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# 2,3,5,6-Tetrakis(phenoxymethyl)-pyrazine and 2,3,5,6-tetrakis(phenylsulfanylmethyl)pyrazine

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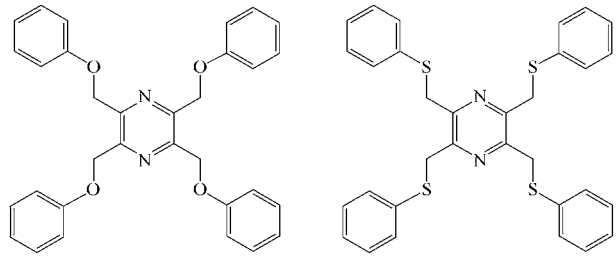
The title compounds, $C_{32}H_{28}N_2O_4$, (I), and $C_{32}H_{28}N_2S_4$, (II), respectively, are tetrasubstituted pyrazines and both possess $C_i$ symmetry. They differ only in the hetero atom ($X$) of the $-CH_2XPh$ side-arm substituents: $X$ = O in (I) and S in (II). Compound (I) has an overall S-shape with a pair of adjacent $-CH_2OPh$ side arms alternately above and below the plane of the central pyrazine ring. The phenyl rings are inclined to one another by 12.63 (18)° and there is one intramolecular C—H···O hydrogen bond involving adjacent $-CH_2OPh$ side arms. In compound (II), adjacent $-CH_2SPh$ side arms point in opposite directions with respect to the pyrazine ring plane, with the phenyl rings inclined at 60.45 (8)°. Both structures have weak C—H···$\pi$ intermolecular interactions.

## Comment

Tetrasubstituted pyrazines have been used now for many years as ligands in coordination chemistry. The most studied compounds are 2,3,5,6-tetra-2-pyridylpyrazine (tppz) (Bock *et al.*, 1992; Greaves & Stoeckli-Evans, 1992) and, to a lesser extent, pyrazine-2,3,5,6-tetracarboxylic acid (pztca) (Vishweshwar *et al.*, 2001). A search of the Cambridge Structural Database (CSD, Version 1.9, last update November 2006; Allen, 2002) indicated the presence of more than 110 structures involving tppz and 23 involving pztca. Another tetrasubstituted pyrazine we have used in coordination chemistry is tetrakis(aminomethyl)pyrazine (Ferigo *et al.*, 1994; Neels & Stoeckli-Evans, 1998; Neels *et al.*, 2003). Two triclinic polymorphs of 2,3,5,6-tetrakis(naphthalen-2-ylsulfanylmethyl)-pyrazine have also been reported (Pacifico & Stoeckli-Evans, 2004); both crystallized in the space group $P\overline{1}$ and, like the title compounds, possess $C_i$ symmetry.

The molecular structures of compounds (I) and (II) are shown in Figs. 1 and 2, respectively. The bond distances




and angles (Tables 1 and 3) are similar to those reported for 2,3,5,6-tetrakis[(naphthalen-2-yloxy)methyl]pyrazine, (III) (Gasser & Stoeckli-Evans, 2007), and the (naphthalen-2-ylsulfanylmethyl) analogue, polymorphs (IV*a*) and (IV*b*), referred to above. Due to steric hindrance involving the H atoms on atoms C3 and C5, and C10 and C16 in (I), the average value of the O1—C4—C5 and O2—C11—C16 angles is 124.7 (2)°. In (II), the steric hindrance involves the H atoms on atoms C3 and C9, and C10 and C16, and the average value of the S1—C4—C9 and S2—C11—C16 angles is 124.22 (8)°. Similar observations can be made for compound (III), and for polymorphs (IV*a*) and (IV*b*).

In compound (I), there is an intramolecular C10—H10*B*···O1 hydrogen bond involving adjacent side arms (Table 2 and Fig. 5). In both compounds, all of the aromatic rings are planar within experimental error. The dihedral angles between the aromatic rings in all four compounds are given in Table 5. Compounds (I) and (II) differ in their overall shape, owing to the different orientation of the adjacent $-CH_2XPH$ substituents with respect to the plane of the pyrazine ring. The overall shape of molecule (I) is very similar to that observed in (III). This is reflected in the similar dihedral angles between the aromatic rings (Table 5), and is illu-

