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Capped-porphyrin precursors

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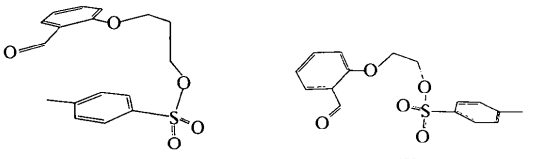
Abstract

In the crystalline state, 2-[3-(tosyloxy)propoxy]benzaldehyde [(I), $C_{17}H_{18}O_5S$] exists in a U-shaped conformation. The benzaldehyde and toluene rings are nearly parallel. Crystals of 2-[2-(tosyloxy)ethoxy]-benzaldehyde occur with two habits. The X-ray structure determinations of these habits reveal an anhydrous form [(II), $C_{16}H_{16}O_5S$] and a hemihydrated form [(III), $C_{16}H_{16}O_5S{\cdot}0.5H_2O$]. In (III), a water molecule bridges two carbonyl functions [O6$\cdots$O1 2.87 (1) Å]. 1,2,4,5-Tetrakis{2-[2-(1,3-dioxolan-2-yl)-phenoxy]ethoxy}benzene [(IV), $C_{50}H_{54}O_{16}$] was prepared by protecting the aldehyde function of (II) or (III) with ethylene glycol and reacting the resulting compound with 1,2,4,5-tetrahydroxybenzene. Compound (IV) has $\bar{1}$ symmetry.

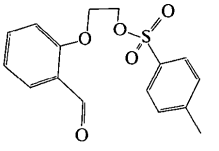
Comment

There is considerable interest in sterically hindered porphyrins as models for heme active sites (Momenteau & Reed, 1994). In particular, a great deal of interest has been paid to model complexes with a high degree of discrimination between O_2 and CO binding (Slebodnick & Ibers, 1997). New models continue to be introduced (Jaquinod *et al.*, 1998; Collman *et al.*, 1997). In the course of our work in this area, three different capped-porphyrin precursors have been structurally characterized. One of these precursors occurs in both anhydrous and hemihydrated crystal forms.

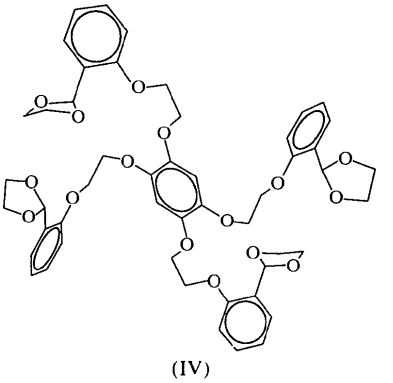
Compound (I), 2-[3-(tosyloxy)propoxy]benzaldehyde, is an intermediate in the synthesis of the sterically hindered five-atom-linked capped porphyrin 5,10,15,20-{benzene-1,2,4,5-tetrakis[(2-phenyloxy)propoxy]-2′,2″,2‴,2⁗-tetrayl}porphyrin (Ma *et al.*, 1993). The



(I) (II)



(III)



(IV)

synthesis involves a condensation proposed by Almog *et al.* (1975), which was more generally elaborated later (Almog *et al.*, 1981). Compound (I) (Fig. 1) contains two symmetry-independent molecules, referred to hereafter as *A* and *B*, related by a pseudo-symmetry center at $x = 0.13$, $y = 0$. For structures with more than one molecule in the asymmetric unit of $Pna2_1$, such symmetry centers are common and they occur predominantly at about $x = \frac{1}{8}$, $y = 0$ (Marsh *et al.*, 1998). In both *A* and *B*, the distance between the two benzene planes is 3.49 (1) Å (measured from the centroid of the toluene to the mean plane of the benzaldehyde), with a dihedral angle of 2.0 (1)° between the planes. The dihedral angle between the two molecules in the asymmetric unit is 3.4 (2)° (measured as the angle between the mean plane of C2–C7 in *A* and the mean plane of C19–C24 in *B*). Equivalent bond lengths between *A* and *B* are nearly identical. Table 1 lists equivalent bond lengths and angles one after another. This appears to be a genuine instance of two nearly identical molecules in the asymmetric unit. The *MISSYM* algorithm (Le Page, 1987, 1988) in the *PLATON* suite of programs (Spek, 1990) revealed no extra symmetry; ex-

