature, see: Davis *et al.* (2002); Mitsui *et al.* (2003); Miyaura & Suzuki (1995); Monti & Sleiter (1990); Smith *et al.* (1985); Sonnet (1972).



Experimental

Crystal data

C_5H_4INO
M_r = 220.99
Monoclinic, $P2_1/c$
a = 10.245 (3) Å
b = 4.726 (2) Å
c = 13.531 (4) Å
β = 92.73 (2)°
V = 654.4 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.79 mm^{-1}
T = 295 (2) K
0.40 × 0.40 × 0.15 mm

Data collection

Rigaku AFC-7*R* diffractometer
Absorption correction: ψ-scan (North *et al.*, 1968)
T_{min} = 0.250, T_{max} = 0.533
(expected range = 0.229–0.487)
1793 measured reflections
1505 independent reflections
1281 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
3 standard reflections
every 150 reflections
intensity decay: 1.8%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.068
S = 1.11
1505 reflections
74 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.69 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^{i}	0.88	2.00	2.843 (5)	161
C5—H5···O2^{ii}	0.95	2.50	3.400 (5)	158

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

Data collection: *MSC/AFC7 Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC7 Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *TEXSAN*; program(s) used to refine structure: *TEXSAN* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2326).

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supplementary materials

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4-Iodo-1*H*-pyrrole-2-carbaldehyde

R. A. Davis, A. R. Carroll, R. J. Quinn, P. C. Healy and A. R. White

Comment

The title compound, (I), (Fig. 1) was synthesized during research aimed at producing suitable halogenated pyrrole building blocks for Suzuki–Miyaura coupling reactions (Miyaura & Suzuki, 1995; Davis *et al.*, 2002). Although compound (I) has been previously synthesized using a variety of methods (Mitsui *et al.*, 2003; Monti & Sleiter 1990; Sonnet, 1972) this is the first report of the X-ray crystal structure for 4-iodo-1*H*-pyrrole-2-carbaldehyde. As observed for related structures (Smith *et al.*, 1985), the molecules are planar and exhibit N—H···O bonding to form centrosymmetric dimers (Fig. 2).

Experimental

The commercial reagent pyrrole-2-carbaldehyde (475 mg, 5 mmol) was added to an argon charged two-necked flask (50 ml) to which dry THF (20 ml) was added and the mixture stirred for 10 min before being cooled to 195 K. *N*-iodosuccinimide (1.12 g, 5 mmol) was added portionwise over 15 min then the mixture was stirred at 195 K for 1 h before being transferred to a 258 K refrigerator for 16 h. The solvent was removed under vacuum and the material was partitioned between H_2O (50 ml) and DCM (2 *x* 50 ml). The organic phase was dried ($MgSO_4$), then the DCM was evaporated under reduced pressure. The resulting residue was dissolved in DMSO (10 ml) then chromatographed over a C_{18} flash column (40 mm *x* 80 mm) using 10% stepwise elutions from 20% MeOH/80% H_2O to 100% MeOH. The 70% MeOH/30% H_2O elution contained a 9:1 mixture of 4-iodo-1*H*-pyrrole-2-carbaldehyde and 5-iodo-1*H*-pyrrole-2-carbaldehyde (165 mg), which proved to be inseparable by reversed-phase HPLC. Fractional crystallization using DCM/hexanes produced pure 4-iodo-1*H*-pyrrole-2-carbaldehyde (72 mg, 6.5% yield). Low yielding di-iodinated and tri-iodinated pyrrole derivatives were also detected during the purification work however no crystalline material was obtained for these compounds. NMR assignments for compound (I) were determined following analysis of the one-dimensional and two-dimensional NMR (1*H*, 13 C, gCOSY, gHSQC, gHMBC) data.

4-iodo-1*H*-pyrrole-2-carbaldehyde (I): clear needles, m.p. 390–391 K. ^{1}H NMR (DMSO-d_6, 600 MHz) δ 7.12 (1*H*, s, H-3), 7.33 (1*H*, s, H-5), 9.43 (1*H*, s, 2-CHO), 12.37 (1*H*, br s, 1-NH). ^{13}C NMR (DMSO-d_6, 150 MHz) δ 62.7 (C-4), 126.0 (C-3), 131.3 (C-5), 134.4 (C-2), 178.7 (2-CHO). (-)-LRESIMS (*rel*. int.) m/*z* 220 (100%) $[M—H, C_5H_3INO]^-$.

Refinement

The carbon-bound H atoms were constrained as riding atoms with C—H = 0.95–0.96 Å. The pyrrole proton was located in a difference Fourier synthesis and constrained with N—H = 0.88 Å. U_{iso}(H) values were set at 1.2U_{eq} of the parent atom.

Figures

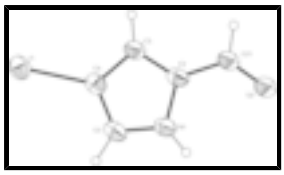

Fig. 1. View of (I) with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.

