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1,2,3,5-Tetramethyl-1*H*-pyrazol-2-ium triiodide

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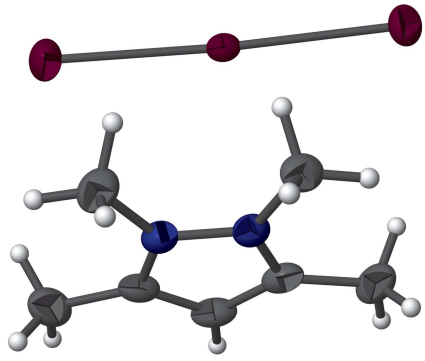
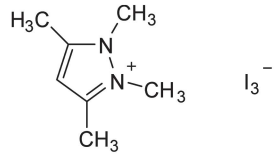
The title salt, $C_7H_{13}N_2^+\cdot I_3^-$, was obtained unintentionally by methylation of 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine and subsequent fragmentation. The pyrazolium ring is almost planar (r.m.s. deviation = 0.003 Å) and the triiodide anion deviates slightly from linearity [I—I—I = 177.099 (12)°]. No directional interactions occur in the crystal.

3D view



Chemical scheme



Structure description

Quaternary pyrazolium salts have been prepared by alkylation of pyrazoles (Elguero *et al.*, 1969) and a one-pot synthesis of the related 1,2,3,5-tetramethylpyrazolium chloride has been reported (Hobbs & Wilson, 1972). Pyrazolium salts are well known plant-growth regulators (Jäger & Lürssen, 1976) and herbicides (Jäger & Eue, 1976).

The molecular structure of the ion pair of the title compound is shown in Fig. 1. The pyrazolium ring is almost perfectly planar (r.m.s. deviation = 0.003 Å). The triiodide ion deviates significantly from linearity with an I1—I2—I3 angle of 177.099 (12)°, which is close to the mean value for triiodide ions taken from the Cambridge Structure Database (Version 5.37; Groom *et al.*, 2016) of 178°. There are no directional classic hydrogen bonds in this structure, although Hirshfeld surface calculation (Spackman & Jayatilaka, 2009) revealed a large percentage of H···I interactions (39.5% of the total surface) with distances to the extent of the sum of van der Waals radii. The crystal packing is shown in Fig. 2.

A few related structures (Han & Huynh, 2007; Han *et al.*, 2007, 2010, 2011) of pyrazolium salts and derived *N*-heterocyclic carbene (NHC) complexes have been reported.

Synthesis and crystallization

A solution of 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (0.5 g, 1.85 mmol; Coburn *et al.*, 1991) and CH_3I (0.46 ml, 7.4 mmol) in $CHCl_3$ (4 ml) was heated at 368 K

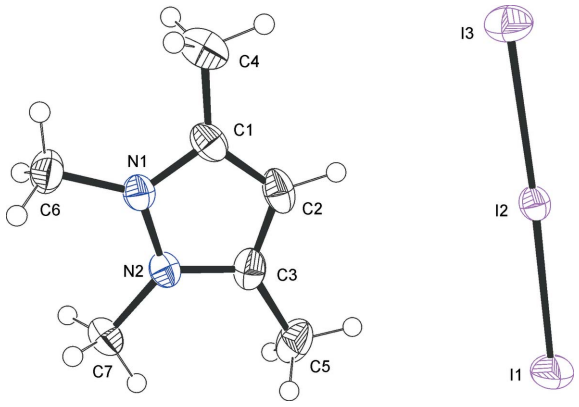


Figure 1
The molecular structure of the ion pair of the title compound, showing the atom labels and 50% probability displacement ellipsoids for non-H atoms.

for five days in a sealed tube. Red crystals (0.89 g, 95%) precipitated which were washed with $CHCl_3$ and dried, m.p. 442 K. The PXRD (Mo Kα radiation) of the bulk material was identical to the one calculated from the single-crystal diffraction data (Fig. 3), indicating phase purity. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.40 (*s*, 6H), 3.89 (*s*, 6H), 6.53 (*s*, 1H) p.p.m. ^{13}C NMR (75 MHz, DMSO-d_6): δ 11.3, 33.5, 106.9, 145.1 p.p.m. IR (neat): ν 3287, 3084, 2991, 2930, 1680, 1609, 1577, 1480, 1420, 1274, 1161, 1077, 1046, 1023, 968, 941, 842, 816, 756, 719, 659, 646, 621, 588, 554, 516, 470, 420 cm^{-1}.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_7H_{13}N_2^+\cdot I_3^-$
M_r	505.89
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	193
a, b, c (Å)	9.6719 (7), 13.4005 (9), 11.1874 (8)
β (°)	112.994 (2)
V (Å^3)	1334.77 (16)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	6.99
Crystal size (mm)	0.16 × 0.13 × 0.08
Data collection	
Diffractometer	Bruker D8 QUEST PHOTON 100
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.397, 0.562
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22167, 2648, 2400
R_{int}	0.028
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.619
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.062, 1.24
No. of reflections	2648
No. of parameters	113
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.40, −1.21

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXTL-XT2014/4* and *SHELXL2014/7* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2006).