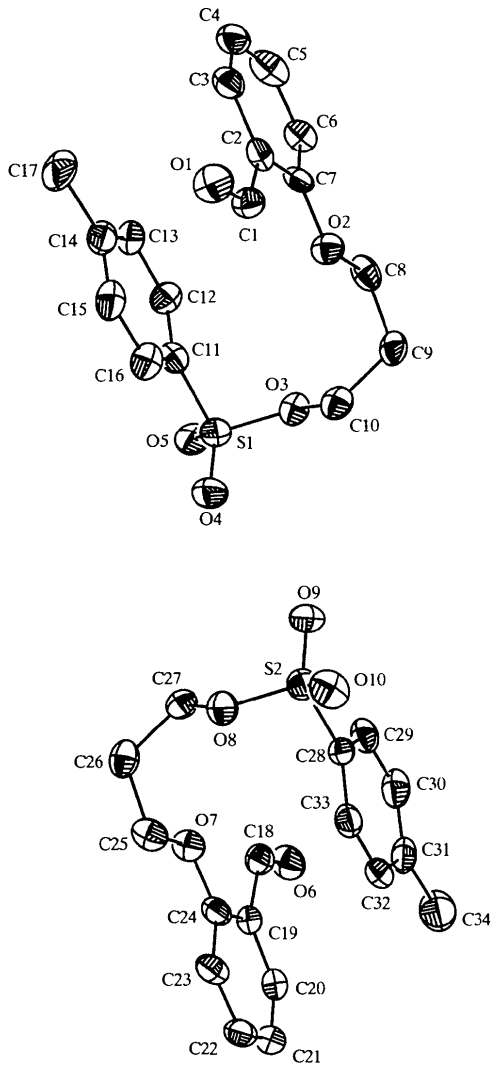


Fig. 1. A view showing 50% probability displacement ellipsoids for the two symmetry-independent molecules of (I) in the asymmetric unit. H atoms have been omitted for clarity. In the text, *A* refers to the top molecule and *B* to the bottom molecule.

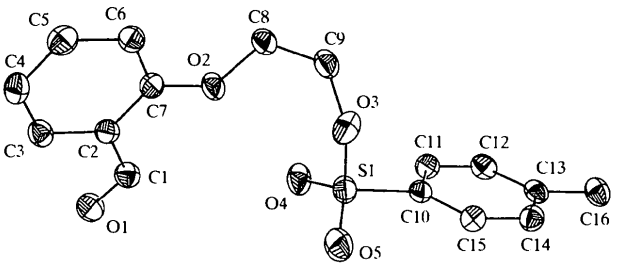


Fig. 2. The structure of the anhydrous form of compound (II) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

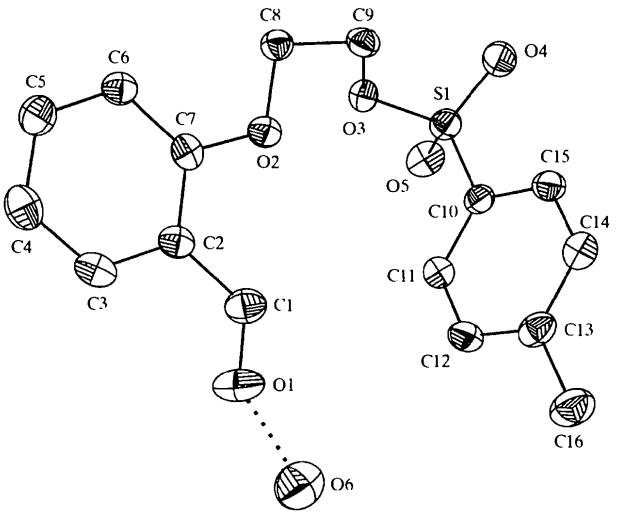


Fig. 3. The structure of the hemihydated form of compound (III) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

amination of H···H intermolecular interactions revealed none shorter than 2.36 Å.

