

2,6-Dibenzyl-1,2,3,5,6,7-hexahydro-2,4,6,8-tetraaza-*s*-indacene and 2,6-bis(4-methoxybenzyl)-1,2,3,5,6,7-hexahydro-2,4,6,8-tetraaza-*s*-indacene

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Received 16 March 2004

Accepted 20 April 2004

Online 22 June 2004

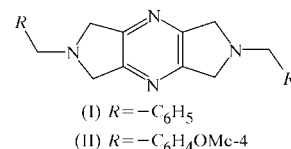
The title compounds, $C_{22}H_{22}N_4$ and $C_{24}H_{26}N_4O_2$ [alternative names: 2,6-dibenzyl-2,3,6,7-tetrahydro-1*H*,5*H*-dipyrrolo[3,4-*b*;3',4'-*e*]pyrazine and 2,6-bis(4-methoxybenzyl)-2,3,6,7-tetrahydro-1*H*,5*H*-dipyrrolo[3,4-*b*;3',4'-*e*]pyrazine], two 1,2,3,5,6,7-hexahydro-2,4,6,8-tetraaza-*s*-indacene derivatives, are both centrosymmetric and have similar S-shaped structures. In the former, there are two independent molecules (*A* and *B*), both of which possess C_i symmetry. These two molecules are arranged such that the benzene ring substituent of molecule *B* is directed towards the plane of the benzene ring substituent of molecule *A*, with a dihedral angle of $55.4(2)^\circ$ between their planes. The shortest C—H...C distance is, however, only 3.21(1) Å. In both compounds, the benzene ring substituents are almost perpendicular to the plane of the central pyrazine ring, and the pyrrolidine rings have perfect envelope conformations. In the crystal structures of both compounds, the molecules pack in a herring-bone arrangement.

Comment

During attempts to prepare 1,2,3,5,6,7-hexahydro-2,4,6,8-tetraaza-*s*-indacene, the title compounds, (I) and (II) were synthesized by the reaction of 2,3,5,6-tetrakis(bromomethyl)-

pyrazine (Ferrigo *et al.*, 1994) with the corresponding amines. Attempts have been made to deprotect these diamines, but with little success so far.

Compound (I), with two benzyl substituents, crystallizes with two independent centrosymmetric molecules (*A* and *B*) in the unit cell. The molecular structure of (I) is illustrated in Fig. 1, and selected geometric parameters are given in Table 1. The bond distances and angles are normal when compared with values found for similar molecules in the Cambridge Structural Database (Allen, 2002).



The molecules have an S shape, the plane of the benzene rings being almost perpendicular to the plane of the pyrazine ring. In molecule *A*, the dihedral angle between the C6–C11 plane and the plane of the pyrazine ring involving atom N1 is $88.2(2)^\circ$. In molecule *B*, the dihedral angle between the planes of the C26–C31 benzene ring and the pyrazine ring involving atom N21 is $88.9(2)^\circ$. The pyrrolidine rings have perfect envelope conformations, with atoms N2 and N22 at the flaps. The two Csp^3 atoms (C3 and C4A in molecule *A*, and C23 and C24 in molecule *B*; see Fig. 1) lie in the plane of the pyrazine ring. The Cremer & Pople (1975) puckering parameters $Q(2)$ and $\varphi(2)$ are 0.289(3) Å and $1.9(6)^\circ$ for molecule *A* (atom N2), and 0.290(3) Å and $182.1(7)^\circ$ for molecule *B* (atom N22).

The two molecules are arranged such that the plane of the benzene ring of molecule *B* (C26–C31) is directed towards the plane of the benzene ring of molecule *A* (C6–C11), as shown in Fig. 1. These rings are inclined to one another by $55.4(2)^\circ$. The shortest C—H...C distance, for the C29—H29A...C9 interaction, is, however, only 3.21(1) Å (for H29...C9).

In the crystal structure, the molecules stack along the *c* axis, with molecules *A* and *B* in separate columns. The molecules are arranged head-to-head (or tail-to-tail) in a herring-bone arrangement, as shown in Fig. 2. There are no short intermolecular contacts (< 3.2 Å) in the crystal structure, apart from the arrangement noted above.

Compound (II), with two 4-methoxybenzyl substituents, also possesses C_i symmetry. The molecular structure of (II) is illustrated in Fig. 3, and selected geometric parameters are

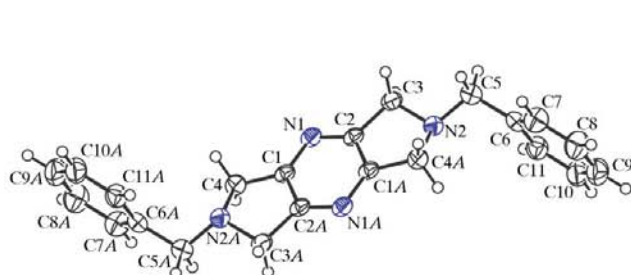
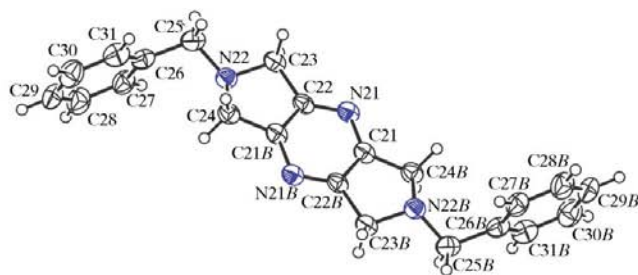


