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Crystal structure of 2,5-bis(4-methylpyridin-2-yl)pyrazine chloroform disolvate

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This work is part of the PhD thesis (Neuchâtel, 2008) of LS.

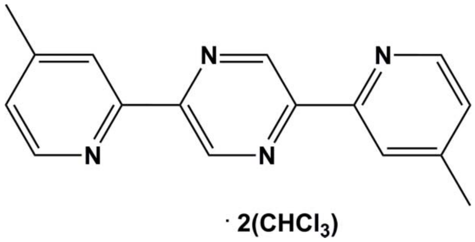
The heterocyclic molecule in the title solvate, $C_{16}H_{14}N_4 \cdot 2CHCl_3$, possesses inversion symmetry, with the inversion centre situated at the centre of the pyrazine ring. The outer pyridine rings are inclined to the central pyrazine ring by 4.89 (9)°. The compound crystallized as a chloroform disolvate with the solvent molecules linked to the title molecule by C—H⋯N hydrogen bonds. In the crystal, molecules are further linked by π–π interactions involving the pyrazine and pyridine rings of neighbouring molecules [inter-centroid distance = 3.5629 (12) Å; symmetry code: x, $y + 1$, $z + 1$].

Keywords: crystal structure; pyrazine; pyridine; bis(2-pyridyl)pyrazine; solvate.

CCDC reference: 1004308

1. Related literature

The title compound is the 4-methylpyridine derivative of the ligand 2,5-bis(pyridin-2-yl)pyrazine (bppz), see: Neels & Stoeckli-Evans (1993); Schmitt (2008). For the synthesis of a number of transition-metal complexes of bppz, especially of copper(II), and for their magnetic properties, see for example: Escuer *et al.* (1993); Neels *et al.* (1995); Yuste *et al.* (2009); Bentama *et al.* (2012).



2. Experimental

2.1. Crystal data

$C_{16}H_{14}N_4 \cdot 2CHCl_3$
$M_r = 501.05$
Monoclinic, $I2/a$
$a = 16.4498\ (17)$ Å
$b = 6.0691\ (4)$ Å
$c = 21.605\ (3)$ Å
$\beta = 93.885\ (9)°$
$V = 2152.0\ (4)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.81$ mm^{-1}
$T = 173$ K
0.45 × 0.29 × 0.23 mm

2.2. Data collection

Stoe IPDS 2 diffractometer
Absorption correction: multi-scan (*MULscanABS* in *PLATON*; Spek, 2009)
$T_{\min} = 0.567$, $T_{\max} = 1.000$
9566 measured reflections
1902 independent reflections
1676 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.066$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.112$
$S = 1.06$
1902 reflections
129 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C10—H10⋯N1	1.00	2.50	3.335 (3)	141

Data collection: *X-AREA* (Stoe & Cie, 2009); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2013*, *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: WM0002).

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S1. Experimental

S1.1. Synthesis and crystallization

The title compound was prepared in 3 stages:

Stage 1. Synthesis of methyl-2-pyridine-4-methyl-ketoxime (1): Hydroxylamine hydrochloride (566 mg, 8.14 mmol) in pyridine (5ml) was added to a solution of 2-acetyl-4-methylpyrine (1.0 g, 7.40 mmol) in pyridine (22 ml) with vigorous stirring for 3 h at room temperature. The colourless solution was then poured into iced water. The oxime that precipitated was filtered and then dried under vacuum, yielding 1.33 g of compound (1) as a white powder. MS (ESI) calc. for $C_8H_{10}N_2O$ $[M+H]^+$: 150.18; found 151.1.

Stage 2. Synthesis of methyl-p-tosyl-2-actelypyridine oxime (2): Tosyl chloride (2.40 g, 7.32 mmol) was added to a solution of (1) [1.0 g, 6.6 mmol] in pyridine (10 ml) with stirring for 20 h. The orange solution obtained was poured into iced water. A white precipitate was obtained which was filtered, washed with cold water and dried, yielding compound (2) as a white powder [Yield 74%; 523 mg]. MS (ESI) calc. for $C_{15}H_{16}N_2O_3S$ $[M+H]^+$: 304.36; found 305.1.

