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(1*S*,2*S*,4*S*,5*S*)-2,5-Dibenzyl-1,4-diazoniabicyclo[2.2.2]octane dichloride methanol solvate

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In the cation of the title compound, $C_{20}H_{26}N_2^{2+}\cdot 2Cl^-\cdot CH_4O$, there is an approximate twofold rotation axis. All the four chiral centers are in the *S* configuration. All three six-membered rings in the central part of the cation adopt a boat conformation. Both chloride anions and the O atom in the solvent molecule form hydrogen bonds with the cation, resulting in a chain along [010].

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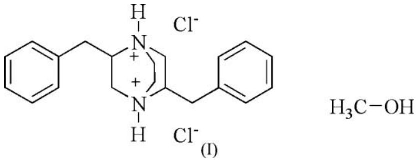
Key indicators

Single-crystal X-ray study
T = 193 K
Mean σ(C–C) = 0.006 Å
R factor = 0.043
wR factor = 0.128
Data-to-parameter ratio = 12.2

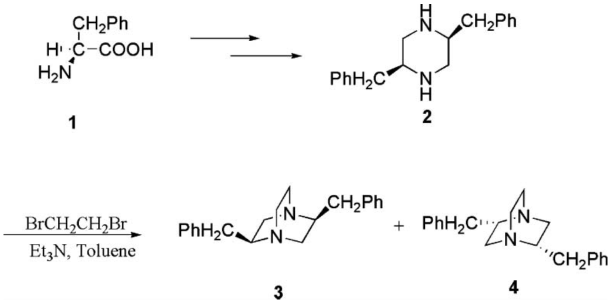
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

1,4-Diazabicyclo[2.2.2]octane (DABCO) has been reported to catalyze many asymmetric organic reactions due to its strong basicity (Minato *et al.*, 1990). Several chiral *trans*-2,3-disubstituted DABCOs have been synthesized and applied to the asymmetric Baylis-Hillman reaction (Oishi *et al.*, 1995). In a broad sense, the Baylis–Hillman reaction (Baylis & Hillman, 1972) can be regarded as a one-pot combination of Michael and aldol reactions. It is an atom-economical C—C bond-forming reaction between the α-position of activated alkenes and carbon electrophiles under the influence of DABCO, producing an interesting class of highly functionalized molecules that have been extensively used in various organic transformation methodologies, often involving high levels of stereoselectivity (Basavaiah *et al.*, 2003). DABCO is also used in vicinal hydroxylation (Oishi & Hirama, 1992) and its bis-ammonium salt is a prospective chiral phase-transfer catalyst. Reported here is the structure of (3) (see reaction scheme), as its dihydrochloride methanol solvate, (I).



(I)



In the central part of the cation, there are three six-membered rings (Fig. 1), *viz*. ring 1 (atoms C1–C4/N1/N2), ring 2 (C1/C2/C5/C6/N1/N2) and ring 3 (C3–C6/N1/N2). Each of these rings adopts a boat conformation. There are four chiral atoms in the cation, namely C1, C3, N1 and N2, and all are in the *S* configuration. A careful comparison of corresponding pairs of geometrical parameters (Table 1), indicates that there is an approximate twofold rotation axis passing through the midpoints of the vector N1···N2 and the bond C5—C6. The maximum differences between the corresponding pairs of bond lengths, angles and torsion angles are 0.02 Å, 2° and 2°, respectively. The pseudo-torsion angles C1—N1···N2—C2, C4—N1···N2—C3 and C5—N1···N2—C6 are 12.4 (3), 12.6 (3) and 10.4 (4)°, respectively..

The title salt crystallized with a methanol solvent molecule. In the crystal structure, both the solvent molecule and the anions form O—H···Cl, N—H···Cl, C—H···O and C—H···Cl hydrogen bonds (Desiraju, 2002) with the cation (Table 2 and Fig. 2), resulting in a chain along [010].

Experimental

The title compound, (I), was simply and conveniently prepared (see reaction scheme) from natural L-phenylalanine in three steps (Qiu *et al.*, 2003). The intermediate (2) (1.00 g, 3.75 mmol) was heated directly with 1,2-dibromoethane (0.43 g, 2.30 mmol) and triethylamine (2 ml) in toluene (10 ml) for 12 h, then cooled to room temperature. The reaction mixture was brought to pH 9–10 with 1 mol l^{-1} aqueous NaOH, and the organic phase was separated. The aqueous phase was extracted three times with chloroform (15 ml). The combined organic phase was dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was placed in a column and eluted with chloroform/methanol (50:1 *v*/*v*) to give compounds (3) and (4). The dihydrochloride of (3) was dissolved in methanol. After standing for a week, suitable crystals of (I) formed gradually.