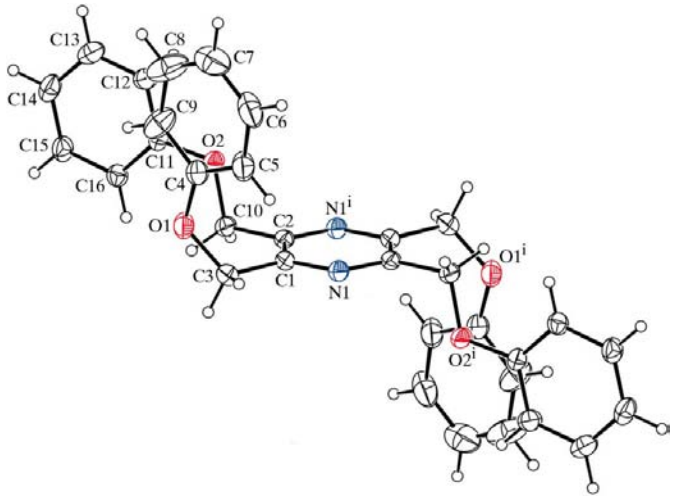



**Figure 1**
A view of the molecular structure of compound (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $1-x, 1-y, 1-z$.]

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strated by the CPK (Corey–Pauling–Koltun) views given in Fig. 3. The overall shape of molecule (II) is intermediate between those observed in polymorphs (IV*a*) and (IV*b*). Again, this is reflected in the dihedral angles between the aromatic rings (Table 5). An inspection of the CPK views given in Fig. 4 shows that, while (II) and (IV*a*) have two opposite side arms almost parallel to the pyrazine ring, the orientation of the other pair of opposite side arms differs by *ca* 180°. The general conformation of (IV*b*) is different from any of the other four arrangements.

In the cell of (I), the molecules form stacks along the *b* axis. The only intermolecular contact is a C—H···$\pi$ interaction (Fig. 5 and Table 2). In (II), the molecules form stacks along

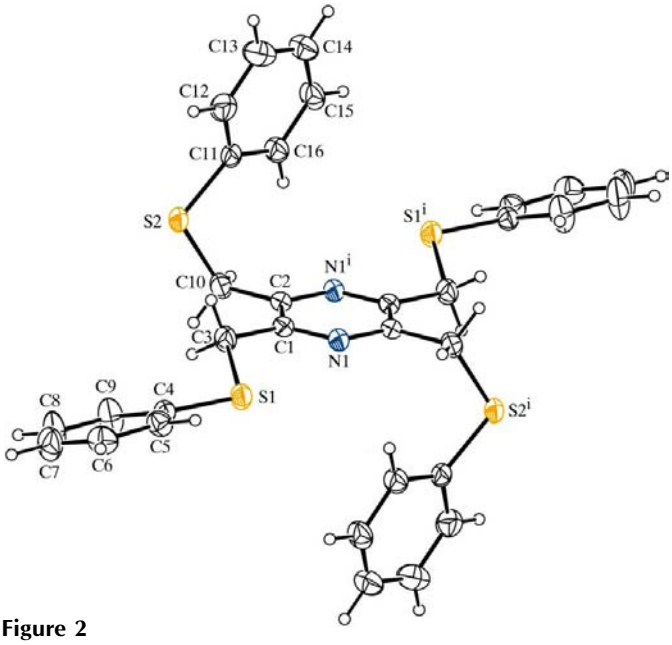


**Figure 2**
A view of the molecular structure of compound (II), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $1-x, 1-y, 1-z$.]

