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2-(4-Iodo-1-methyl-1*H*-pyrazol-3-yl)pyridinium dichloroiodide

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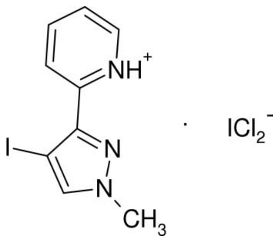
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; R factor = 0.027; wR factor = 0.069; data-to-parameter ratio = 16.8.

In the title molecular salt, $C_9H_9IN_3^+\cdot ICl_2^-$, the dihedral angle between the aromatic rings in the cation is 14.9 (2)°. The I—Cl bond lengths of the anion are distinctly different, by 0.149 (2) Å. The most significant interaction in the crystal structure is a bifurcated N—H···(N,Cl) hydrogen bond.

Related literature

For background, see: Rømming (1958); Greenwood & Earnshaw (1997); Wang *et al.* (1999). For reference structural data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_9H_9IN_3^+\cdot Cl_2I^-$
M_r = 483.89
Monoclinic, $P2_1/c$
a = 8.4261 (4) Å
b = 8.0183 (4) Å
c = 21.4692 (10) Å
β = 98.604 (1)°
V = 1434.20 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.74 mm^{-1}
T = 293 (2) K
0.29 × 0.19 × 0.12 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.340, T_{max} = 0.601 (expected range = 0.320–0.566)
8399 measured reflections
2523 independent reflections
2256 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.069
S = 1.04
2523 reflections
150 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.35 e Å^{-3}
$\Delta\rho_{min}$ = −1.15 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

I2—Cl2	2.4819 (13)	I2—Cl1	2.6308 (13)
Cl2—I2—Cl1	178.86 (5)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N2	0.78 (5)	2.32 (5)	2.683 (5)	109 (4)
N1—H1···Cl1	0.78 (5)	2.54 (5)	3.216 (4)	146 (5)
C2—H2···Cl2^{i}	0.93	2.77	3.664 (5)	160

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

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The author thanks M. R. St J. Foreman and M. John Plater for supplying the sample.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2504).

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supplementary materials

Acta Cryst. (2007). E**63**, o4045 [**doi:10.1107/S1600536807044169**]

2-(4-Iodo-1-methyl-1*H*-pyrazol-3-yl)-pyridinium dichloroiodide

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Comment

The title compound, (I), is a molecular salt (Fig. 1), with normal geometrical parameters for the organic component (Allen *et al.*, 1995). The dihedral angle betwen the N1/C1—C5 and N2/N3/C6—C8 rings in the cation is 14.9 (2)°. The C1—N1—C5 bond angle of 124.2 (4)° is typically expanded due to the protonation of N1 (Wang *et al.*, 1999).

The two I—Cl bond lengths (Table 1) in the ICl_2^- anion in (I) are significantly different, by some 0.149 (2) Å. Sometimes (Wang *et al.*, 1999) the two bond lengths in the ICl_2^- anion are constrained to be the same by symmetry. However, in $C_4H_{12}N_2{\cdot}(ICl_2)_2$, the difference between the two bonds of 0.22Å (Romming, 1958) is even greater than seen here. In all cases, the Cl—I—Cl bond angle is close to linear, in accordance with the predictions of VSEPR or qualitative MO theory (Greenwood & Earnshaw, 1997).

In the crystal, the components interact by way of an intra/intermolecular bifurcated N—H···(N,Cl) hydrogen bond (Table 2). A weak C—H···Cl contact also occurs. The separation of I1 and $Cl1^{ii}$ (ii = x, $1/2 - y$, $z - 1/2$) of 3.5275 (13)Å is some 0.2 Å less than the van der Waals separation of I and Cl of 3.73 Å. If this is considered to be a bonding interaction, [001] chains of ion-pairs are the result (Fig. 2).

Experimental

The title compound arose from the attempted methylation (with MeI) of 3-(2-pyridine)-pyrazole hydrochloride. Orange blocks of (I) were recoverd from the reaction. Their composition could not be determined on the basis of spectroscopic measurements and the single-crystal study was performed to identify the title compound. The mechanism of formation of (I) requires further investigation.

Refinement

The N-bound H atom was located in a difference map and its position were freely refined with $U_{iso}(H) = 1.2U_{eq}(N)$.

The C-bound H atoms were placed geometrically (C—H = 0.93–0.96 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(carrier)$ or $1.5U_{eq}$(methyl C). The methyl group was allowed to rotate, but not to tip, to best fit the electron density.