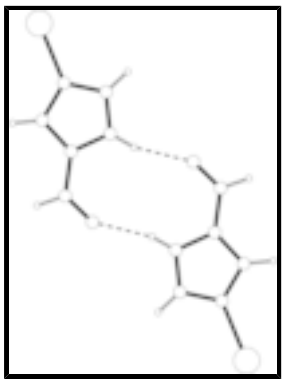

Fig. 2. View of the centrosymmetric dimers of (I).

4-iodo-1*H*-pyrrole-2-carbaldehyde

Crystal data

C_5H_4INO	F_{000} = 408
M_r = 220.99	D_x = 2.243 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71069 Å
Hall symbol: -P 2ybc	Cell parameters from 25 reflections
a = 10.245 (3) Å	θ = 12.5–16.3º
b = 4.726 (2) Å	μ = 4.79 mm^{-1}
c = 13.531 (4) Å	T = 295 (2) K
β = 92.73 (2)º	Plate, colourless
V = 654.4 (4) Å^3	0.40 × 0.40 × 0.15 mm
Z = 4	

Data collection

Rigaku AFC-7R diffractometer	R_{int} = 0.018
Radiation source: Rigaku rotating anode	θ_{max} = 27.5º
Monochromator: graphite	θ_{min} = 3.0º
T = 295 K	h = −13→13
ω/2θ scans	k = −2→6
Absorption correction: ψ scan (North *et al.*, 1968)	l = −7→17
T_{min} = 0.250, T_{max} = 0.533	3 standard reflections
1793 measured reflections	every 150 reflections
1505 independent reflections	intensity decay: 1.8%

1281 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.026$	$w = 1/[\sigma^2(F_o^2) + (0.0254P)^2 + 0.8517P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.068$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.11$	$\Delta\rho_{max} = 0.56$ e Å^{-3}
1505 reflections	$\Delta\rho_{min} = -0.69$ e Å^{-3}
74 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^*=kFc[1+0.001Fc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0057 (6)
Secondary atom site location: difference Fourier map	

Special details

Experimental. The scan width was (1.79 + 0.30tanθ)° with an ω scan speed of 16° per minute (up to 5 scans to achieve I/σ(I) > 10). Stationary background counts were recorded at each end of the scan, and the scan time:background time ratio was 2:1.

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodness of fit values S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The observed criterion of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating –*R*-factor-obs *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.10101 (3)	0.11438 (6)	0.17038 (2)	0.0593 (1)
O2	0.4065 (3)	0.9850 (9)	−0.1241 (2)	0.0696 (10)
N1	0.3783 (3)	0.6731 (8)	0.0582 (2)	0.0536 (10)
C2	0.2945 (4)	0.6628 (9)	−0.0239 (3)	0.0521 (13)
C3	0.1952 (4)	0.4801 (10)	−0.0045 (3)	0.0531 (11)
C4	0.2196 (4)	0.3788 (8)	0.0908 (3)	0.0490 (11)
C5	0.3333 (4)	0.5006 (10)	0.1282 (3)	0.0547 (13)
C21	0.3154 (4)	0.8263 (11)	−0.1112 (3)	0.0601 (14)
H1	0.45070	0.77370	0.06420	0.0630*
H2	0.25140	0.80760	−0.16460	0.0710*
H3	0.12300	0.42850	−0.04790	0.0630*
H5	0.37100	0.46580	0.19280	0.0640*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0656 (2)	0.0567 (2)	0.0560 (2)	0.0093 (1)	0.0078 (1)	0.0053 (1)
O2	0.0663 (18)	0.096 (2)	0.0456 (15)	−0.0168 (18)	−0.0061 (13)	0.0071 (17)
N1	0.0476 (16)	0.071 (2)	0.0417 (16)	0.0030 (16)	−0.0029 (13)	−0.0036 (16)
C2	0.053 (2)	0.065 (3)	0.0376 (17)	0.0046 (19)	−0.0053 (15)	−0.0039 (17)
C3	0.053 (2)	0.062 (2)	0.0435 (19)	−0.0021 (19)	−0.0067 (16)	−0.0025 (19)
C4	0.0533 (19)	0.052 (2)	0.0418 (18)	0.0109 (17)	0.0035 (15)	−0.0023 (17)
C5	0.056 (2)	0.069 (3)	0.0387 (18)	0.013 (2)	−0.0017 (16)	−0.0012 (19)
C21	0.058 (2)	0.081 (3)	0.0404 (19)	−0.008 (2)	−0.0070 (16)	0.002 (2)

Geometric parameters (Å, °)

