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Two triclinic polymorphs of 2,3,5,6-tetrakis(naphthalen-2-ylsulfanylmethyl)pyrazine

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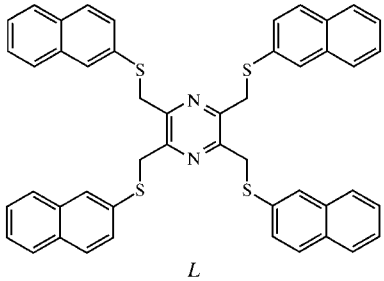
The title compound, $C_{48}H_{36}N_2S_4$, can be crystallized as two polymorphic structures, (I) and (II), both of which are in the triclinic space group $P\overline{1}$ and possess C_i symmetry. In the crystal structure of polymorph (I), the adjacent naphthalene moieties are orientated towards one another and are inclined to one another by 78.7 (1)°, resulting in weak C—H$\cdots\pi$ interactions. In polymorph (II), the adjacent substituents are orientated away from one another, enclosing the pyrazine N atoms. In this way, the S atom of one substituent sits below the plane of the naphthalene ring of the other substituent.

Comment

Tetrasubstituted pyrazine derivatives have been used for a number of years as ligands in coordination chemistry, and a search of the Cambridge Structural Database (Version 5.25 of November 2003; Allen, 2002) indicated the presence of more than 40 such complexes. The majority include mono- and binuclear coordination complexes, and some coordination polymers, involving the ligands 2,3,5,6-tetra(2-pyridyl)-pyrazine and 2,3,5,6-pyrazinetetracarboxylic acid.



L

Two cases of polymorphs of tetrasubstituted pyrazine derivatives are also known, namely 2,3,5,6-tetraphenyl-pyrazine (Bartnik *et al.*, 1999) and 2,3,5,6-tetra(2-pyridyl)-pyrazine (Bock *et al.*, 1992; Greaves & Stoeckli-Evans, 1992). The title compound, *L*, which possesses four extended 'arms', was synthesized in order to explore its coordination behaviour with first-row transition metals. Two polymorphic forms, (I) and (II), have been isolated. Both crystallize in space group $P\overline{1}$ and possess C_i symmetry.

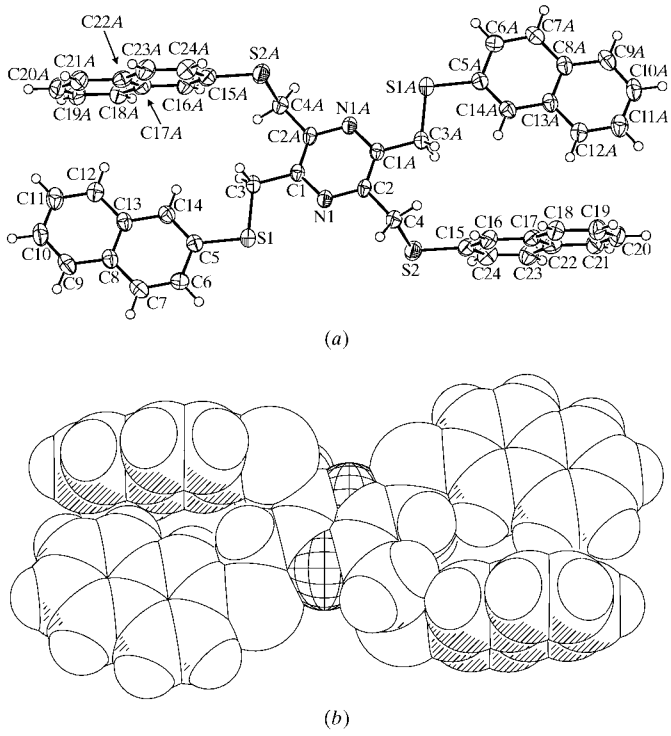


Figure 1
(*a*) A view of polymorph (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size. Atoms labelled with the additional letter *A* are at the symmetry position $(1-x, 2-y, 1-z)$. (*b*) A CPK view of polymorph (I).