Compounds (II) (Fig. 2) and (III) (Fig. 3) are the anhydrous and hemihydrated forms, respectively, of 2-[2-(tosyloxy)ethoxy]benzaldehyde, an intermediate in the synthesis of the sterically hindered four-atom-linked capped porphyrin 5,10,15,20-{benzene-1,2,4,5-tetrakis-[(2-phenyloxy)ethoxy]-2′,2″,2‴,2⁗-tetrayl}porphyrin (Johnson *et al.*, 1991). This precursor forms the ether–phenyl linkages from the porphyrin to the benzene cap.

The difference in conformation between the two forms involves rotation about the C9—C8 and O3—S1 bonds, and opening of the C9—O3—S1 bond angle. Although other bond lengths and angles are quite close (see Tables 2 and 3), the C9—O3—S1 bond angle opens up to 121.5 (1)° in (II) *versus* 117.1 (1)° in (III). As a result of these conformational changes, the average intramolecular distance between the toluene and the benzaldehyde moieties shrinks from 8.9 (1) Å in (II) to 5.1 (1) Å in (III). In both cases, the distance is measured from the centroid of C2–C7 to the centroid of C10–C15. The two moieties have a dihedral angle of 107.2 (1)° in (II) and 70.1 (1)° in (III). The different conformation in (III) may be explained by the presence of a water molecule. After locating the atoms of the precursor, a strong peak of electron density remained on a twofold axis. It was refined as O6, the O atom of a water molecule. The O6 atom is 2.87 (1) Å from O1 and O1′ of the aldehydes on two adjacent molecules. The O1′···O6···O1 angle is 107.92 (11) Å. The water H atom was not assigned.

Compound (IV) (Fig. 4) is also an intermediate in the synthesis of the sterically hindered four-atom-linked capped porphyrin 5,10,15,20-{benzene-1,2,4,5-tetrakis-[(2-phenyloxy)ethoxy]-2′,2″,2‴,2⁗-tetrayl}porphyrin (Johnson *et al.*, 1991). When cyclized, it forms the cap and linkages to the porphyrin.

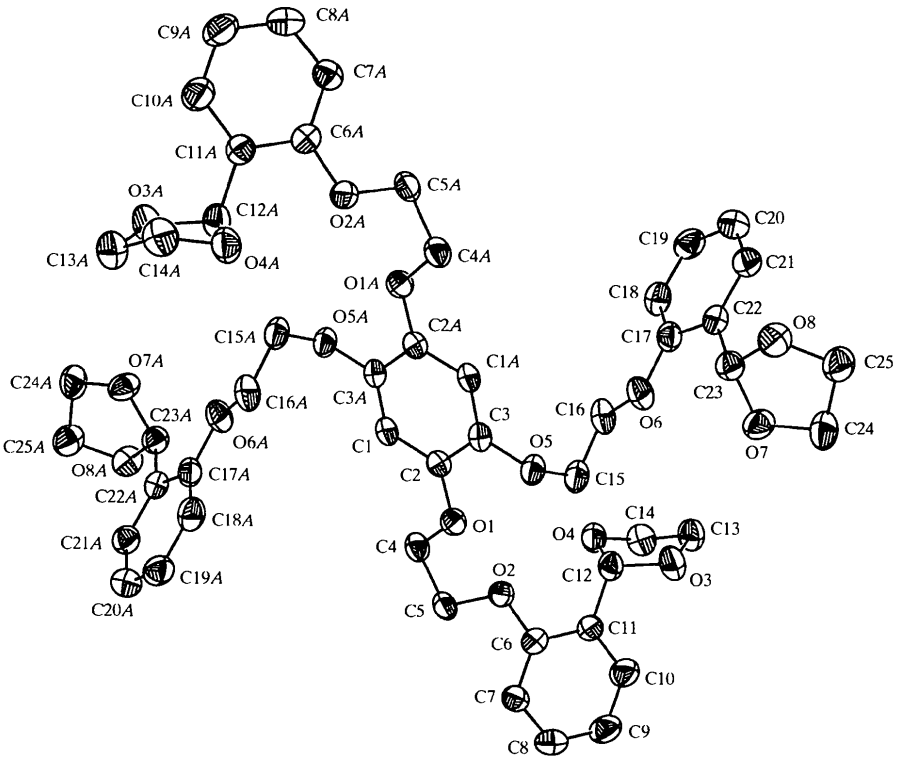


Fig. 4. The structure of compound (IV) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The molecule of (IV) is located on an inversion center. The asymmetric unit contains one-half of the molecule. The central benzene ring (C1, C2, C3, C1*A*, C2*A* and C3*A*) forms a dihedral angle of 54.5 (1)° with benzene ring *C* (C6–C11) and an angle of 55.6 (1)° with benzene ring *D* (C17–C22). Rings *C* and *D* have a dihedral angle of 80.0 (1)° relative to each other.