Figures

Fig. 1. The molecular structure of (I) (50% displacement ellipsoids, arbitrary spheres for the H atoms, hydrogen bonds indicated by double dashed lines).

Fig. 2. An [001] chain in (I) arising from N—H···Cl hydrogen bonds and possible I···Cl interactions. Symmetry code: (ii) x, $1/2 - y$, $z - 1/2$.

2-(4-Iodo-1-methyl-1*H*-pyrazol-3-yl)-pyridinium dichloroiodide

Crystal data

$C_9H_9IN_3{}^{+}\cdot Cl_2I^{-}$
$M_r = 483.89$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 8.4261$ (4) Å
$b = 8.0183$ (4) Å
$c = 21.4692$ (10) Å
$\beta = 98.604$ (1)°
$V = 1434.20$ (12) Å^3
$Z = 4$

$F_{000} = 896$
$D_x = 2.241$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 5028 reflections
$\theta = 2.5$–25.0°
$\mu = 4.74$ mm^{-1}
$T = 293$ (2) K
Block, orange
0.29 × 0.19 × 0.12 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Radiation source: fine-focus sealed tube
Monochromator: graphite
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ω scans
Absorption correction: multi-scan (SADABS; Bruker, 1999)
$T_{\min} = 0.340$, $T_{\max} = 0.601$
8399 measured reflections

2523 independent reflections
2256 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.029$
$\theta_{\max} = 25.0$°
$\theta_{\min} = 1.9$°
$h = -10 \rightarrow 9$
$k = -7 \rightarrow 9$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.027$

Hydrogen site location: difmap and geom
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o{}^2) + (0.0376P)^2 + 1.477P]$

	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.069$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.04$	$\Delta\rho_{max} = 1.35$ e Å^{-3}
2523 reflections	$\Delta\rho_{min} = -1.15$ e Å^{-3}
150 parameters	Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0015 (2)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2sigma(F^2)$ is used only for calculating *R*-factors(gt) *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}
C1	0.3644 (5)	0.1154 (6)	0.6860 (2)	0.0506 (11)
H1A	0.3397	0.0788	0.7246	0.061*
C2	0.2569 (6)	0.0942 (7)	0.6326 (2)	0.0626 (13)
H2	0.1585	0.0429	0.6339	0.075*
C3	0.2985 (6)	0.1513 (8)	0.5760 (2)	0.0641 (14)
H3	0.2264	0.1396	0.5390	0.077*
C4	0.4438 (6)	0.2244 (6)	0.5744 (2)	0.0526 (11)
H4	0.4704	0.2620	0.5363	0.063*
C5	0.5527 (5)	0.2428 (5)	0.62949 (19)	0.0361 (8)
C6	0.7118 (5)	0.3184 (5)	0.63513 (18)	0.0362 (8)
C7	0.8107 (5)	0.3601 (5)	0.59068 (18)	0.0401 (9)
C8	0.9446 (5)	0.4287 (5)	0.6250 (2)	0.0444 (10)
H8	1.0336	0.4701	0.6091	0.053*
C9	1.0300 (6)	0.4922 (8)	0.7394 (2)	0.0732 (17)
H9A	1.0087	0.4379	0.7771	0.110*
H9B	1.0117	0.6099	0.7426	0.110*
H9C	1.1395	0.4730	0.7340	0.110*
N1	0.5052 (4)	0.1889 (4)	0.68311 (17)	0.0395 (8)
H1	0.570 (6)	0.193 (6)	0.713 (2)	0.047*
N2	0.7823 (4)	0.3587 (4)	0.69377 (15)	0.0396 (8)
N3	0.9241 (4)	0.4256 (5)	0.68572 (16)	0.0437 (8)
I1	0.77668 (4)	0.33639 (5)	0.493422 (14)	0.06943 (16)
I2	0.37423 (3)	0.26801 (3)	0.869408 (12)	0.04377 (12)