Crystal data

$C_{20}H_{26}N_2^{2+}\cdot 2Cl^-\cdot CH_4O$
M_r = 397.37
Monoclinic, $P2_1$
a = 11.7262 (13) Å
b = 7.6968 (7) Å
c = 11.8788 (13) Å
β = 109.970 (5)°
V = 1007.65 (18) Å^3
Z = 2
D_x = 1.310 Mg m$^{-3$}
Mo *Kα* radiation
Cell parameters from 3734 reflections
θ = 3.0–25.5°
μ = 0.34 mm^{-1}
T = 193 (2) K
Prism, colorless
0.70 × 0.50 × 0.50 mm

Data collection

Rigaku Mercury diffractometer
ω scans
Absorption correction: multi-scan (Jacobson, 1998)
T_{min} = 0.799, T_{max} = 0.850
6594 measured reflections
2874 independent reflections
2855 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 25.5°
h = −14 → 14
k = −9 → 8
l = −13 → 14

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.128
S = 1.13
2874 reflections
236 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0733P)^2 + 0.7886P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.60 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}
Absolute structure: Flack (1983), 855 Friedel pairs
Flack parameter: 0.02 (9)

Table 1
Selected geometric parameters (Å, °).

O1—C21	1.401 (10)	C1—C7	1.522 (5)
N1—C5	1.492 (5)	C1—C2	1.543 (5)
N1—C1	1.507 (4)	C3—C14	1.525 (5)
N1—C4	1.507 (4)	C3—C4	1.532 (5)
N2—C2	1.495 (4)	C5—C6	1.532 (5)
N2—C3	1.512 (5)	C7—C8	1.517 (5)
N2—C6	1.512 (4)	C14—C15	1.508 (5)
C5—N1—C1	111.2 (3)	N2—C3—C14	110.5 (3)
C5—N1—C4	108.7 (3)	N2—C3—C4	106.6 (2)
C1—N1—C4	109.0 (3)	C14—C3—C4	114.3 (3)
C2—N2—C3	109.3 (3)	N1—C4—C3	108.4 (3)
C2—N2—C6	109.5 (3)	N1—C5—C6	108.6 (3)
C3—N2—C6	110.9 (3)	N2—C6—C5	107.4 (3)
N1—C1—C7	110.6 (3)	C8—C7—C1	113.7 (3)
N1—C1—C2	107.2 (3)	C13—C8—C9	117.9 (3)
C7—C1—C2	113.2 (3)	C15—C14—C3	112.6 (3)
N2—C2—C1	107.8 (3)	C16—C15—C20	118.5 (3)
C5—N1—C1—C7	−76.2 (4)	C4—N1—C5—C6	50.3 (3)
C4—N1—C1—C7	164.0 (3)	C2—N2—C6—C5	50.7 (4)
C5—N1—C1—C2	47.7 (3)	C3—N2—C6—C5	−70.1 (4)
C4—N1—C1—C2	−72.1 (3)	N1—C5—C6—N2	16.8 (4)
C3—N2—C2—C1	49.2 (3)	N1—C1—C7—C8	−176.4 (3)
C6—N2—C2—C1	−72.6 (3)	C2—C1—C7—C8	63.2 (4)
N1—C1—C2—N2	19.9 (3)	C1—C7—C8—C13	−146.2 (3)
C7—C1—C2—N2	142.2 (3)	C1—C7—C8—C9	36.1 (5)
C2—N2—C3—C14	162.0 (3)	C7—C8—C9—C10	177.6 (4)
C6—N2—C3—C14	−77.0 (3)	C7—C8—C13—C12	−177.4 (3)
C2—N2—C3—C4	−73.3 (3)	N2—C3—C14—C15	−177.2 (2)
C6—N2—C3—C4	47.7 (4)	C4—C3—C14—C15	62.6 (4)
C5—N1—C4—C3	−73.3 (3)	C3—C14—C15—C16	−123.7 (4)
C1—N1—C4—C3	48.1 (4)	C3—C14—C15—C20	62.5 (4)
N2—C3—C4—N1	20.5 (3)	C14—C15—C16—C17	−174.1 (5)
C14—C3—C4—N1	142.8 (3)	C14—C15—C20—C19	174.4 (4)
C1—N1—C5—C6	−69.7 (4)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···Cl1	0.94 (4)	2.03 (4)	2.967 (3)	176 (4)
C5—H5*A*···O1	0.99	2.51	3.331 (7)	140
N2—H2···Cl2^{i}	0.92 (5)	2.18 (5)	3.045 (3)	157 (4)
C6—H6*A*···Cl1^{i}	0.99	2.75	3.563 (4)	139
O1—H1···Cl2^{ii}	0.82	2.38	3.201 (4)	180
C6—H6*B*···O1^{ii}	0.99	2.41	3.151 (9)	131
C14—H14*B*···O1^{ii}	0.99	2.68	3.389 (7)	129
C6—H6*B*···Cl1^{ii}	0.99	2.94	3.715 (4)	136
C4—H4*A*···O1^{iii}	0.99	2.51	3.329 (8)	140
C3—H3···Cl2^{iv}	0.99	2.68	3.526 (4)	142