The molecular structures of polymorphs (I) and (II) are shown in Figs. 1(*a*) and 2(*a*), respectively. The bond distances and angles are normal for such compounds, and selected geometric parameters are given in Tables 1 and 2. The molecular structures of (I) and (II) differ in the orientation of the naphthalen-2-ylsulfanyl moieties with respect to the plane of the pyrazine ring. This difference is reflected in the torsion angles about the C1—C3 and C2—C4, and S1—C3 and S2—C4 bonds, which are quite different in the two polymorphs (see Tables 1 and 2). It can be seen that opposite naphthalene moieties are parallel to one another by symmetry. The various dihedral angles formed by the naphthalene and pyrazine rings are given in Table 3.

In polymorph (I), adjacent naphthalene ring planes are inclined to one another by 78.7 (1)°, resulting in a weak C—H$\cdots\pi$ interaction involving atom C12 and the centroid of the plane formed by atoms C17*A*–C22*A* [the C—H$\cdots$centroid distance is 2.64 (3) Å; symmetry code: (*A*) $1-x, 2-y, 1-z$]. This structure is illustrated in the CPK (Corey–Pauling–Koltun) view of (I) given in Fig. 1(*b*).

In polymorph (II), the adjacent substituents are orientated away from one another, enclosing the pyrazine N atoms. The plane of the naphthalene moiety defined by atoms C5–C14 is inclined to the plane of the second naphthalene moiety (C15–C24) by 57.0 (1)°. In this way, atom S2 of one substituent sits below the plane of the naphthalene ring of the other substi-

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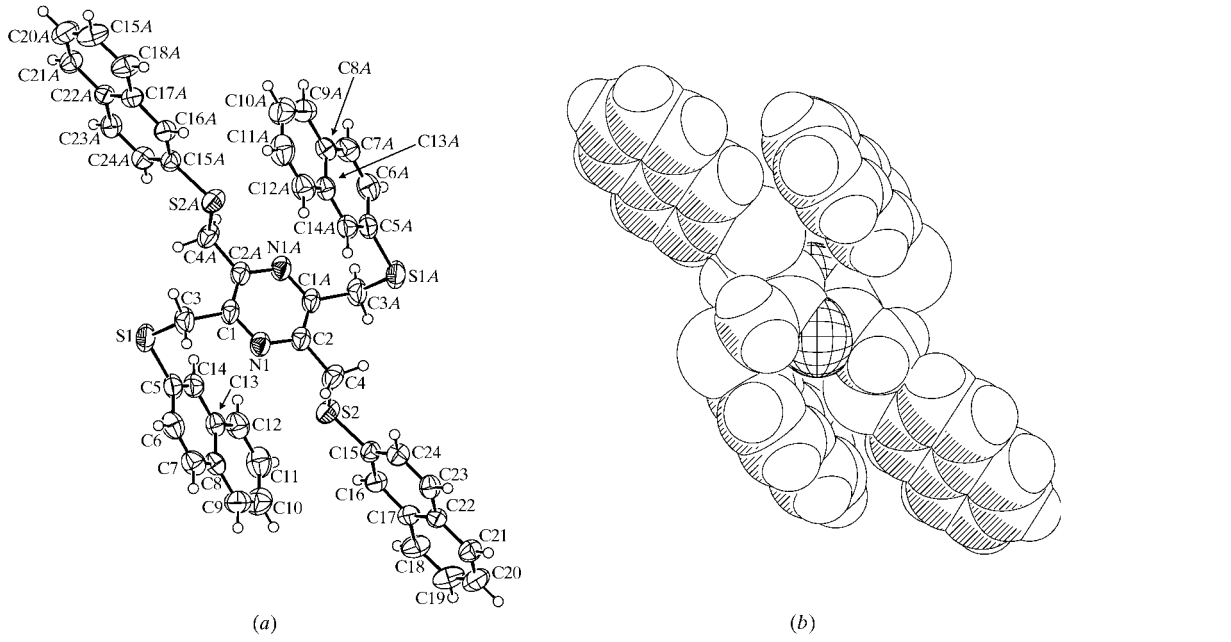

Figure 2
(*a*) A view of polymorph (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size. Atoms labelled with the additional letter *A* are at the symmetry position $(1-x, -y, -z)$. (*b*) A CPK view of polymorph (II).