Cl1	0.62989 (15)	0.1392 (2)	0.83096 (6)	0.0648 (3)
Cl2	0.13126 (16)	0.3839 (2)	0.90614 (6)	0.0740 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.045 (2)	0.060 (3)	0.049 (3)	−0.008 (2)	0.017 (2)	−0.002 (2)
C2	0.041 (2)	0.082 (4)	0.065 (3)	−0.024 (2)	0.008 (2)	−0.010 (3)
C3	0.049 (3)	0.092 (4)	0.048 (3)	−0.012 (3)	−0.002 (2)	−0.006 (3)
C4	0.050 (3)	0.070 (3)	0.036 (2)	−0.012 (2)	0.002 (2)	0.002 (2)
C5	0.040 (2)	0.035 (2)	0.033 (2)	−0.0018 (16)	0.0070 (16)	−0.0017 (16)
C6	0.041 (2)	0.0326 (19)	0.035 (2)	−0.0001 (16)	0.0065 (17)	0.0037 (16)
C7	0.044 (2)	0.047 (2)	0.030 (2)	−0.0020 (18)	0.0090 (17)	0.0002 (17)
C8	0.042 (2)	0.050 (2)	0.044 (2)	−0.0015 (19)	0.0155 (18)	0.0034 (19)
C9	0.056 (3)	0.112 (5)	0.048 (3)	−0.034 (3)	−0.006 (2)	−0.004 (3)
N1	0.0387 (19)	0.0448 (19)	0.0348 (18)	−0.0024 (15)	0.0047 (14)	0.0016 (15)
N2	0.0344 (17)	0.051 (2)	0.0330 (17)	−0.0054 (15)	0.0022 (14)	0.0047 (15)
N3	0.0359 (17)	0.055 (2)	0.0395 (19)	−0.0069 (16)	0.0026 (14)	0.0007 (16)
I1	0.0779 (3)	0.0981 (3)	0.03559 (19)	−0.0296 (2)	0.01929 (16)	−0.00920 (16)
I2	0.04535 (18)	0.04520 (18)	0.03920 (18)	−0.00216 (12)	0.00128 (12)	0.00301 (11)
Cl1	0.0531 (6)	0.0988 (10)	0.0434 (6)	0.0133 (6)	0.0107 (5)	0.0076 (6)
Cl2	0.0652 (8)	0.0984 (10)	0.0581 (8)	0.0316 (8)	0.0079 (6)	−0.0003 (7)

Geometric parameters (Å, °)

C1—N1	1.334 (6)	C7—C8	1.367 (6)
C1—C2	1.361 (7)	C7—I1	2.073 (4)
C1—H1A	0.9300	C8—N3	1.341 (5)
C2—C3	1.391 (7)	C8—H8	0.9300
C2—H2	0.9300	C9—N3	1.449 (6)
C3—C4	1.363 (7)	C9—H9A	0.9600
C3—H3	0.9300	C9—H9B	0.9600
C4—C5	1.392 (6)	C9—H9C	0.9600
C4—H4	0.9300	N1—H1	0.78 (5)
C5—N1	1.346 (5)	N2—N3	1.345 (4)
C5—C6	1.460 (6)	I2—Cl2	2.4819 (13)
C6—N2	1.348 (5)	I2—Cl1	2.6308 (13)
C6—C7	1.398 (5)		
N1—C1—C2	120.0 (4)	C8—C7—I1	123.9 (3)
N1—C1—H1A	120.0	C6—C7—I1	131.2 (3)
C2—C1—H1A	120.0	N3—C8—C7	107.5 (4)
C1—C2—C3	118.1 (4)	N3—C8—H8	126.2
C1—C2—H2	120.9	C7—C8—H8	126.2
C3—C2—H2	120.9	N3—C9—H9A	109.5
C4—C3—C2	120.6 (4)	N3—C9—H9B	109.5
C4—C3—H3	119.7	H9A—C9—H9B	109.5
C2—C3—H3	119.7	N3—C9—H9C	109.5
C3—C4—C5	120.3 (4)	H9A—C9—H9C	109.5

C3—C4—H4	119.9	H9B—C9—H9C	109.5
C5—C4—H4	119.9	C1—N1—C5	124.2 (4)
N1—C5—C4	116.8 (4)	C1—N1—H1	120 (4)
N1—C5—C6	116.7 (4)	C5—N1—H1	116 (4)
C4—C5—C6	126.5 (4)	N3—N2—C6	104.6 (3)
N2—C6—C7	110.8 (3)	C8—N3—N2	112.2 (3)
N2—C6—C5	116.6 (3)	C8—N3—C9	127.8 (4)
C7—C6—C5	132.6 (4)	N2—N3—C9	119.9 (4)
C8—C7—C6	104.8 (3)	Cl2—I2—Cl1	178.86 (5)