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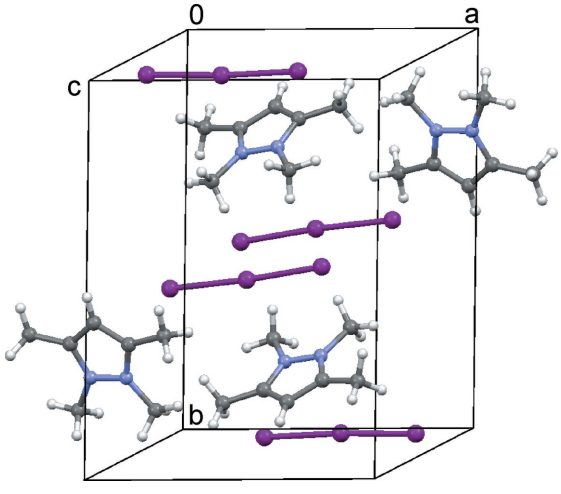

Figure 2
Crystal packing of the title compound.

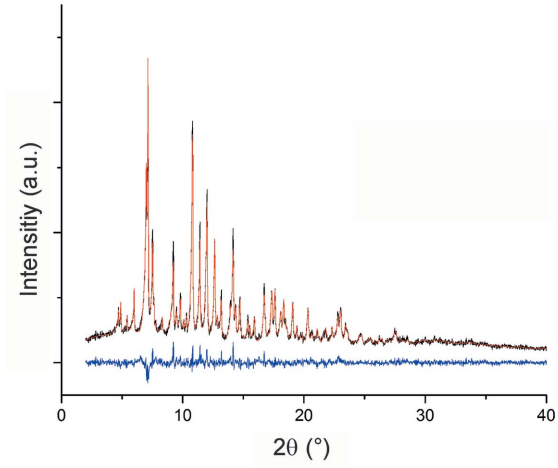

Figure 3
Pawley fit (R_{wp} = 6.62%, R_{exp} = 6.43%, R_p = 5.23%, gof = 1.03) of the PXRD data with a model calculated from the structural data of the single-crystal structure determination. Black dots indicate raw data, while the red line indicates the calculated model. The difference curve is shown in blue.

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full crystallographic data

IUCrData (2016). **1**, x161331 [doi:10.1107/S2414314616013316]

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Crystal data

$C_7H_{13}N_2^+\cdot I_3^-$
M_r = 505.89
Monoclinic, $P2_1/n$
a = 9.6719 (7) Å
b = 13.4005 (9) Å
c = 11.1874 (8) Å
β = 112.994 (2)°
V = 1334.77 (16) Å^3
Z = 4
$F(000)$ = 912
D_x = 2.517 Mg m^{-3}
Melting point: 442 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9875 reflections
θ = 2.4–26.0°
μ = 6.99 mm^{-1}
T = 193 K
Prism, red
0.16 × 0.13 × 0.08 mm

Data collection

Bruker D8 QUEST PHOTON 100 diffractometer
Radiation source: Incoatec Microfocus
Multi layered optics monochromator
Detector resolution: 10.4 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
T_{min} = 0.397, T_{max} = 0.562
22167 measured reflections
2648 independent reflections
2400 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 26.1°, θ_{min} = 2.4°
h = −11→11
k = −16→16
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.062
S = 1.24
2648 reflections
113 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0207P)^2 + 3.0909P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −1.21 e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.53163 (4)	0.57210 (2)	0.18064 (3)	0.04747 (10)
I2	0.31387 (3)	0.58881 (2)	0.29850 (2)	0.02818 (8)
I3	0.09003 (3)	0.59495 (2)	0.41519 (3)	0.04406 (10)
C1	0.6156 (5)	0.8272 (3)	0.4063 (4)	0.0339 (9)
C2	0.4931 (5)	0.8817 (3)	0.4027 (4)	0.0368 (9)
H2	0.4512	0.9379	0.3490	0.044*
C3	0.4422 (4)	0.8404 (3)	0.4907 (4)	0.0337 (9)
C4	0.7113 (6)	0.8394 (4)	0.3308 (5)	0.0484 (11)
H4A	0.8144	0.8549	0.3901	0.073*
H4B	0.6719	0.8939	0.2683	0.073*
H4C	0.7107	0.7774	0.2842	0.073*
C5	0.3137 (5)	0.8684 (4)	0.5255 (5)	0.0458 (11)
H5A	0.2409	0.8136	0.5030	0.069*
H5B	0.2652	0.9285	0.4774	0.069*
H5C	0.3503	0.8816	0.6190	0.069*
C6	0.7544 (5)	0.6788 (3)	0.5368 (4)	0.0408 (10)
H6A	0.8132	0.6818	0.4827	0.061*
H6B	0.7076	0.6128	0.5282	0.061*
H6C	0.8207	0.6903	0.6278	0.061*
C7	0.5258 (5)	0.6932 (3)	0.6445 (4)	0.0361 (9)
H7A	0.4429	0.7120	0.6696	0.054*
H7B	0.6206	0.6954	0.7210	0.054*
H7C	0.5092	0.6255	0.6086	0.054*
N1	0.6383 (4)	0.7550 (2)	0.4950 (3)	0.0294 (7)
N2	0.5329 (4)	0.7627 (2)	0.5471 (3)	0.0295 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.04624 (18)	0.05257 (19)	0.0537 (2)	−0.00103 (13)	0.03051 (15)	−0.00763 (14)
I2	0.03148 (14)	0.02296 (13)	0.02863 (14)	−0.00115 (9)	0.01014 (11)	−0.00118 (9)
I3	0.04725 (18)	0.04483 (18)	0.05066 (19)	0.00210 (12)	0.03060 (15)	0.00475 (13)
C1	0.043 (2)	0.0233 (18)	0.033 (2)	−0.0066 (16)	0.0124 (17)	−0.0009 (15)
C2	0.046 (2)	0.0222 (18)	0.033 (2)	0.0001 (17)	0.0053 (18)	0.0019 (16)
C3	0.033 (2)	0.0242 (18)	0.036 (2)	0.0010 (15)	0.0043 (17)	−0.0058 (16)
C4	0.060 (3)	0.044 (3)	0.046 (3)	−0.010 (2)	0.026 (2)	0.002 (2)
C5	0.038 (2)	0.039 (2)	0.058 (3)	0.0099 (19)	0.017 (2)	−0.006 (2)
C6	0.041 (2)	0.037 (2)	0.043 (2)	0.0130 (18)	0.0160 (19)	0.0050 (19)
C7	0.046 (2)	0.030 (2)	0.032 (2)	0.0008 (17)	0.0161 (18)	0.0053 (16)
N1	0.0321 (16)	0.0241 (16)	0.0311 (16)	0.0013 (13)	0.0114 (13)	0.0003 (12)
N2	0.0341 (17)	0.0245 (15)	0.0294 (16)	0.0015 (13)	0.0117 (14)	0.0010 (13)