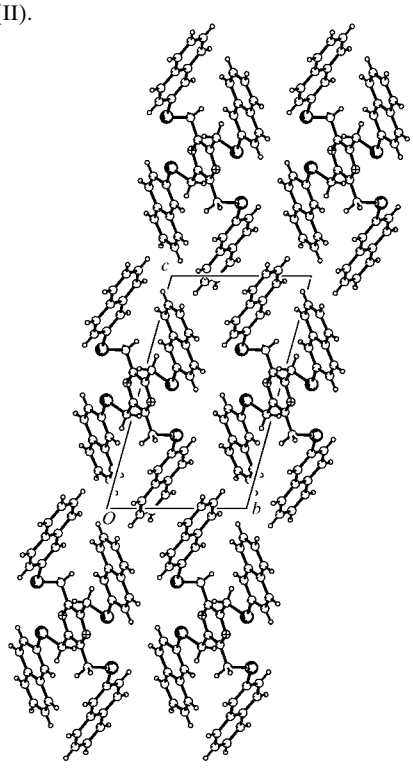

Figure 3
The molecular packing of polymorph (I), viewed along the *a* axis.

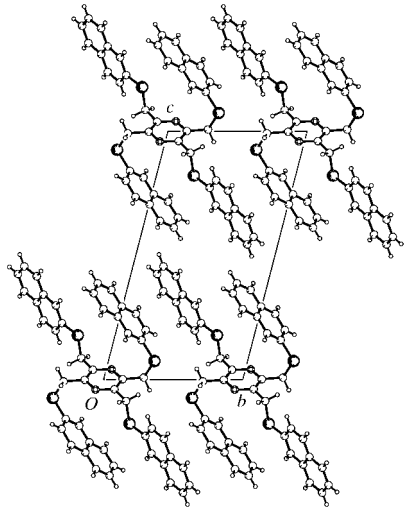

Figure 4
The molecular packing of polymorph (II), viewed along the *a* axis.

tuent. This conformation is illustrated in the CPK view of (II) given in Fig. 2(*b*). However, there are no short intramolecular interactions; for example, atom S2 is more than 3.7 Å from atom C12.

In the crystal packing of (I) and (II), the molecules stack along the *a* axes, as shown in Figs. 3 and 4, respectively. There are no short intermolecular interactions between symmetry-related molecules in either structure.

Experimental

In a 200 ml three-necked flask, NaOH (575 mg, 14.4 mmol, 4.4 equivalents) was dissolved in refluxing tetrahydrofuran (THF; 45 ml) and water (5 ml). Naphthalene-2-thiol (2.188 g, 13.7 mmol, 4.1 equivalents) dissolved in THF (45 ml) was then added dropwise. The deprotonation of naphthalene-2-thiol occurred in 1 h. To this solution, a solution of 2,3,5,6-tetrakis(bromomethyl)pyrazine (TBr; 1.515 g, 3.3 mmol, 1 equivalent) in THF (75 ml) was added dropwise, and the resulting mixture was left to reflux for 29 h. The solvent was removed using a rotary evaporator and a yellow powder (2.250 g) was obtained. The compound was purified on a chromatography column using CH_2Cl_2–toluene (10:3) as eluant (yield 42%). After evaporation of the solvent, a colourless powder was obtained. Crystals of polymorph (I) suitable for X-ray analysis were prepared by diffusion