Experimental

Crystals of compound (I) were prepared according to the literature method of Ma *et al.* (1993), and ^{1}H NMR spectra match the reported results. IR experiments were performed on samples of compound (I). The spectra show two bands attributable to the methyl group at ν_{CH} 2972 and 2884 cm^{-1}, a carbonyl band at ν_{CO} 1683 cm^{-1}, and bands associated with symmetric and antisymmetric S=O stretches at ν_{sym} 1173 and at ν_{anti} 1349 cm^{-1}, respectively.

Crystals of compounds (II) and (III) were prepared according to the literature method of Johnson *et al.* (1996), and ^{1}H NMR spectra match the reported results. Crystals of both forms are products of the same reaction. Each form has a different crystal morphology. Compound (II) appears as colorless prisms, and compound (III) as colorless plates. Crystals of (III) were the predominant product. The source of water is incomplete drying of the wet organic layer with sodium sulfate before crystallization. Rapid crystallization (1–2 h) and limited availability of water may account for the mixture of products.

Crystals of compound (IV) were prepared by the reaction of 1,2,4,5-tetrahydroxybenzene with excess 2-{2-[2-(tosyloxy)ethoxy]phenyl}-1,3-dioxolane and powdered potassium hydroxide in dimethyl sulfoxide. The resulting solution was extracted with brine, and the semi-solid residue that formed was extracted with chloroform and purified by column chromatography (60 Å silica, 2% methanol/98% chloroform). Crystals formed from the slow evaporation of the appropriate fraction (m.p. 396–398 K). ^{1}H NMR ($CDCl_3$): δ 3.96 (*m*, 8H, acetal CH_2), 4.10 (*m*, 8H, acetal CH_2), 4.26 [*m*, 8H, $C_6H_2(OCH_2CH_2OR)_4$], 4.30 [*m*, 8H, $C_6H_2(OCH_2CH_2OR)_4$], 6.13 (*s*, 4H, acetal *CH*), 6.74 [*s*, 2H, $C_6H_2(OCH_2CH_2OR)_4$], 6.88 (*d*, 4H, 3-position phenyl proton), 6.98 (*t*, 4H, 4-position phenyl proton), 7.28 (*t*, 4H, 5-position phenyl proton), 7.52 (*m*, 2H, 6-position phenyl proton).

Compound (I)

Crystal data

$C_{17}H_{18}O_5S$
M_r = 334.37
Orthorhombic
$Pna2_1$
a = 13.887 (1) Å
b = 7.162 (1) Å
c = 32.124 (3) Å
V = 3194.8 (5) Å^3
Z = 8
D_x = 1.390 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 3750 reflections
θ = 2.54–25.50°
μ = 0.226 mm^{-1}
T = 153 (2) K
Triangular plate
0.18 × 0.15 × 0.10 mm
Colorless

Data collection

Bruker SMART1000 CCD diffractometer
ω scans
Absorption correction: numerical, face-indexed (Sheldrick, 1997)
T_{min} = 0.95, T_{max} = 0.98
16 483 measured reflections
3032 independent reflections (plus 2872 Friedel-related reflections)
3563 reflections with $I > 2\sigma(I)$
R_{int} = 0.063
θ_{max} = 25.5°
$h = -16 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = -38 \rightarrow 38$
Intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.11
S = 0.91
5904 reflections
415 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$(\Delta/\sigma)_{max}$ = 0.006
$\Delta\rho_{max}$ = 0.62 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.13 (10)