Stage 3. Synthesis of 2,5-bis(4-methyl-2-yl)-pyrazine: Potassium tert-butoxide (516 mg, 4.60 mmol) was added in small portions to a solution of (2) [1.0 g, 3.286 mmol] in dry ethanol (15 ml). The mixture was stirred at room temperature for 20 h. The precipitate of potassium p-toluenesulfonate that formed was filtered off and washed with ether. The filtrate and the washed fractions were collected. This process was repeated until no further precipitation occurred. An aqueous solution of hydrogen peroxide (30%, 4 ml) was then added to the assembled filtrates and washed fractions. When the exothermic reaction had stopped, the mixture was placed in a refrigerator over night yielding the title compound. It was filtered off and washed with water/methanol (1/1, v/v) and dried (yield 5%, 43 mg). MS (ESI) calc. for $C_{16}H_{14}N_4$ $[M+H]^+$: 262.31, found 263.13. The colourless rod-like crystals used for X-ray diffraction analysis were obtained by slow evaporation of a solution in chloroform.

S1.2. Refinement

The C-bound H atoms were included in calculated positions and treated as riding atoms: C—H = 0.95 - 1.00 Å with $U_{iso}(H) = 1.5U_{eq}$(C-methyl) and = $1.2U_{eq}(C)$ for other H atoms.

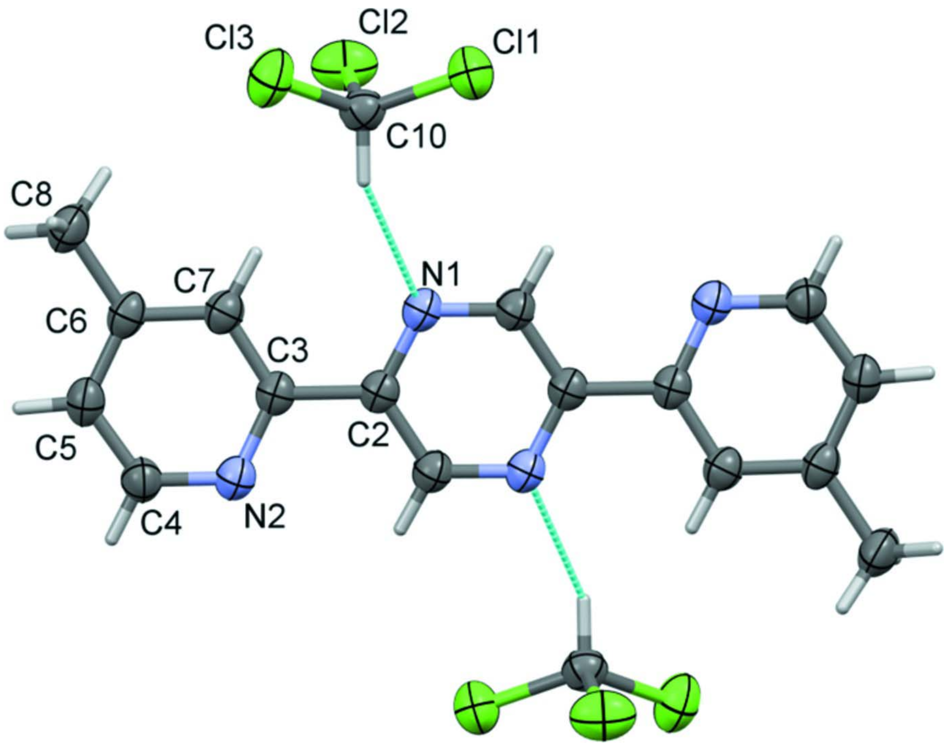

Figure 1

A view of the molecular structure of the title compound, with atom labelling [unlabelled atoms are generated by inversion symmetry (symmetry code: -*x* + 3/2, -*y* + 3/2, -*z* + 1/2)]. Displacement ellipsoids are drawn at the 50% probability level. The C—H···N hydrogen bonds are shown as dashed lines (see Table 1 for details).