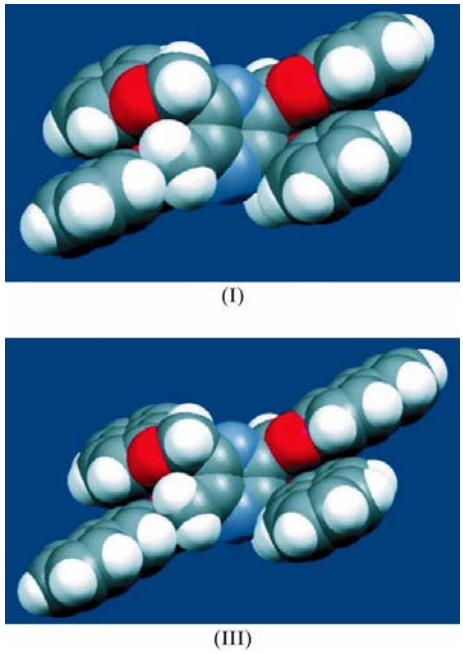


**Figure 3**
CPK views of compounds (I) and (III).

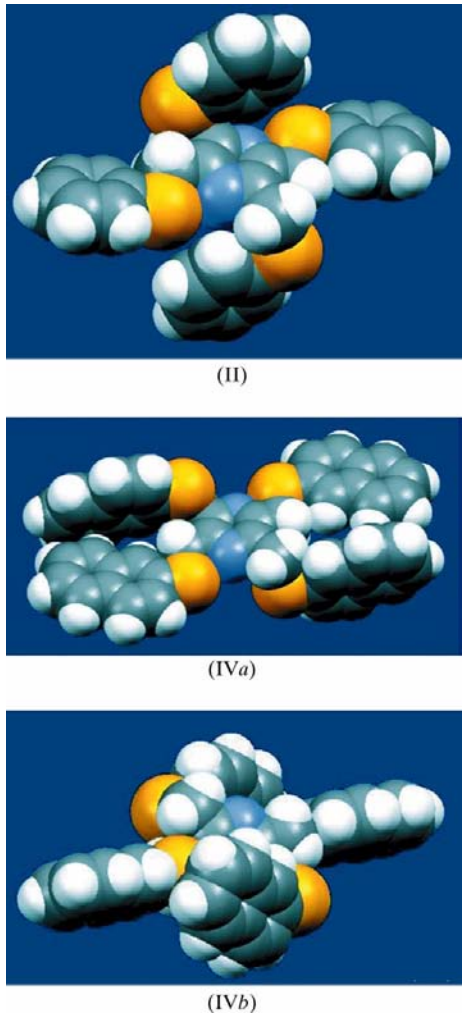


**Figure 4**
CPK views of compound (II), and polymorphs (IV*a*) and (IV*b*).

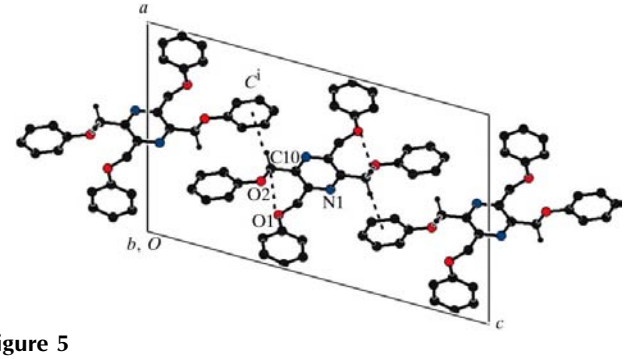


**Figure 5**
The crystal packing of compound (I), viewed down the *b* axis. The C—H···O intramolecular hydrogen bonds and C—H···$\pi$ interactions are shown as dashed lines [plane *C* = phenyl ring C11–C16; symmetry code: (i) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$].

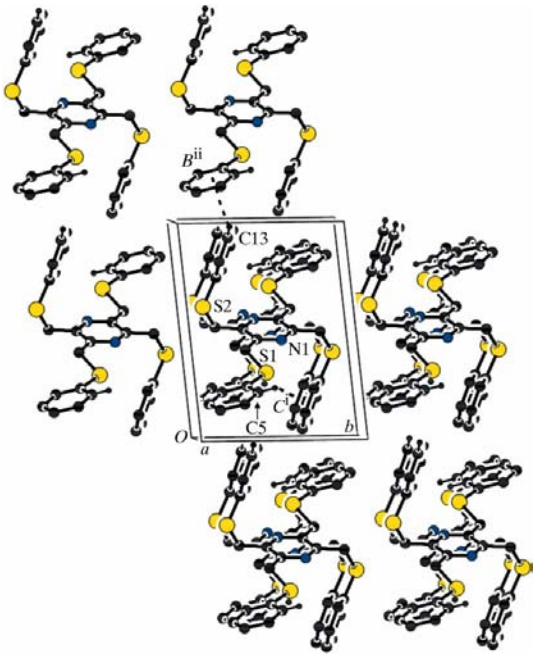


**Figure 6**
The crystal packing of compound (II), viewed down the *a* axis. The C—H···$\pi$ interactions are shown as dashed lines [plane *B* = phenyl ring C4–C9; plane *C* = phenyl ring C11–C16; symmetry codes: (i) $2-x, 1-y, 1-z$; (ii) $x, y, 1+z$].

the *a* direction. Here, there are two intermolecular C—H···$\pi$ interactions (Fig. 6 and Table 4).