I1—C4	2.079 (4)	C2—C21	1.436 (6)
O2—C21	1.216 (6)	C3—C4	1.387 (6)
N1—C2	1.372 (5)	C4—C5	1.374 (6)
N1—C5	1.348 (5)	C3—H3	0.9500
N1—H1	0.8800	C5—H5	0.9500
C2—C3	1.369 (6)	C21—H2	0.9600
I1···C4^{i}	3.853 (4)	C4···I1^{vii}	3.853 (4)
I1···C5^{i}	3.812 (5)	C5···I1^{vii}	3.812 (5)
I1···I1^{ii}	3.8646 (17)	C5···O2^{viii}	3.400 (5)
I1···I1^{iii}	3.8646 (17)	C21···H1^{vi}	3.0900
I1···H2^{iv}	3.3200	C21···H5^{v}	2.9100
O2···N1	2.900 (5)	H1···O2	2.7500
O2···C5^{v}	3.400 (5)	H1···O2^{vi}	2.0000
O2···N1^{vi}	2.843 (5)	H1···C21^{vi}	3.0900
O2···H1^{vi}	2.0000	H2···I1^{ix}	3.3200
O2···H1	2.7500	H2···H5^{v}	2.5700
O2···H5^{v}	2.5000	H5···O2^{viii}	2.5000
N1···O2	2.900 (5)	H5···C21^{viii}	2.9100
N1···O2^{vi}	2.843 (5)	H5···H2^{viii}	2.5700
C2—N1—C5	109.0 (3)	C3—C4—C5	108.1 (4)
C5—N1—H1	125.00	N1—C5—C4	107.9 (3)
C2—N1—H1	126.00	O2—C21—C2	126.5 (4)
N1—C2—C21	122.3 (4)	C2—C3—H3	127.00
N1—C2—C3	108.0 (4)	C4—C3—H3	126.00
C3—C2—C21	129.7 (4)	N1—C5—H5	128.00
C2—C3—C4	107.1 (4)	C4—C5—H5	124.00
I1—C4—C5	124.6 (3)	O2—C21—H2	117.00
I1—C4—C3	127.2 (3)	C2—C21—H2	117.00
C5—N1—C2—C3	0.0 (5)	C3—C2—C21—O2	−179.7 (5)
C5—N1—C2—C21	179.5 (4)	C2—C3—C4—I1	175.5 (3)
C2—N1—C5—C4	−0.1 (5)	C2—C3—C4—C5	0.0 (5)

N1—C2—C3—C4	0.0 (5)	I1—C4—C5—N1	−175.6 (3)
C21—C2—C3—C4	−179.4 (4)	C3—C4—C5—N1	0.1 (5)
N1—C2—C21—O2	1.1 (7)		

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*, *y*−1/2, −*z*+1/2; (iii) −*x*, *y*+1/2, −*z*+1/2; (iv) *x*, −*y*+1/2, *z*+1/2; (v) *x*, −*y*+3/2, *z*−1/2; (vi) −*x*+1, −*y*+2, −*z*; (vii) *x*, *y*+1, *z*; (viii) *x*, −*y*+3/2, *z*+1/2; (ix) *x*, −*y*+1/2, *z*−1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2^{vi}	0.88	2.00	2.843 (5)	161
C5—H5···O2^{viii}	0.95	2.50	3.400 (5)	158

Symmetry codes: (vi) −*x*+1, −*y*+2, −*z*; (viii) *x*, −*y*+3/2, *z*+1/2.

Fig. 1

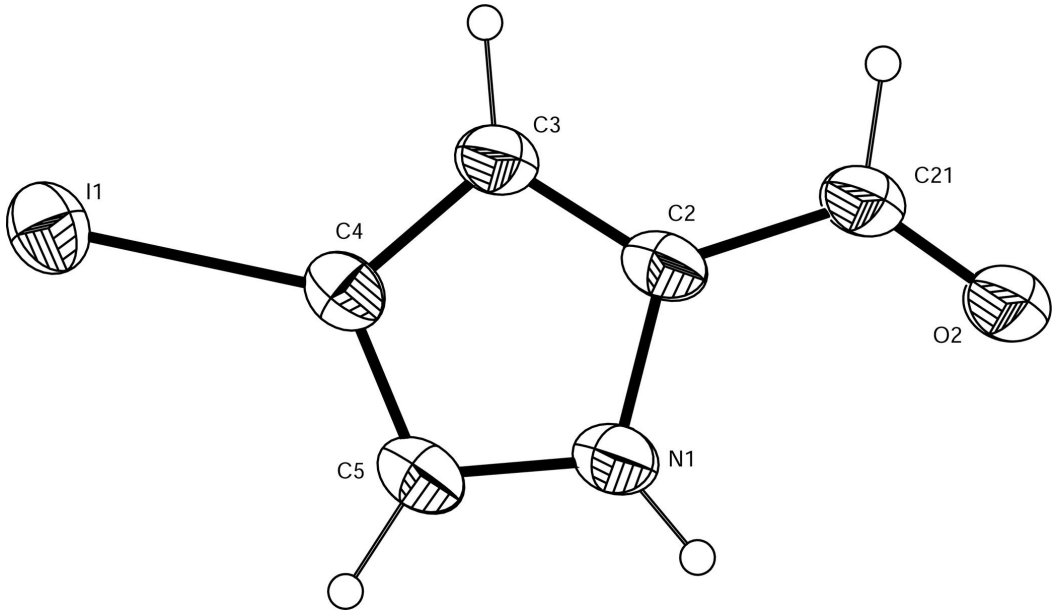

Fig. 2