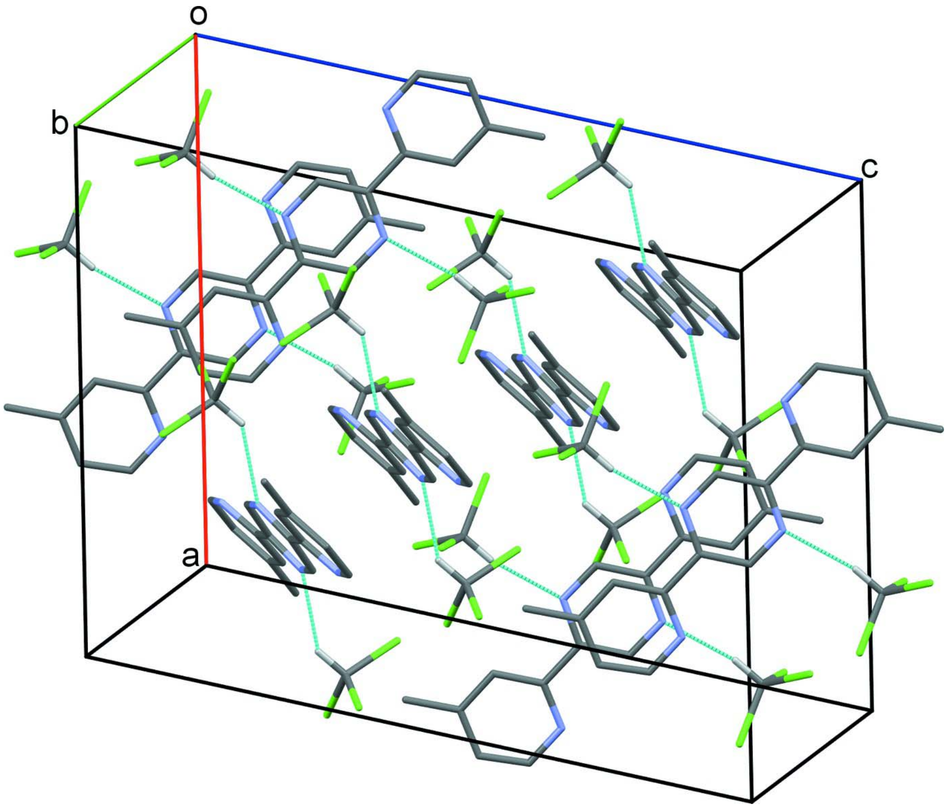

Figure 2

A view of the crystal packing of the title compound, illustrating the overlap of the pyrazine and pyridine rings of neighbouring molecules.

2,5-Bis(4-methylpyridin-2-yl)pyrazine chloroform disolvate

Crystal data

$C_{16}H_{14}N_4 \cdot 2CHCl_3$	$F(000) = 1016$
$M_r = 501.05$	$D_x = 1.546$ Mg m^{-3}
Monoclinic, *I*2/*a*	Mo *Kα* radiation, $\lambda = 0.71073$ Å
$a = 16.4498$ (17) Å	Cell parameters from 12496 reflections
$b = 6.0691$ (4) Å	$\theta = 1.5$–25.6°
$c = 21.605$ (3) Å	$\mu = 0.81$ mm^{-1}
$\beta = 93.885$ (9)°	$T = 173$ K
$V = 2152.0$ (4) Å^3	Rod, colourless
$Z = 4$	0.45 × 0.29 × 0.23 mm

