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

N1—C11	1.310 (4)	N2—C8	1.345 (4)
N1—C10	1.349 (4)	Cl—C11	1.750 (3)
N2—C11	1.325 (4)		
C11—N1—C10	115.7 (2)	C6—C7—C8	118.3 (3)
C11—N2—C8	113.6 (2)	N2—C8—C9	122.6 (3)
O—C7—C6	122.7 (3)	N1—C10—C9	120.0 (3)
O—C7—C8	119.0 (3)	N1—C11—N2	130.1 (3)
C1—C6—C7—O	135.7 (3)	O—C7—C8—N2	153.3 (3)
C1—C6—C7—C8	−45.8 (4)	C6—C7—C8—C9	157.3 (3)
C5—C6—C7—C8	135.8 (3)	C9—C10—C12—C17	−167.6 (3)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *MULTAN*88 (Debaerdemaeker *et al.*, 1988). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1294). Services for accessing these data are described at the back of the journal.

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A cyclam-like macrocycle side-bridged by a propyl chain

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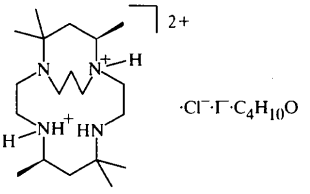
Abstract

The preparation and crystal structure of *meso*-5,5,7,12,12,14-hexamethyl-1,8-diazonia-4,11-diazabicyclo-[9.3.3]heptadecane chloride iodide 0.5-diethyl ether solvate, $C_{19}H_{42}N_4^{2+}\cdot Cl^-\cdot I^-\cdot 0.5C_4H_{10}O$, are described. The 14-membered macrocycle has an extended conformation with the $-(CH_2)_3-$ bridge to one side. It contains two N—H···Cl hydrogen bonds.

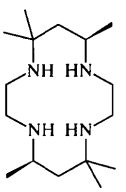
Comment

The compound *meso*-5,5,7,12,12,14-hexamethyl-1,8-diazonia-4,11-diazabicyclo[9.3.3]heptadecane chloride iodide 0.5-diethyl ether solvate, (1), was synthesized unexpectedly during our study of the transition metal complexes of cross-bridged tetraazamacrocycles (Hubin *et al.*, 1998). Generally, ethylene bridges across non-adjacent N atoms of tetraazamacrocycles are obtained by the condensation of NH with glyoxal, selective alkylation at two non-adjacent N atoms, and finally, ring-opening reduction of the diquat intermediate (Weisman *et al.*, 1996). However, substituted macrocycles, like *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, (2), are more difficult to bridge by this route because of the added steric bulk of the six C-methyl groups (Hubin *et al.*, 1999). We have explored another route to the cross-bridged analogue of (2) based on the successful *trans*-dialkylation of (2), in which the geminal dimethyl groups apparently sterically protect two of the four secondary amines of the macrocycle from reaction (Hay *et al.*, 1996). We chose 1,3-diiodopropane as the bis-electrophile in our bridging reaction because 1,2-dihaloethanes have been shown to preferentially bridge adjacent N atoms of tetraazamacrocycles giving the stable piperazine derivatives, which we wanted to avoid (Wainwright, 1980; Ramasubbu & Wainwright, 1982). However, rather than the expected cross-bridged product, we isolated (1), in which the trimethylene group has bridged adjacent N atoms N1 and N11, giving an eight-membered ring as part of the bicyclic product. The structure determination also revealed one H atom on N8,

one on N11, two on N4 and none on N1; thus, N4 and N11 have been protonated to give the dication. Iodide and chloride counter-ions (apparently originating from chloroform used during the synthesis) and a disordered diethyl ether molecule of crystallization complete the structure (modelled as four 50% and two 25% occupancy C atoms).



(1)



(2)

No other side-bridged 14-membered tetraazamacrocycles have been structurally characterized that include bridges across two N atoms separated by three C atoms in the starting macrocycle. An eight-membered ring incorporating N1, N11 and two trimethylene groups has been produced in preference to the cross-bridged product, despite the steric bulk of the geminal dimethyl group α to N1 which prohibits alkylation by non-bridging groups (Hay *et al.*, 1996). The geometry of the two trimethylene groups is very similar (bridge torsion angles equivalent within 1°). The main macrocyclic ring has an extended conformation (Fig. 1). The chloride anion forms N—H···Cl hydrogen bonds to N4 [3.130 (2) Å] and to N8($1-x$, $-y$, $1-z$) [3.269 (2) Å].

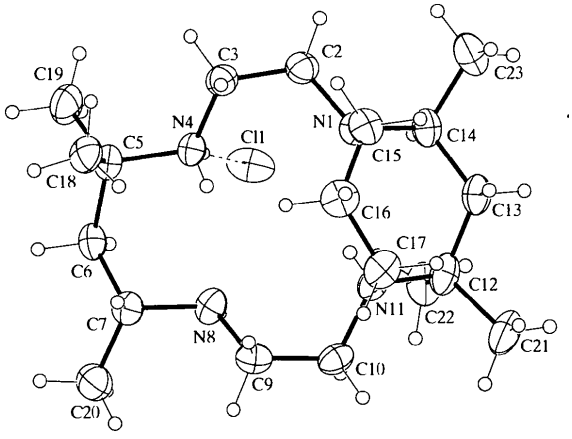


Fig. 1. View of the title molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Compound (1) was obtained as follows: a solution of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, (2) (2 g, 0.006 mol) (obtained by literature procedures; Hay *et al.*, 1975), dissolved in MeOH (5 ml) and MeCN (55 ml), and a solution of 1,3-diiodopropane (1.78 g, 0.006 mol) in MeCN (60 ml) were added at a rate of 1 ml h^{-1} from separate syringes to refluxing MeCN (500 ml) and sodium carbonate (17.7 g, 0.17 mol) in a 1 l three-neck round-bottom flask under nitrogen. After a total of 72 h reaction time, the mixture was evaporated to dryness, dissolved in 4 *M* KOH (250 ml) and extracted with benzene (4 × 200 ml). The organic fraction was dried over sodium sulfate, then evaporated to give a crude solid, which was stirred in chloroform (100 ml) and filtered to give a white solid product. X-ray quality crystals were obtained by the diffusion of ether into a methanol solution.

Crystal data

$C_{19}H_{42}N_4^{2+}\cdot Cl^-\cdot I^-\cdot 0.5C_4H_{10}O$ (see below)
M_r = 525.91
Triclinic
$P\overline{1}$
a = 8.8253 (7) Å
b = 11.5326 (9) Å
c = 14.3441 (11) Å
α = 69.839 (1)°
β = 77.083 (1)°
γ = 87.933 (1)°
V = 1334.45 (18) Å^3
Z = 2
D_x = 1.272 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 3926 reflections
θ = 3–20°
μ = 1.309 mm^{-1}
T = 180 (2) K
Needle
0.25 × 0.10 × 0.10 mm
Colourless

Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.75, T_{max} = 0.93
6454 measured reflections
4364 independent reflections
3119 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 24.5°
$h = -9 \rightarrow 10$
$k = -13 \rightarrow 10$
$l = -16 \rightarrow 16$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.134
S = 1.032
4364 reflections
279 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0760P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.045
$\Delta\rho_{max}$ = 0.977 e Å^{-3}
$\Delta\rho_{min}$ = −1.169 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

A disordered solvent molecule was modelled as 4 × 0.5 and 2 × 0.25 C atoms.

Data collection: *SMART* (Siemens, 1994). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *SHELXTL* (Sheldrick, 1997*b*). Software used to prepare material for publication: *SHELXTL*.

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