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Crystal structure of 2,3,5,6-tetrakis[(methylsulfanyl)methyl]pyrazine

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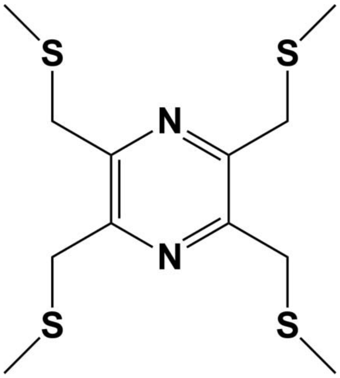
The title compound, $C_{12}H_{20}N_2S_4$, synthesized by the reaction of 2,3,5,6-tetrakis(bromomethyl)pyrazine with sodium methanethiolate, crystallizes with a half -molecule in the asymmetric unit. The whole molecule is generated by inversion symmetry; the inversion centre being located in the centre of the pyrazine ring. The molecule has an S-shaped conformation with two (methylsulfanyl)methyl substituent arms directed above the plane of the pyrazine ring and two below. The $C(H_3)—S—C(H_2)—C$(aromatic) torsion angles are 70.47 (18) and −67.65 (17)°, respectively. In the crystal, molecules are linked *via* weak C—H⋯S hydrogen bonds, forming chains along [001] and enclosing $R_2^2(12)$ ring motifs. The chains are linked by further weak C—H⋯S hydrogen bonds, forming sheets lying parallel to (101).

Keywords: crystal structure; tetrakis-substituted; pyrazine; sulfanyl-methyl derivative; inversion symmetry.

CCDC reference: 1004261

1. Related literature

For syntheses of the starting reagent, 2,3,5,6-tetrakis(bromomethyl)pyrazine, see: Ferigo *et al.* (1994); Assoumatine (1999); Assoumatine & Stoeckli-Evans (2014). For the crystal structures of similar sulfanylmethyl derivatives of pyrazine, such as two triclinic polymorphs of 2,3,5,6 tetrakis(naphthalen-2-ylsulfanylmethyl)pyrazine both possessing inversion symmetry, see: Pacifico & Stoeckli-Evans (2004), and for 2,3,5,6-tetrakis(phenylsulfanylmethyl)pyrazine, which also crystallizes in space group $P\bar{1}$ and possesses inversion symmetry, see: Assoumatine *et al.* (2007).



2. Experimental

2.1. Crystal data

$C_{12}H_{20}N_2S_4$
$M_r = 320.54$
Triclinic, $P\bar{1}$
$a = 6.6773$ (6) Å
$b = 6.9433$ (4) Å
$c = 9.5135$ (5) Å
$\alpha = 102.635$ (6)°
$\beta = 107.539$ (5)°
$\gamma = 99.462$ (9)°
$V = 397.61$ (5) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.58$ mm^{-1}
$T = 293$ K
0.40 × 0.40 × 0.23 mm

2.2. Data collection

Stoe AED2 four-circle diffractometer
2960 measured reflections
1478 independent reflections
1283 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
3 standard reflections every 60 min
intensity decay: 1%

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.088$
$S = 1.08$
1478 reflections
85 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C3—H3A⋯S2^{i}	0.97	2.89	3.589 (2)	130
C5—H5B⋯S1^{ii}	0.97	2.95	3.7395 (19)	139
C5—H5B⋯S1^{i}	0.97	2.93	3.614 (2)	128

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $x, y, z+1$.

Data collection: *STADI4* (Stoe & Cie, 1997); cell refinement: *STADI4*; data reduction: *X-RED* (Stoe & Cie, 1997); 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: HB0006).

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supporting information

Acta Cryst. (2014). E**70**, o887–o888 [doi:10.1107/S1600536814011246]