Geometric parameters (Å, º)

I1—I2	2.8972 (4)	C5—H5A	0.9800
I2—I3	2.9336 (4)	C5—H5B	0.9800
C1—N1	1.340 (5)	C5—H5C	0.9800
C1—C2	1.379 (6)	C6—N1	1.454 (5)
C1—C4	1.486 (6)	C6—H6A	0.9800
C2—C3	1.377 (6)	C6—H6B	0.9800
C2—H2	0.9500	C6—H6C	0.9800
C3—N2	1.350 (5)	C7—N2	1.456 (5)
C3—C5	1.488 (6)	C7—H7A	0.9800
C4—H4A	0.9800	C7—H7B	0.9800
C4—H4B	0.9800	C7—H7C	0.9800
C4—H4C	0.9800	N1—N2	1.361 (4)
I1—I2—I3	177.099 (12)	H5A—C5—H5C	109.5
N1—C1—C2	107.1 (4)	H5B—C5—H5C	109.5
N1—C1—C4	122.8 (4)	N1—C6—H6A	109.5
C2—C1—C4	130.1 (4)	N1—C6—H6B	109.5
C3—C2—C1	108.0 (4)	H6A—C6—H6B	109.5
C3—C2—H2	126.0	N1—C6—H6C	109.5
C1—C2—H2	126.0	H6A—C6—H6C	109.5
N2—C3—C2	107.1 (4)	H6B—C6—H6C	109.5
N2—C3—C5	122.0 (4)	N2—C7—H7A	109.5
C2—C3—C5	130.8 (4)	N2—C7—H7B	109.5
C1—C4—H4A	109.5	H7A—C7—H7B	109.5
C1—C4—H4B	109.5	N2—C7—H7C	109.5
H4A—C4—H4B	109.5	H7A—C7—H7C	109.5
C1—C4—H4C	109.5	H7B—C7—H7C	109.5
H4A—C4—H4C	109.5	C1—N1—N2	109.2 (3)
H4B—C4—H4C	109.5	C1—N1—C6	128.9 (4)
C3—C5—H5A	109.5	N2—N1—C6	121.9 (3)
C3—C5—H5B	109.5	C3—N2—N1	108.5 (3)
H5A—C5—H5B	109.5	C3—N2—C7	129.1 (4)
C3—C5—H5C	109.5	N1—N2—C7	122.3 (3)
N1—C1—C2—C3	−0.3 (5)	C2—C3—N2—N1	−0.3 (4)
C4—C1—C2—C3	179.5 (4)	C5—C3—N2—N1	179.4 (4)
C1—C2—C3—N2	0.4 (4)	C2—C3—N2—C7	−178.6 (4)
C1—C2—C3—C5	−179.3 (4)	C5—C3—N2—C7	1.1 (6)
C2—C1—N1—N2	0.2 (4)	C1—N1—N2—C3	0.1 (4)
C4—C1—N1—N2	−179.7 (4)	C6—N1—N2—C3	179.3 (3)
C2—C1—N1—C6	−179.0 (4)	C1—N1—N2—C7	178.6 (3)
C4—C1—N1—C6	1.1 (6)	C6—N1—N2—C7	−2.2 (5)