of an equal volume of methanol into a toluene solution containing the product. Suitable crystals of polymorph (II) were prepared by slow evaporation of a chloroform–methanol (1:1) mixture after heating for 1 h under reflux. In both cases, the crystals were colourless. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84 (*m*, 8H, H6,9), 7.76 (*m*, 8H, H7,11), 7.48 [*dd*, 4H, ^3J(12,11) = 9.4 Hz, ^4J(12,4) = 1.9 Hz, H12], 7.47 (*s*, 4H, H4), 7.39 [*dd*, 4H, ^3J(8,7) = 8.6 Hz, ^4J(8,6/9) = 1.9 Hz, H8], 4.49 (*s*, 8H, H2); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 149.59 (4C, C1), 134.21 (4C, C3), 133.88 (4C, C5), 132.43 (4C, C10), 129.13 (4C, C11), 128.38 (12C, C6,8,9), 127.91 (4C, C7), 127.38 (4C, C12), 126.70 (4C, C4), 37.25 (4C, C2); ESI–MS: 769.09 $[M+H]^+$; IR (KBr disc, cm^{-1}): 3049 (*w*), 2926 (*w*), 1622 (*m*), 1582 (*m*), 1500 (*m*), 1446 (*m*), 1402 (*s*), 1336 (*w*), 1269 (*w*), 1243 (*w*), 1199 (*w*), 1131 (*m*), 1077 (*m*), 1013 (*w*), 957 (*w*), 942 (*w*), 902 (*w*), 885 (*w*), 863 (*w*), 852 (*s*), 821 (*s*), 806 (*s*), 798 (*s*), 763 (*w*), 749 (*s*), 737 (*s*), 636 (*w*), 598 (*w*), 479 (*s*), 469 (*s*). Analysis calculated for $C_{48}H_{36}N_2S_4$: C 74.96, H 4.72, N 3.64%; found: C 74.90, H 4.93, N 3.41%.

Compound (I)

Crystal data

$C_{48}H_{36}N_2S_4$
M_r = 769.09
Triclinic, $P\overline{1}$
a = 6.8780 (10) Å
b = 9.0432 (14) Å
c = 15.613 (2) Å
α = 73.631 (17)°
β = 82.265 (16)°
γ = 82.091 (18)°
V = 918.2 (2) Å^3
Z = 1
D_x = 1.391 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3169 reflections
θ = 2.4–25.9°
μ = 0.30 mm^{-1}
T = 153 (2) K
Rod, colourless
0.45 × 0.20 × 0.10 mm

Data collection

Stoe IPDS diffractometer
φ oscillation scans
7208 measured reflections
3332 independent reflections
1735 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
θ_{max} = 25.9°
$h = -8 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -18 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.082
S = 1.00
3332 reflections
244 parameters
H-atom parameters constrained
$w = \{\exp[3(\sin\theta/\lambda)^2]\}/[\sigma^2(F_o^2) + (0.0281P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

N1—C1	1.342 (3)	S2—C4	1.820 (3)
N1—C2	1.345 (3)	C1—C2^{i}	1.392 (4)
S1—C5	1.761 (2)	C1—C3	1.501 (3)
S1—C3	1.809 (3)	C2—C4	1.512 (3)
S2—C15	1.764 (3)		
C1—N1—C2	117.5 (2)	N1—C2—C1^{i}	121.7 (2)
C5—S1—C3	101.12 (12)	N1—C2—C4	115.2 (2)
C15—S2—C4	105.59 (13)	C1^{i}—C2—C4	123.0 (2)
N1—C1—C2^{i}	120.8 (2)	C1—C3—S1	110.34 (17)
N1—C1—C3	117.8 (2)	C2—C4—S2	108.9 (2)
C2^{i}—C1—C3	121.5 (2)		
N1—C1—C3—S1	−15.3 (3)	N1—C2—C4—S2	95.7 (2)
C5—S1—C3—C1	−178.9 (2)	C15—S2—C4—C2	125.36 (19)

Symmetry code: (i) $1-x, 2-y, 1-z$.