Crystal structure of 2,3,5,6-tetrakis[(methylsulfanyl)methyl]pyrazine

Tokouré Assoumatine and Helen Stoeckli-Evans

S1. Experimental

S1.1. Synthesis and crystallization

A mixture of sodium methanethiolate (0.94 g, 13 mmol, Fluka 95%) in ethanol (50 ml) was added slowly and drop wise with stirring to a refluxed solution of 2,3,5,6-tetrakis(bromomethyl)pyrazine [Assoumatine & Stoeckli-Evans, 2014], (1.5 g, 3.32 mmol) in ethanol (50 ml). Refluxing and stirring were continued for 4 h. The solvent was removed under reduced pressure and the resultant residue diluted with CH_2Cl_2 (200 ml). The organic layer was washed with water (3 × 30 ml) and saturated NaCl (30 ml), then dried over anhydrous $MgSO_4$ and evaporated to dryness after filtration. The brown residue obtained was washed with acetonitrile till this solvent became colourless, yielding the title compound which was further dried under vacuum [Yield 0.55 g (52%), M.p. 418-419 K]; Rf 0.48 (solvent : CH_2Cl_2, eluent : toluene/$MeCO_2Et$, 10/1 v/v). Diffusion of an equal volume of ethanol into a concentrated $CHCl_3$ (4 ml) solution of the title compound in a 16 mm diameter glass tube yielded suitable yellow plate-like crystals for X-ray diffraction analysis. Spectroscopic data: ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 3.97 (s, 8H, Pz—CH_2—S), 2.13 (s, 12H, S—CH_3) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 149.50, 35.89, 15.65 ppm. Anal. for $C_{12}H_{20}N_2S_4$ (Mr = 320.58 g/mol) Calc. (%): C 44.96; H 6.30; N 8.74; S 40.00. Found (%): C 44.65; H 6.24; N 8.76; S 40.03. MS (EI, 70 eV), m/z (%): 320 ([M$^+$], 89.4), 274 (95.2), 257 (50.1), 227 (100), 210 (25.4), 194 (37.9), 181 (54.2), 164 (29.2), 135 (28.1), 97 (23.8). IR (KBr disc, cm^{-1}): 2967 w, 2915 w, 1425 ms, 1394 vs, 1311 w, 1248 w, 1218 s, 1120 ms, 988 ms, 903 w, 795 w, 754 w, 720 w, 679 w, 484 w.

S1.2. Refinement

The H atoms were included in calculated positions and treated as riding atoms: C—H = 0.96 - 0.97 Å with $U_{iso}(H) = 1.5U_{eq}$(C-methyl) and = $1.2U_{eq}(C)$ for other H atoms. No absorption correction was applied owing to the irregular shape of the crystal, and as there were no suitable reflections for psi scans.

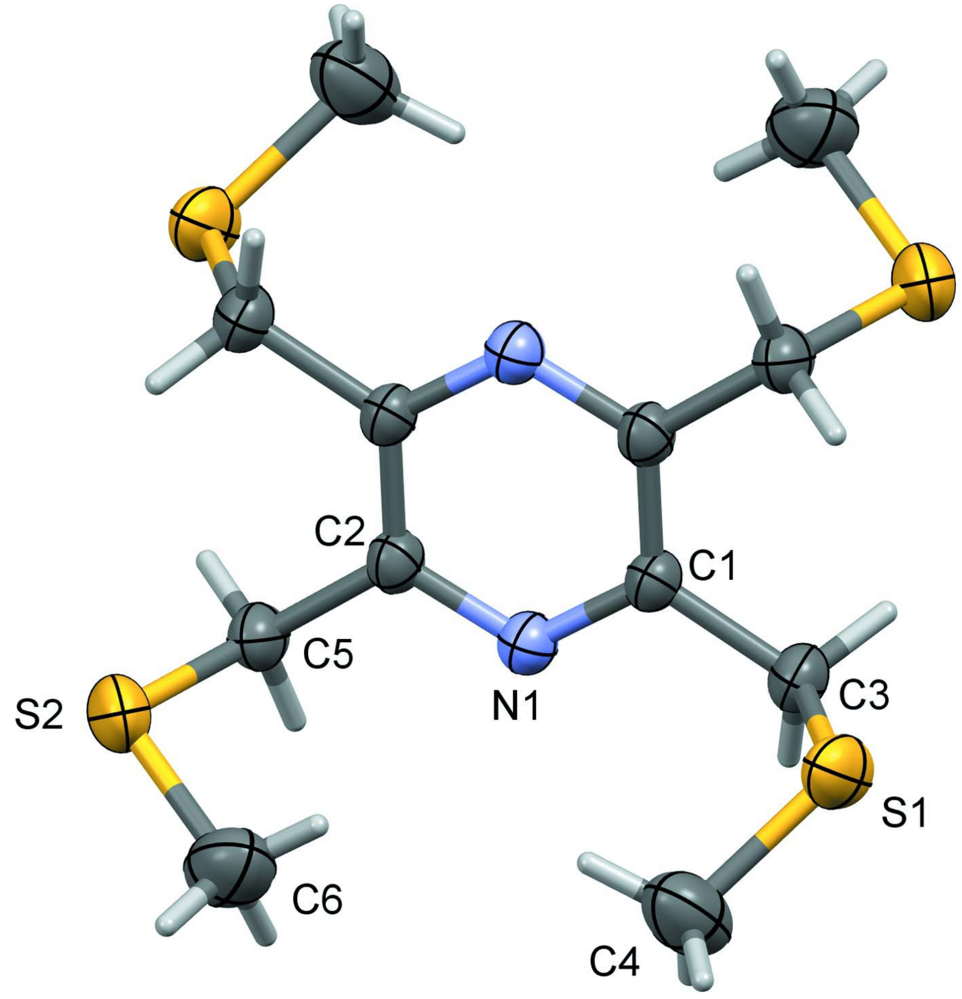

Figure 1

A view of the molecular structure of the title molecule, with atom labelling (unlabelled atoms are generated by inversion symmetry with symmetry code: -*x*, -*y+1*, -*z* + 1). Displacement ellipsoids are drawn at the 50% probability level.