Figure 1

A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (*A*) $1 - x, 2 - y, -z$; (*B*) $-x, 1 - y, -z$.]



given in Table 2. The overall structure is similar to that of (I) and, again, the bond distances and angles are normal (Allen, 2002). The molecule has an S shape (Fig. 3), the plane of the benzene ring being inclined to the plane of the pyrazine ring by $86.6(1)^\circ$. The pyrrolidine rings have perfect envelope conformations, with atom N2 at the flap. The two Csp^3 atoms (C3 and C4) lie in the plane of the pyrazine ring. The Cremer & Pople (1975) puckering parameters $Q(2)$ and $\varphi(2)$ are $0.288(1) \text{ \AA}$ and $178.2(3)^\circ$, respectively. The methoxy substituent on the benzene ring lies in the plane of the ring, with a C12—O1—C9—C10 torsion angle of $-179.85(13)^\circ$.

In the crystal structure of (II), the molecules stack along the c axis and are arranged head-to-head (or tail-to-tail) in a herring-bone arrangement, as shown in Fig. 4. Again, there are no short intermolecular contacts ($< 3.2 \text{ \AA}$) in the crystal structure.

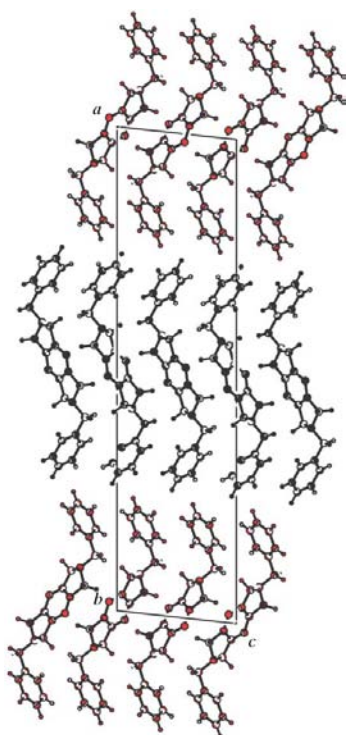


Figure 2
The molecular packing of (I), viewed down the b axis. Molecules A are centred about $x = \frac{1}{2}$.

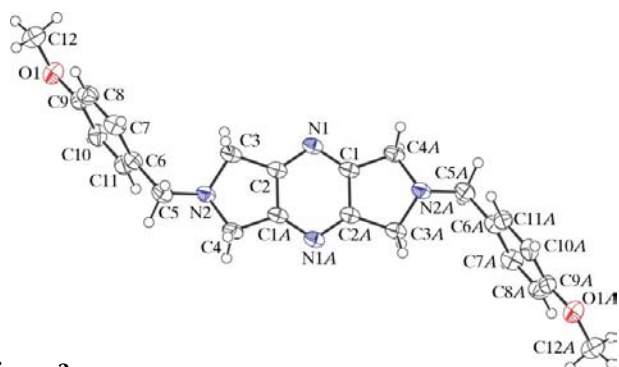


Figure 3
A view of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (A) $-x, 1 - y, 1 - z$.]

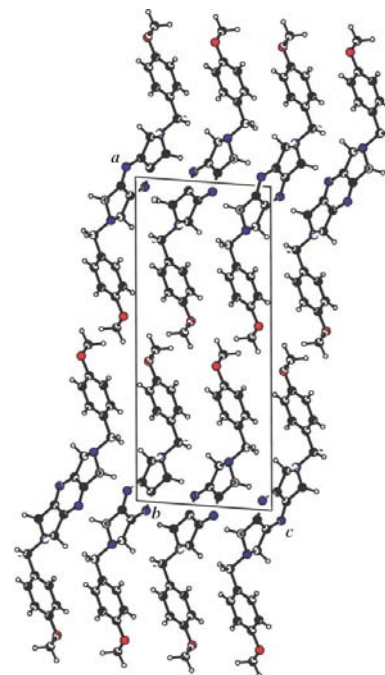


Figure 4
The molecular packing of (II), viewed down the b axis.

Experimental

Compounds (I) and (II) were prepared by the reaction of 2,3,4,5-tetrakis(bromomethyl)pyrazine (Ferrigo *et al.*, 1994) with benzylamine [for (I)] or 4-methoxybenzylamine [for (II)], both in dry methanol. Crystals suitable for X-ray analysis were obtained by slow evaporation of solutions of pure (I) and (II) in CHCl_3 over a period of about one week.