Data collection

Stoe IPDS 2 diffractometer	9566 measured reflections
Radiation source: fine-focus sealed tube	1902 independent reflections
Plane graphite monochromator	1676 reflections with $I > 2\sigma(I)$
$\varphi + \omega$ scans	$R_{int} = 0.066$
Absorption correction: multi-scan (*MULscanABS* in *PLATON*; Spek, 2009)	$\theta_{max} = 25.2°$, $\theta_{min} = 1.9°$
$T_{min} = 0.567$, $T_{max} = 1.000$	$h = -19 \rightarrow 19$
	$k = -7 \rightarrow 7$
	$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.112$
$S = 1.06$
1902 reflections
129 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0725P)^2 + 0.8241P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Extinction correction: *SHELXL2013* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0064 (11)

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.72397 (10)	0.6344 (3)	0.19653 (8)	0.0368 (4)
N2	0.89303 (10)	0.2947 (3)	0.25318 (8)	0.0394 (4)
C1	0.68638 (12)	0.8157 (3)	0.21400 (9)	0.0374 (4)
H1	0.6406	0.8677	0.1890	0.045*
C2	0.78878 (11)	0.5676 (3)	0.23260 (8)	0.0328 (4)
C3	0.83238 (11)	0.3674 (3)	0.21341 (9)	0.0328 (4)
C4	0.93307 (13)	0.1154 (3)	0.23585 (10)	0.0418 (5)
H4	0.9771	0.0635	0.2627	0.050*
C5	0.91455 (13)	0.0006 (3)	0.18141 (10)	0.0401 (5)
H5	0.9446	−0.1274	0.1720	0.048*
C6	0.85181 (12)	0.0739 (3)	0.14075 (9)	0.0376 (5)
C7	0.81112 (11)	0.2637 (3)	0.15755 (9)	0.0378 (5)
H7	0.7685	0.3224	0.1305	0.045*
C8	0.82828 (15)	−0.0466 (4)	0.08138 (11)	0.0510 (6)
H8A	0.7910	−0.1672	0.0898	0.077*
H8B	0.8772	−0.1066	0.0642	0.077*
H8C	0.8012	0.0556	0.0515	0.077*
Cl1	0.50499 (4)	0.55130 (10)	0.09961 (3)	0.0569 (2)
Cl2	0.65296 (4)	0.52518 (12)	0.03495 (3)	0.0617 (3)
Cl3	0.57200 (4)	0.12697 (10)	0.06982 (3)	0.0582 (2)
C10	0.59461 (13)	0.4006 (3)	0.09061 (10)	0.0416 (5)
H10	0.6275	0.3999	0.1312	0.050*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0398 (9)	0.0332 (9)	0.0377 (9)	−0.0008 (7)	0.0045 (7)	−0.0041 (7)
N2	0.0429 (9)	0.0351 (9)	0.0405 (9)	0.0005 (7)	0.0053 (7)	−0.0032 (7)
C1	0.0404 (10)	0.0333 (10)	0.0385 (10)	−0.0002 (8)	0.0035 (8)	−0.0027 (8)

C2	0.0356 (10)	0.0294 (10)	0.0340 (10)	−0.0039 (8)	0.0075 (7)	0.0008 (8)
C3	0.0343 (9)	0.0290 (9)	0.0358 (10)	−0.0042 (7)	0.0090 (7)	−0.0001 (7)
C4	0.0467 (11)	0.0374 (11)	0.0417 (11)	0.0052 (9)	0.0054 (8)	−0.0004 (8)
C5	0.0460 (11)	0.0326 (10)	0.0433 (11)	0.0022 (8)	0.0140 (9)	−0.0003 (8)
C6	0.0424 (10)	0.0343 (10)	0.0377 (10)	−0.0038 (8)	0.0136 (8)	−0.0047 (8)
C7	0.0388 (10)	0.0381 (11)	0.0372 (10)	−0.0011 (8)	0.0077 (8)	−0.0025 (8)
C8	0.0578 (13)	0.0499 (13)	0.0460 (12)	0.0046 (10)	0.0076 (10)	−0.0152 (10)
Cl1	0.0557 (4)	0.0538 (4)	0.0613 (4)	0.0130 (3)	0.0040 (3)	−0.0024 (3)
Cl2	0.0589 (4)	0.0759 (5)	0.0507 (4)	−0.0204 (3)	0.0069 (3)	0.0140 (3)
Cl3	0.0758 (5)	0.0417 (4)	0.0594 (4)	−0.0037 (3)	0.0207 (3)	−0.0062 (2)
C10	0.0449 (11)	0.0426 (11)	0.0376 (11)	−0.0012 (9)	0.0041 (8)	0.0024 (9)