## Experimental

Compound (I) was prepared by reacting tetrakis(bromomethyl)-pyrazine (TBr4) (Ferigo *et al.*, 1994) with phenol in the presence of NaH. In a three-necked 100 ml flask under $N_2$ were added successively NaH (0.12 g, 4.8 mmol, 4.8 equivalents), which had been washed with dry pentane to remove its dispersion oil, and tetrahydrofuran (THF) (10 ml). Phenol (0.41 g, 4.4 mmol, 4.4 equivalents) dissolved in dry THF (20 ml) was then added dropwise, firstly over an ice bath, then at room temperature, followed by a water bath and finally an oil bath at 343 K, all over a period of 90 min. The mixture was then cooled to room temperature and TBr4 (0.45 g, 1 mmol, 1 equivalent) dissolved in dry THF (20 ml) was added dropwise over a period of 30 min. The solution turned yellow and was then heated under reflux for 2 h. The mixture, which had turned brown and from which a white solid (NaBr) had precipitated, was then allowed to cool to room temperature. A few drops of water were added cautiously to the mixture in order to destroy excess NaH. The mixture was then filtered to remove NaBr and the solvent was eliminated from the filtrate by rotary evaporation. The residual solid was dissolved in diethyl ether (50 ml). The unreacted phenol was removed by extraction using 3 × 50 ml of 0.25 *N* NaOH. The organic phases were collected, dried over $MgSO_4$ and filtered. The solvents were eliminated by evaporation. The light-brown paste obtained was dried under vacuum and purified by flash chromatography using $CH_2Cl_2$–toluene (10:3 *v*/*v*) to give compound (I) as a white solid (yield 0.13 g, 26%). Further analytical data are available in the archived CIF. Crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of a solution of (I) in $CHCl_3$.

Compound (II) was prepared by reacting TBr4 with the sodium salt of thiophenol. To a solution of EtOH (200 ml) containing the thiophenol sodium salt (4.10 g, 31 mmol; Fluka, 97%) was added TBr4 (1 g, 2.21 mmol). The mixture was heated under reflux with stirring for 5 h. After cooling in an ice bath, the white precipitate that had formed was filtered off, washed with EtOH and dried under vacuum to give (II) (yield 1.14 g, 90%). Further analytical data are available in the archived CIF. Crystals suitable for X-ray crystallographic analysis were prepared by diffusion of an equal volume of ethanol into a $CHCl_3$ solution of (II).

### Compound (I)

*Crystal data*

$C_{32}H_{28}N_2O_4$
$M_r$ = 504.56
Monoclinic, $P2_1/c$
$a$ = 12.4717 (15) Å
$b$ = 5.0859 (6) Å
$c$ = 21.0412 (19) Å
$\beta$ = 105.243 (11)°
$V$ = 1287.7 (2) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.09 mm$^{-1}$
$T$ = 223 (2) K
0.49 × 0.46 × 0.11 mm

*Data collection*

Stoe AED2 four-circle diffractometer
4618 measured reflections
2391 independent reflections
1373 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.053
2 standard reflections
frequency: 60 min
intensity decay: 1%

*Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.150
$S$ = 1.10
2391 reflections
172 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.16 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.20 e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| O1—C3 | 1.428 (4) | O2—C10 | 1.434 (4) |
| O1—C4 | 1.376 (4) | O2—C11 | 1.381 (3) |
| C3—O1—C4 | 118.5 (2) | O1—C4—C9 | 114.9 (3) |
| C10—O2—C11 | 116.9 (2) | O2—C10—C2 | 106.4 (2) |
| O1—C3—C1 | 112.8 (2) | O2—C11—C12 | 115.8 (3) |
| O1—C4—C5 | 125.6 (3) | O2—C11—C16 | 123.8 (3) |

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

*Cg* is the centroid of the C11–C16 ring.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C10—H10*B*···O1 | 0.98 | 2.53 | 2.977 (3) | 108 |
| C10—H10*A*···*Cg*$^{i}$ | 0.98 | 2.89 | 3.741 (3) | 147 |