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+1, y-\frac{1}{2}, -z+1$; (iii) $-x+1, y+\frac{1}{2}, -z+1$; (iv) $-x, y-\frac{1}{2}, -z+1$.

H atoms attached to N atoms were refined freely [N1—H1*A* = 0.94 (4) Å and N2—H2 = 0.92 (5) Å]. H atoms attached to C and O were positioned geometrically (C—H = 0.95–1.00 Å and O—H = 0.84 Å) and treated as riding, with $U_{iso}(H) = xU_{eq}$(carrier atom),- where *x* = 1.5 for methyl C and O, and *x* = 1.2 for all other C atoms.

Data collection: *CRYSTALCLEAR* (Rigaku, 1990); cell refinement: *CRYSTALCLEAR*; data reduction: *CrystalStructure* (Rigaku/MSC, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* for Windows

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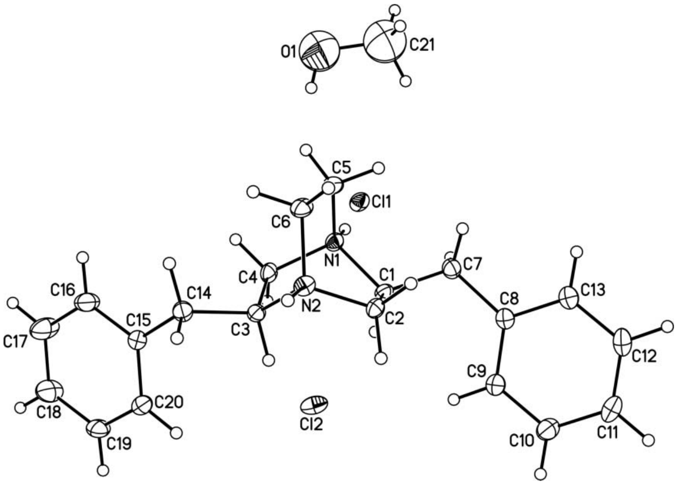

Figure 1
A view of the title compound. Displacement ellipsoids are drawn at the 40% probablitity level.

(Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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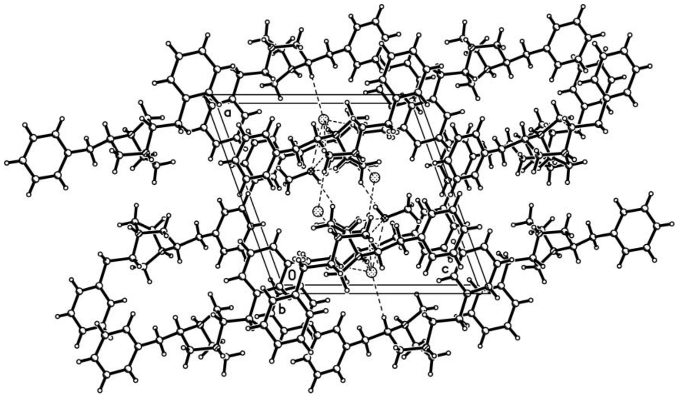

Figure 2
A packing diagram, viewed down the *b* axis. Dashed lines indicate hydrogen bonds.

o2670 Qiu *et al.* • $C_{20}H_{26}N_2^{2+}\cdot 2Cl^{-}\cdot CH_4O$ *Acta Cryst.* (2005). E**61**, o2668–o2670