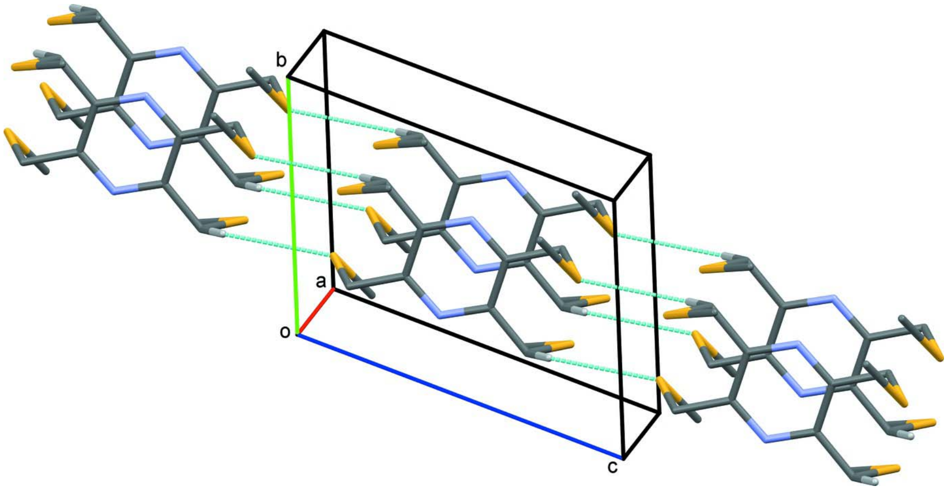

Figure 2

A partial view along the *a* axis of the crystal packing of the title compound, showing the formation of the C—H···S hydrogen-bonded chains along [001], enclosing $R^2_2(12)$ ring motifs (H atoms not involved in these hydrogen bonds have been omitted for clarity).

2,3,5,6-Tetrakis[(methylsulfanyl)methyl]pyrazine

Crystal data

$C_{12}H_{20}N_2S_4$
$M_r = 320.54$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
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$c = 9.5135$ (5) Å
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$\beta = 107.539$ (5)°
$\gamma = 99.462$ (9)°
$V = 397.61$ (5) Å^3

$Z = 1$
$F(000) = 170$
$D_x = 1.339$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 33 reflections
$\theta = 14.2$–18.8°
$\mu = 0.58$ mm^{-1}
$T = 293$ K
Plate, yellow
0.40 × 0.40 × 0.23 mm

Data collection

Stoe AED2 four-circle diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$2\theta/\omega$ scans
2960 measured reflections
1478 independent reflections
1283 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.018$
$\theta_{\max} = 25.5°$, $\theta_{\min} = 2.3°$
$h = -8 \rightarrow 7$
$k = -8 \rightarrow 8$
$l = 0 \rightarrow 11$
3 standard reflections every 60 min
intensity decay: 1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.088$
$S = 1.08$
1478 reflections
85 parameters

0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.1143P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.24$ e Å^{-3}

$\Delta\rho_{min} = -0.20$ e Å^{-3}

Extinction correction: *SHELXL2013* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.064 (11)