Geometric parameters (Å, º)

N1—C1	1.329 (3)	C5—H5	0.9500
N1—C2	1.340 (3)	C6—C7	1.393 (3)
N2—C4	1.339 (3)	C6—C8	1.504 (3)
N2—C3	1.346 (3)	C7—H7	0.9500
C1—C2^{i}	1.391 (3)	C8—H8A	0.9800
C1—H1	0.9500	C8—H8B	0.9800
C2—C1^{i}	1.391 (3)	C8—H8C	0.9800
C2—C3	1.484 (3)	Cl1—C10	1.757 (2)
C3—C7	1.385 (3)	Cl2—C10	1.760 (2)
C4—C5	1.383 (3)	Cl3—C10	1.753 (2)
C4—H4	0.9500	C10—H10	1.0000
C5—C6	1.383 (3)		
C1—N1—C2	116.90 (17)	C5—C6—C8	121.56 (19)
C4—N2—C3	116.44 (17)	C7—C6—C8	121.58 (19)
N1—C1—C2^{i}	122.74 (18)	C3—C7—C6	120.36 (18)
N1—C1—H1	118.6	C3—C7—H7	119.8
C2^{i}—C1—H1	118.6	C6—C7—H7	119.8
N1—C2—C1^{i}	120.36 (17)	C6—C8—H8A	109.5
N1—C2—C3	117.77 (16)	C6—C8—H8B	109.5
C1^{i}—C2—C3	121.87 (17)	H8A—C8—H8B	109.5
N2—C3—C7	122.68 (17)	C6—C8—H8C	109.5
N2—C3—C2	116.19 (16)	H8A—C8—H8C	109.5
C7—C3—C2	121.13 (17)	H8B—C8—H8C	109.5
N2—C4—C5	124.3 (2)	Cl3—C10—Cl1	110.88 (12)
N2—C4—H4	117.9	Cl3—C10—Cl2	110.37 (12)
C5—C4—H4	117.9	Cl1—C10—Cl2	110.64 (12)
C6—C5—C4	119.35 (19)	Cl3—C10—H10	108.3
C6—C5—H5	120.3	Cl1—C10—H10	108.3
C4—C5—H5	120.3	Cl2—C10—H10	108.3
C5—C6—C7	116.86 (18)		
C2—N1—C1—C2^{i}	−0.8 (3)	C3—N2—C4—C5	−1.7 (3)
C1—N1—C2—C1^{i}	0.7 (3)	N2—C4—C5—C6	1.2 (3)

C1—N1—C2—C3	−179.12 (16)	C4—C5—C6—C7	0.6 (3)
C4—N2—C3—C7	0.5 (3)	C4—C5—C6—C8	−179.05 (19)
C4—N2—C3—C2	−179.40 (16)	N2—C3—C7—C6	1.2 (3)
N1—C2—C3—N2	−174.82 (17)	C2—C3—C7—C6	−178.94 (16)
C1^{i}—C2—C3—N2	5.3 (3)	C5—C6—C7—C3	−1.7 (3)
N1—C2—C3—C7	5.3 (3)	C8—C6—C7—C3	177.96 (19)
C1^{i}—C2—C3—C7	−174.56 (18)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10···N1	1.00	2.50	3.335 (3)	141