Compound (I)

Crystal data

$\text{C}_{22}\text{H}_{22}\text{N}_4$
 $M_r = 342.44$
Monoclinic, $P2_1/c$
 $a = 36.228(3) \text{ \AA}$
 $b = 5.5729(6) \text{ \AA}$
 $c = 8.9677(7) \text{ \AA}$
 $\beta = 96.205(9)^\circ$
 $V = 1799.9(3) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.264 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 5182 reflections
 $\theta = 2.3\text{--}26.0^\circ$
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 153(2) \text{ K}$
Plate, colourless
 $0.40 \times 0.40 \times 0.10 \text{ mm}$

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I).

N1—C1	1.338 (4)	N21—C21	1.343 (4)
N1—C2	1.342 (4)	N21—C22	1.342 (4)
N2—C5	1.466 (4)	N22—C25	1.454 (4)
N2—C3	1.471 (4)	N22—C23	1.470 (4)
N2—C4 ⁱ	1.472 (4)	N22—C24	1.475 (4)
C1—C2 ⁱ	1.395 (4)	C21—C22 ⁱⁱ	1.389 (4)
C1—C4	1.495 (4)	C21—C24 ⁱⁱ	1.483 (5)
C2—C3	1.493 (5)	C22—C23	1.491 (5)
C1—N1—C2	112.4 (3)	C22—N21—C21	111.9 (3)
C5—N2—C3	113.2 (3)	C25—N22—C23	113.8 (3)
C5—N2—C4 ⁱ	113.6 (3)	C25—N22—C24	113.9 (3)
C3—N2—C4 ⁱ	108.0 (2)	C23—N22—C24	107.1 (2)

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

Data collection

Stoe Image-Plate diffractometer	$R_{\text{int}} = 0.087$
φ scans	$\theta_{\text{max}} = 26.0^\circ$
12 398 measured reflections	$h = -44 \rightarrow 44$
3324 independent reflections	$k = -6 \rightarrow 6$
1882 reflections with $I > 2\sigma(I)$	$l = -9 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0662P)^2 + 1.3228P]$
$R[F^2 > 2\sigma(F^2)] = 0.068$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.181$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.19 \text{ e } \text{\AA}^{-3}$
3324 reflections	$\Delta\rho_{\text{min}} = -0.18 \text{ e } \text{\AA}^{-3}$
235 parameters	
H-atom parameters constrained	

Compound (II)

Crystal data

$\text{C}_{24}\text{H}_{26}\text{N}_4\text{O}_2$	$D_x = 1.308 \text{ Mg m}^{-3}$
$M_r = 402.49$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3858 reflections
$a = 20.852 (2) \text{ \AA}$	$\theta = 2.9\text{--}25.9^\circ$
$b = 5.6574 (5) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$c = 8.6905 (9) \text{ \AA}$	$T = 153 (2) \text{ K}$
$\beta = 94.400 (13)^\circ$	Plate, colourless
$V = 1022.17 (18) \text{ \AA}^3$	$0.50 \times 0.40 \times 0.10 \text{ mm}$
$Z = 2$	

Data collection

Stoe Image-Plate diffractometer	$R_{\text{int}} = 0.075$
φ scans	$\theta_{\text{max}} = 25.9^\circ$
7540 measured reflections	$h = -25 \rightarrow 25$
1985 independent reflections	$k = -6 \rightarrow 6$
1152 reflections with $I > 2\sigma(I)$	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.030$	$w = 1/[\sigma^2(F_o^2) + (0.0278P)^2]$
$wR(F^2) = 0.071$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.81$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1985 reflections	$\Delta\rho_{\text{max}} = 0.14 \text{ e } \text{\AA}^{-3}$
137 parameters	$\Delta\rho_{\text{min}} = -0.13 \text{ e } \text{\AA}^{-3}$

For both (I) and (II), H atoms were included in calculated positions and treated as riding atoms, to ensure as high a parameter/

Table 2

Selected geometric parameters (\AA , $^\circ$) for (II).

N1—C1	1.3389 (17)	O1—C9	1.3744 (18)
N1—C2	1.3392 (18)	O1—C12	1.4247 (18)
N2—C5	1.4588 (18)	C1—C2 ⁱⁱⁱ	1.3956 (18)
N2—C3	1.4716 (17)	C1—C4 ⁱⁱⁱ	1.487 (2)
N2—C4	1.4764 (17)	C2—C3	1.491 (2)
C1—N1—C2	112.46 (11)	C3—N2—C4	107.41 (10)
C5—N2—C3	113.82 (11)	C9—O1—C12	117.36 (12)
C5—N2—C4	113.51 (11)		

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

reflection ratio as possible [aromatic C—H = 0.95 \AA and CH_2 C—H = 0.99 \AA , with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, and methyl C—H = 0.98 \AA , with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$].

For both compounds, data collection: *EXPOSE* (Stoe & Cie, 2000); cell refinement: *CELL* (Stoe & Cie, 2000); data reduction: *INTEGRATE* (Stoe & Cie, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

Financial support from the Swiss National Science Foundation is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1478). Services for accessing these data are described at the back of the journal.

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