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

S1—O3	1.572 (3)	O2—C7	1.363 (6)
S2—O8	1.572 (3)	O7—C24	1.366 (6)
S1—O4	1.429 (3)	O2—C8	1.452 (6)
S2—O9	1.421 (3)	O7—C25	1.430 (7)
S1—O5	1.417 (4)	O3—C10	1.475 (6)
S2—O10	1.432 (4)	O8—C27	1.479 (6)
S1—C11	1.764 (5)	C8—C9	1.512 (7)
S2—C28	1.749 (4)	C25—C26	1.494 (7)
O1—C1	1.221 (5)	C9—C10	1.494 (6)
O6—C18	1.206 (5)	C26—C27	1.508 (6)
O5—S1—O4	118.9 (2)	O10—S2—C28	108.7 (2)
O9—S2—O10	119.5 (2)	O4—S1—C11	109.3 (2)
O5—S1—O3	104.8 (2)	O9—S2—C28	109.4 (2)
O10—S2—O8	104.3 (2)	O3—S1—C11	103.1 (2)
O4—S1—O3	110.4 (2)	O8—S2—C28	103.6 (2)
O9—S2—O8	110.1 (2)	C10—O3—S1	117.1 (3)
O5—S1—C11	109.1 (2)	C27—O8—S2	116.6 (3)

Compound (II)

Crystal data

$C_{16}H_{16}O_5S$
M_r = 320.35
Triclinic
$P\bar{1}$
a = 8.532 (1) Å
b = 9.576 (1) Å
c = 9.953 (1) Å
α = 76.679 (1)°
β = 84.054 (1)°
γ = 70.290 (1)°
V = 744.7 (1) Å^3
Z = 2
D_x = 1.429 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 3092 reflections
θ = 2.10–28.31°
μ = 0.239 mm^{-1}
T = 153 (2) K
Prism
0.254 × 0.210 × 0.176 mm
Colorless

Data collection

Bruker SMART1000 CCD diffractometer
ω scans
Absorption correction: numerical, face indexed (Sheldrick, 1997)
T_{min} = 0.94, T_{max} = 0.96
6761 measured reflections
3415 independent reflections
2661 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 28.31°
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$
Intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.11
S = 1.41
3415 reflections
199 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$(\Delta/\sigma)_{max}$ = 0.007
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1—O5	1.427 (1)	O2—C7	1.367 (2)
S1—O4	1.428 (1)	O2—C8	1.430 (2)
S1—O3	1.573 (1)	O3—C9	1.453 (2)
S1—C10	1.747 (2)	C1—C2	1.478 (2)
O1—C1	1.216 (2)	C8—C9	1.505 (2)
O5—S1—O4	120.17 (8)	O2—C7—C6	123.75 (15)
O5—S1—O3	103.91 (8)	O2—C7—C2	115.93 (14)
O4—S1—O3	109.55 (7)	C6—C7—C2	120.28 (16)
O5—S1—C10	108.83 (8)	O2—C8—C9	106.78 (13)
O4—S1—C10	109.26 (8)	O3—C9—C8	107.76 (14)
O3—S1—C10	103.83 (8)	C11—C10—C15	120.80 (16)
C7—O2—C8	118.88 (13)	C11—C10—S1	119.75 (13)
C9—O3—S1	121.54 (11)	C15—C10—S1	119.42 (13)
O1—C1—C2	123.48 (16)		
S1—O3—C9—C8	113.7 (1)	C9—C8—O2—C7	168.6 (1)
O3—C9—C8—O2	−68.9 (1)		

Compound (III)

Crystal data

$C_{16}H_{16}O_5S{\cdot}0.5H_2O$
M_r = 329.36
Orthorhombic
Pbcn
a = 14.415 (1) Å
b = 6.693 (1) Å
c = 31.692 (2) Å
V = 3057.5 (4) Å^3
Z = 8
D_x = 1.427 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 3194 reflections
θ = 1.91–25.50°
μ = 0.237 mm^{-1}
T = 153 (2) K
Plate
0.276 × 0.144 × 0.082 mm
Colorless