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.10172 (10)	0.33963 (9)	0.10899 (6)	0.0509 (2)
S2	0.37011 (9)	0.28482 (9)	0.80525 (6)	0.0515 (2)
N1	−0.0169 (2)	0.2930 (2)	0.44718 (16)	0.0326 (4)
C1	−0.0580 (3)	0.4056 (3)	0.34870 (19)	0.0311 (5)
C2	0.0402 (3)	0.3854 (3)	0.59786 (19)	0.0313 (5)
C3	−0.1194 (3)	0.2955 (3)	0.1806 (2)	0.0390 (6)
C4	0.2772 (5)	0.2016 (4)	0.2027 (3)	0.0684 (10)
C5	0.0843 (3)	0.2519 (3)	0.7029 (2)	0.0376 (6)
C6	0.4534 (4)	0.1829 (4)	0.6484 (3)	0.0665 (9)
H3A	−0.23980	0.33950	0.12120	0.0470*
H3B	−0.16800	0.15040	0.16540	0.0470*
H4A	0.33380	0.26610	0.31160	0.1030*
H4B	0.39480	0.20040	0.16450	0.1030*
H4C	0.19730	0.06420	0.18230	0.1030*
H5A	0.02160	0.11060	0.64270	0.0450*
H5B	0.01290	0.28160	0.77720	0.0450*
H6A	0.36700	0.04660	0.59450	0.1000*
H6B	0.60330	0.18130	0.68720	0.1000*
H6C	0.43450	0.26620	0.57940	0.1000*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0731 (4)	0.0608 (4)	0.0394 (3)	0.0318 (3)	0.0335 (3)	0.0242 (3)
S2	0.0568 (4)	0.0584 (4)	0.0352 (3)	0.0256 (3)	0.0050 (2)	0.0128 (2)
N1	0.0386 (8)	0.0332 (8)	0.0285 (7)	0.0114 (6)	0.0133 (6)	0.0097 (6)
C1	0.0355 (9)	0.0350 (9)	0.0252 (8)	0.0112 (7)	0.0123 (7)	0.0092 (7)
C2	0.0340 (9)	0.0371 (9)	0.0272 (8)	0.0112 (7)	0.0134 (7)	0.0123 (7)
C3	0.0492 (11)	0.0408 (10)	0.0265 (9)	0.0141 (8)	0.0124 (8)	0.0076 (8)
C4	0.0750 (17)	0.0855 (19)	0.0741 (17)	0.0467 (15)	0.0399 (14)	0.0415 (15)
C5	0.0493 (11)	0.0384 (10)	0.0307 (9)	0.0154 (8)	0.0164 (8)	0.0145 (8)
C6	0.0570 (15)	0.0784 (18)	0.0633 (16)	0.0307 (13)	0.0207 (12)	0.0090 (13)

Geometric parameters (Å, º)

S1—C3	1.813 (2)	C3—H3B	0.9700
S1—C4	1.789 (3)	C4—H4A	0.9600
S2—C5	1.812 (2)	C4—H4B	0.9600
S2—C6	1.790 (3)	C4—H4C	0.9600
N1—C1	1.342 (2)	C5—H5A	0.9700
N1—C2	1.342 (2)	C5—H5B	0.9700
C1—C3	1.509 (2)	C6—H6A	0.9600
C1—C2^{i}	1.401 (3)	C6—H6B	0.9600
C2—C5	1.504 (3)	C6—H6C	0.9600
C3—H3A	0.9700		
C3—S1—C4	101.45 (13)	S1—C4—H4B	109.00
C5—S2—C6	100.09 (11)	S1—C4—H4C	109.00
C1—N1—C2	118.31 (16)	H4A—C4—H4B	109.00
N1—C1—C3	116.40 (17)	H4A—C4—H4C	109.00
N1—C1—C2^{i}	120.78 (15)	H4B—C4—H4C	109.00
C2^{i}—C1—C3	122.82 (17)	S2—C5—H5A	109.00
N1—C2—C5	116.03 (17)	S2—C5—H5B	109.00
N1—C2—C1^{i}	120.91 (17)	C2—C5—H5A	109.00
C1^{i}—C2—C5	123.05 (15)	C2—C5—H5B	109.00
S1—C3—C1	113.18 (14)	H5A—C5—H5B	108.00
S2—C5—C2	113.56 (15)	S2—C6—H6A	109.00
S1—C3—H3A	109.00	S2—C6—H6B	109.00
S1—C3—H3B	109.00	S2—C6—H6C	109.00
C1—C3—H3A	109.00	H6A—C6—H6B	110.00
C1—C3—H3B	109.00	H6A—C6—H6C	109.00
H3A—C3—H3B	108.00	H6B—C6—H6C	109.00
S1—C4—H4A	109.00		
C4—S1—C3—C1	70.47 (18)	C2^{i}—C1—C3—S1	77.1 (2)
C6—S2—C5—C2	−67.65 (17)	N1—C1—C2^{i}—N1^{i}	−0.5 (3)
C2—N1—C1—C3	179.41 (18)	N1—C1—C2^{i}—C5^{i}	−180.00 (19)
C2—N1—C1—C2^{i}	0.4 (3)	C3—C1—C2^{i}—N1^{i}	−179.35 (18)
C1—N1—C2—C5	179.98 (18)	C3—C1—C2^{i}—C5^{i}	1.1 (3)
C1—N1—C2—C1^{i}	−0.4 (3)	N1—C2—C5—S2	103.98 (18)
N1—C1—C3—S1	−101.84 (19)	C1^{i}—C2—C5—S2	−75.6 (2)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3*A*···S2^{i}	0.97	2.89	3.589 (2)	130
C5—H5*B*···S1^{ii}	0.97	2.95	3.7395 (19)	139
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Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) *x*, *y*, *z*+1.