N1—C1—C2—C3	−0.2 (8)	C5—C6—C7—I1	0.9 (7)
C1—C2—C3—C4	0.9 (9)	C6—C7—C8—N3	0.4 (5)
C2—C3—C4—C5	−0.1 (8)	I1—C7—C8—N3	179.1 (3)
C3—C4—C5—N1	−1.4 (7)	C2—C1—N1—C5	−1.4 (7)
C3—C4—C5—C6	−179.8 (5)	C4—C5—N1—C1	2.1 (6)
N1—C5—C6—N2	−13.3 (5)	C6—C5—N1—C1	−179.3 (4)
C4—C5—C6—N2	165.1 (4)	C7—C6—N2—N3	0.2 (4)
N1—C5—C6—C7	166.8 (4)	C5—C6—N2—N3	−179.7 (3)
C4—C5—C6—C7	−14.7 (7)	C7—C8—N3—N2	−0.3 (5)
N2—C6—C7—C8	−0.4 (5)	C7—C8—N3—C9	−176.6 (5)
C5—C6—C7—C8	179.4 (4)	C6—N2—N3—C8	0.1 (5)
N2—C6—C7—I1	−179.0 (3)	C6—N2—N3—C9	176.7 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N2	0.78 (5)	2.32 (5)	2.683 (5)	109 (4)
N1—H1···Cl1	0.78 (5)	2.54 (5)	3.216 (4)	146 (5)
C2—H2···Cl2^{i}	0.93	2.77	3.664 (5)	160

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

Fig. 1

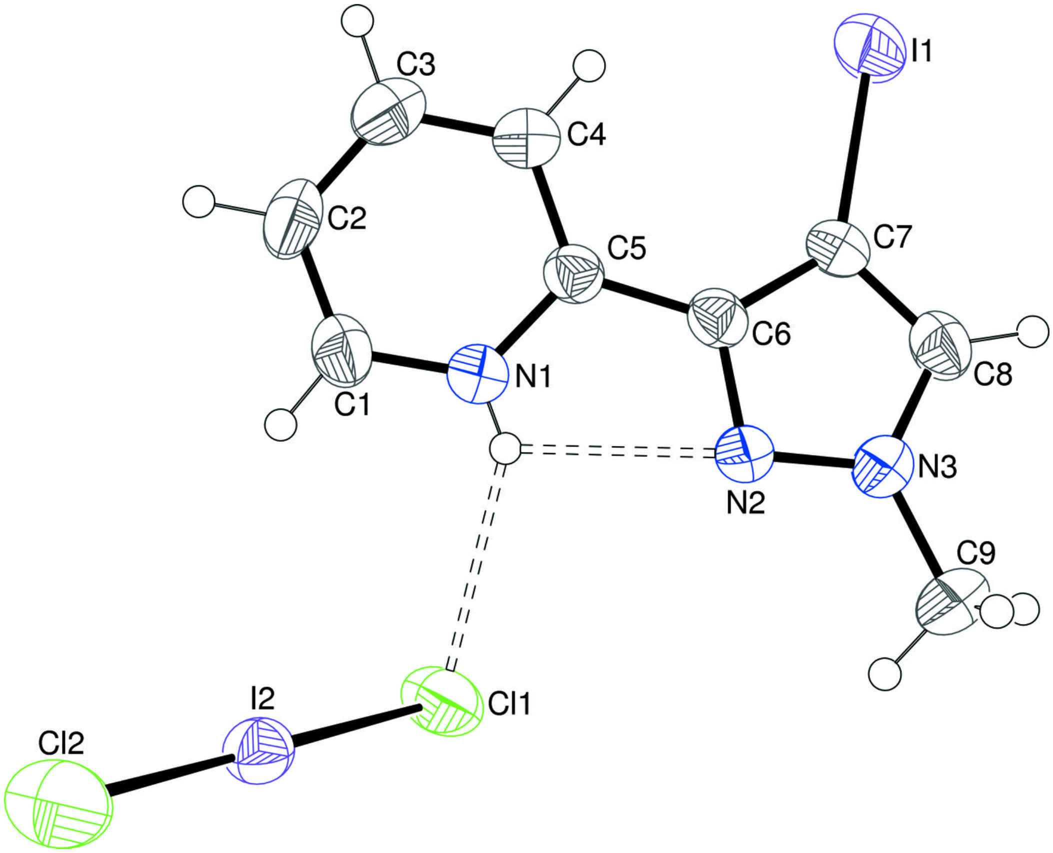

Fig. 2