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

### Compound (II)

*Crystal data*

$C_{32}H_{28}N_2S_4$
$M_r$ = 568.80
Triclinic, $P\overline{1}$
$a$ = 6.4278 (7) Å
$b$ = 9.7152 (12) Å
$c$ = 12.0602 (12) Å
$\alpha$ = 91.152 (10)°
$\beta$ = 102.748 (8)°
$\gamma$ = 107.217 (8)°
$V$ = 698.69 (13) Å$^3$
$Z$ = 1
Mo $K\alpha$ radiation
$\mu$ = 0.37 mm$^{-1}$
$T$ = 173 (2) K
0.37 × 0.14 × 0.12 mm

*Data collection*

| | |
|---|---|
| Stoe IPDSII diffractometer | 13473 measured reflections |
| Absorption correction: multi-scan (*PLATON*; Spek, 2003) | 3763 independent reflections |
| $T_{min}$ = 0.741, $T_{max}$ = 0.956 | 3155 reflections with $I > 2\sigma(I)$ |
| | $R_{int}$ = 0.032 |

*Refinement*

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.033 | 172 parameters |
| $wR(F^2)$ = 0.082 | H-atom parameters constrained |
| $S$ = 1.04 | $\Delta\rho_{max}$ = 0.27 e Å$^{-3}$ |
| 3763 reflections | $\Delta\rho_{min}$ = −0.25 e Å$^{-3}$ |

**Table 3**
Selected geometric parameters (Å, °) for (II).

| | | | |
|---|---|---|---|
| S1—C3 | 1.8159 (15) | S2—C10 | 1.8189 (14) |
| S1—C4 | 1.7752 (14) | S2—C11 | 1.7687 (14) |
| | | | |
| C3—S1—C4 | 101.23 (6) | S1—C4—C9 | 124.32 (12) |
| C10—S2—C11 | 104.03 (6) | S2—C10—C2 | 113.40 (9) |
| S1—C3—C1 | 109.96 (9) | S2—C11—C12 | 116.25 (11) |
| S1—C4—C5 | 116.52 (10) | S2—C11—C16 | 124.12 (11) |

**Table 4**
Hydrogen-bond geometry (Å, °) for (II).

*Cg*1 and *Cg*2 denote the centroids of the C4–C9 and C11–C16 rings, respectively.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C5—H5···*Cg*1$^{i}$ | 0.95 | 2.74 | 3.528 (2) | 141 |
| C13—H13···*Cg*2$^{ii}$ | 0.95 | 2.81 | 3.528 (29 | 133 |

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x, y, z+1$.

**Table 5**
Dihedral angles (°) between aromatic rings in compounds (I), (III) and (II), and polymorphs (IV*a*) and (IV*b*).

| Plane–plane† | (I) | (III) | (II) | (IV*a*)‡ | (IV*b*)§ |
|---|---|---|---|---|---|
| *A*—*B* | 87.64 (17) | 85.2 (3) | 19.15 (7) | 6.8 (1) | 39.8 (1) |
| *A*—*C* | 88.18 (14) | 84.9 (3) | 79.58 (7) | 75.3 (1) | 82.6 (1) |
| *B*—*C* | 12.63 (18) | 0.6 (3) | 60.45 (8) | 78.7(19 | 57.081) |

† Plane *A* = pyrazine ring; plane *B* = phenyl or naphthyl ring attached to heteroatom O1 or S1; plane *C* = phenyl or naphthyl ring attached to heteroatom O2 or S2. ‡ (IV*a*) = CSD refcode INOHIC01 (Pacifico & Stoeckli-Evans, 2004). § (IV*b*) = CSD refcode INOHIC (Pacifico & Stoeckli-Evans, 2004).

In both compounds, the H atoms were included in calculated positions and refined as riding atoms, with C—H distances in the range 0.94–0.98 Å in (I) and 0.95–0.99 Å in (II), and with $U_{iso}$(H) = 1.2$U_{eq}$(C).

Data collection: *STADI4* (Stoe & Cie, 1997) for (I); *X-AREA* (Stoe & Cie, 2006) for (II). Cell refinement: *STADI4* for (I); *X-AREA* for (II). Data reduction: *X-RED* (Stoe & Cie, 1997) for (I); *X-RED32* (Stoe & Cie, 2006) for (II). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *MERCURY* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3041). Services for accessing these data are described at the back of the journal.

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