Data collection

Bruker SMART1000 CCD diffractometer
ω scans
Absorption correction: numerical, face-indexed (Sheldrick, 1997)
T_{min} = 0.95, T_{max} = 0.98
15 612 measured reflections
2844 independent reflections
1948 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 25.50°
$h = -16 \rightarrow 17$
$k = -8 \rightarrow 8$
$l = -31 \rightarrow 38$
Intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.097$
$S = 1.13$
2844 reflections
205 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$(\Delta/\sigma)_{max} = 0.023$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

S1—O5	1.4243 (16)	O2—C7	1.366 (3)
S1—O4	1.4311 (16)	O2—C8	1.426 (2)
S1—O3	1.5726 (15)	O3—C9	1.458 (2)
S1—C10	1.750 (2)	C1—C2	1.460 (3)
O1—C1	1.217 (3)	C8—C9	1.491 (3)
O6—O1	2.871 (2)		
O1^{i}—O6—O1	107.92 (11)	O1—C1—C2	124.2 (2)
O5—S1—O4	119.64 (10)	O2—C7—C6	123.89 (19)
O5—S1—O3	104.08 (9)	O2—C7—C2	115.97 (19)
O4—S1—O3	109.32 (9)	C6—C7—C2	120.1 (2)
O5—S1—C10	110.15 (10)	O2—C8—C9	107.02 (17)
O4—S1—C10	108.70 (10)	O3—C9—C8	107.82 (17)
O3—S1—C10	103.74 (9)	C15—C10—C11	120.6 (2)
C7—O2—C8	118.40 (16)	C15—C10—S1	120.17 (17)
C9—O3—S1	117.06 (13)	C11—C10—S1	119.27 (18)
S1—O3—C9—C8	−160.1 (1)	C9—C8—O2—C7	174.5 (1)
O3—C9—C8—O2	66.8 (1)		

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

Compound (IV)

Crystal data

$C_{50}H_{54}O_{16}$
$M_r = 910.93$
Monoclinic
$P2_1/c$
$a = 7.685$ (1) Å
$b = 9.042$ (1) Å
$c = 32.071$ (3) Å
$\beta = 93.46$ (1)°
$V = 2224.5$ (3) Å^3
$Z = 2$
$D_x = 1.360$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 2602 reflections
$\theta = 2.34$–$25.25°$
$\mu = 0.101$ mm^{-1}
$T = 153$ (2) K
Prism
0.222 × 0.128 × 0.056 mm
Colourless

Data collection

Bruker SMART1000 CCD diffractometer
ω scans
Absorption correction: numerical, face-indexed (Sheldrick, 1997)
$T_{min} = 0.98$, $T_{max} = 0.99$
16 685 measured reflections
4023 independent reflections
2249 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 25.25°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -38 \rightarrow 38$
Intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.092$
$S = 0.88$
4023 reflections
298 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 4. *Selected geometric parameters (Å, °) for (IV)*

O1—C2	1.372 (2)	O7—C23	1.433 (2)
O5—C3	1.384 (2)	O4—C12	1.419 (2)
O1—C4	1.426 (2)	O8—C23	1.402 (2)
O5—C15	1.436 (2)	O7—C24	1.430 (2)
C4—C5	1.492 (3)	O4—C14	1.429 (2)
C15—C16	1.488 (3)	O8—C25	1.440 (3)
O2—C5	1.438 (2)	O3—C13	1.419 (2)
O6—C16	1.431 (2)	C13—C14	1.505 (3)
O2—C6	1.369 (2)	C24—C25	1.479 (3)
O6—C17	1.380 (2)	C1—C3^{i}	1.380 (3)
C11—C12	1.512 (3)	C1—C2	1.391 (3)
C22—C23	1.508 (3)	C2—C3	1.393 (3)
O3—C12	1.413 (2)		
C12—O3—C13	108.54 (16)	O8—C23—O7	106.96 (16)
C24—O7—C23	108.03 (16)	O3—C13—C14	103.94 (17)
C12—O4—C14	106.58 (15)	O7—C24—C25	104.32 (18)
C23—O8—C25	105.73 (16)	O4—C14—C13	101.83 (17)
O3—C12—O4	106.96 (16)	O8—C25—C24	103.39 (18)

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

For all compounds, the crystal-to-detector distance was 5.023 cm. Each exposure was 30 s [except compound (II), which was 15 s] and covered −0.3° in ω. Anisotropic displacement parameters were used for all non-H atoms. H atoms were placed at calculated positions and refined with a riding model (methylene C—H = 0.99, methyl C—H = 0.98 and aromatic C—H = 0.95 Å). For compounds (I) and (III), data were collected in groups of 606, 435, and 230 frames at φ settings of 0, 90, and 180°, respectively. For compounds (II) and (IV), data were collected in groups of 606 frames at φ settings of 0, 120, and 240°, respectively. While immersed in Krytox oil crystals of compounds (II) and (III) were cut to appropriate dimensions with a razor .