Compound (II)

Crystal data

$C_{48}H_{36}N_2S_4$
M_r = 769.09
Triclinic, $P\overline{1}$
a = 5.7641 (11) Å
b = 9.7771 (19) Å
c = 18.006 (4) Å
α = 75.40 (2)°
β = 87.87 (2)°
γ = 86.66 (2)°
V = 980.1 (3) Å^3
Z = 1
D_x = 1.303 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2628 reflections
θ = 2.2–26.0°
μ = 0.28 mm^{-1}
T = 293 (2) K
Plate, colourless
0.50 × 0.30 × 0.03 mm

Data collection

Stoe IPDS diffractometer
φ oscillation scans
7633 measured reflections
3545 independent reflections
1467 reflections with $I > 2\sigma(I)$
R_{int} = 0.062
θ_{max} = 26.0°
$h = -7 \rightarrow 7$
$k = -11 \rightarrow 12$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.086
S = 1.01
3545 reflections
245 parameters
H-atom parameters constrained
$w = \{\exp[4(\sin\theta/\lambda)^2]\}/[\sigma^2(F_o^2) + (0.0241P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0125 (14)

Table 2
Selected geometric parameters (Å, °) for (II).

N1—C1	1.339 (4)	S2—C4	1.807 (3)
N1—C2	1.341 (4)	C1—C2^{ii}	1.403 (4)
S1—C5	1.777 (3)	C1—C3	1.506 (4)
S1—C3	1.822 (3)	C2—C4	1.506 (4)
S2—C15	1.765 (3)		
C1—N1—C2	117.7 (3)	N1—C2—C1^{ii}	120.8 (3)
C5—S1—C3	100.06 (15)	N1—C2—C4	115.7 (3)
C15—S2—C4	104.07 (14)	C1^{ii}—C2—C4	123.4 (3)
N1—C1—C2^{ii}	121.5 (3)	C1—C3—S1	111.3 (2)
N1—C1—C3	115.4 (3)	C2—C4—S2	105.7 (2)
C2^{ii}—C1—C3	123.0 (3)		
N1—C1—C3—S1	−101.8 (3)	N1—C2—C4—S2	93.8 (3)
C5—S1—C3—C1	58.9 (3)	C15—S2—C4—C2	173.1 (2)

Symmetry code: (ii) $1-x, -y, -z$.

Table 3
Dihedral angles (°) between aromatic rings in polymorphs (I) and (II).

Plane *A* is the pyrazine ring, plane *B* is the naphthalene plane containing atom S1 and plane *C* is the naphthalene plane containing atom S2.

Polymorph (I)		Polymorph (II)	
Plane–plane	Angle (°)	Plane–plane	Angle (°)
A–*B*	6.8 (1)	*A*–*B*	39.8 (1)
A–*C*	75.3 (1)	*A*–*C*	82.6 (1)
B–*C*	78.7 (1)	*B*–*C*	57.0 (1)

Crystals of polymorphs (I) and (II) diffracted weakly and the ratios of observed reflections to the number of parameters were low (∼7). It was only possible to access ∼93% of the Ewald sphere in the triclinic system using the image-plate diffraction system if maximum atomic resolution was to be obtained, *i.e.* 0.81 Å. All H atoms were initially located in difference Fourier maps, and were subsequently included in the refinement in calculated positions and treated as riding atoms, using *SHELXL*97 (Sheldrick, 1997) default parameters. Polymorph (I) was measured at 153 K, and hence the C—H distances were 0.95–0.99 Å; polymorph (II) was measured at 293 K, and hence the C—H distances were 0.93–0.97 Å. In both cases, U_{iso}(H) values were taken to be equal to $1.2U_{eq}$(C).

For both polymorphs, data collection: *EXPOSE* (Stoe & Cie, 2000); cell refinement: *CELL* (Stoe & Cie, 2000); data reduction: *INTEGRATE* (Stoe & Cie, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990) for both polymorphs and *PLUTON* (Spek, 1990) for (II).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1045). Services for accessing these data are described at the back of the journal.

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