For all compounds, data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXTL/PC* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1170). Services for accessing these data are described at the back of the journal.

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(1′*R*,2′*R*)-3-[(*cis*-2′-Cyclohexylmethylcyclopentyl)imino]-2-azabicyclo[2.2.2]octane hydrobromide, a hypoglycaemic semicyclic amidine

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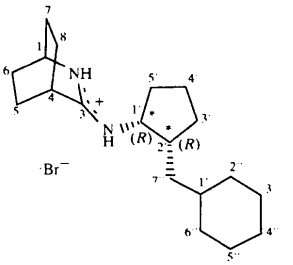
Abstract

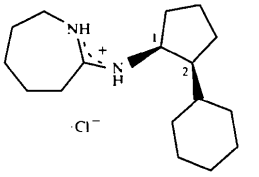
The title compound, $C_{19}H_{33}N_2^+{\cdot}Br^-$, shows dynamic equilibrium in solution between the *Z* and *E* isomers, enabled by the delocalization of the C=N double bond (C···N ~ 1.317 Å) of the amidine function. In the solid state, the absolute configuration has been determined as 1′*R*,2′*R* by X-ray analysis exploiting anomalous-dispersion effects. The double bond displays the *Z* configuration, consistent with *like-induction* in asymmetric reductive amination of prochiral cycloalkanones. Within the crystal structure the molecules are linked into chains by hydrogen bonds to the Br^- ions.

Comment

The title compound, (I), a semicyclic amidine, is a representative of an analogous series of optically pure amidines that stimulate insulin release in pancreatic B cells. The hypoglycaemic activity of racemic 2-[(*cis*-2′-cyclohexylcyclopentyl)imino]hexahydroazepine hydrochloride, (II), was first described by Grisar *et al.* (1973). Improvement of antidiabetic activity was correlated with increasing steric hindrance of the C1 atom, which is attached to the lactamimide function. Until now, however, no experiments concerning the enantiomeric differentiation of the hypoglycaemic effect have been carried out. Therefore, we synthesized two different series of optically pure amidines with variable substituents in position 2′ of the cyclopentane moiety, containing either a caprolactam or an isoquinuclidone ring system. Replacement of the seven-membered ring in compound (II) with a bicyclic ring system allows for separate investigation of the influence of increasing steric hindrance of the lactamimide moiety by itself. Substituents at position 2′ of the cyclopentane ring include isopropyl, phenyl, cyclohexyl, benzyl, cyclohexylmethyl and cyclopentyl residues.



(I)



(II)

In solution, these compounds show dynamic equilibration; their characterization by ^1H, ^{13}C and ^{15}N NMR techniques has been reported separately (Hartmann *et al.*, 1999). Here we are especially interested in establishing the *Z* configuration of the C=N double bond (relating to the position of the cyclopentane residue and the endocyclic N atom) in the solid state, and in elucidating the absolute configuration of the chiral centres C1′ and C2′.

The structure analysis of (I) (Fig. 1) shows that both the endocyclic and the semicyclic N atoms bear one H atom. Bond lengths between the atoms of the amidine function are nearly identical [N1—C3 1.316 (2) and N2—C3 1.319 (2) Å]. These values indicate delocalized bonding between 1.38 Å for an sp^2 C—N single bond and 1.28 Å for an sp^2 C=N double bond (Allen *et al.*, 1987). This partial sp^2 character of the semicyclic C···N bond allows two different configurations: the cyclopentane residue and the endocyclic-N atom located on the same side (*Z*) or on opposite sides (*E*) of the double bond. Earlier time-dependent ^1H NMR