C(7)—C(8)	1.498 (4)	C(8)—C(9)	1.350 (3)
C(8)—C(14)	1.435 (3)	C(9)—C(10)	1.415 (4)
C(10)—C(11)	1.353 (4)	C(11)—C(12)	1.396 (4)
C(12)—C(13)	1.331 (4)		
C(2)—O(1)—C(5)	106.3 (2)	C(10)—O(2)—C(13)	105.7 (2)
C(6)—N(1)—C(7)	121.9 (2)	O(1)—C(2)—C(3)	109.0 (2)
O(1)—C(2)—C(6)	117.1 (2)	C(3)—C(2)—C(6)	133.7 (2)
C(2)—C(3)—C(4)	107.7 (3)	C(3)—C(4)—C(5)	106.4 (3)
O(1)—C(5)—C(4)	110.5 (3)	N(1)—C(6)—C(2)	114.3 (2)
O(3)—C(7)—N(1)	122.4 (2)	O(3)—C(7)—C(8)	121.2 (2)
N(1)—C(7)—C(8)	116.4 (2)	C(7)—C(8)—C(9)	118.6 (2)
C(7)—C(8)—C(14)	118.0 (2)	C(9)—C(8)—C(14)	123.4 (2)
C(8)—C(9)—C(10)	130.8 (2)	O(2)—C(10)—C(9)	120.9 (2)
O(2)—C(10)—C(11)	109.0 (2)	C(9)—C(10)—C(11)	130.1 (3)
C(10)—C(11)—C(12)	107.6 (3)	C(11)—C(12)—C(13)	106.3 (3)
O(2)—C(13)—C(12)	111.4 (3)	N(2)—C(14)—C(8)	174.3 (3)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N(1)—H(1)···N(2)	0.82 (3)	2.80 (3)	3.396 (3)	131 (2)
	1.03*	2.67*		128*
C(6)—H(5)···O(3)	1.01 (3)	2.53 (3)	2.770 (4)	92 (1)
	1.08*	2.53*		91*
C(9)—H(7)···O(3)	0.94 (3)	2.41 (3)	2.784 (4)	103 (2)
	1.08*	2.39*		100*
N(1)—H(1)···N(2^{i})	0.82 (3)	2.42 (2)	3.123 (3)	145 (2)
C(4)—H(3)···O(2^{ii})	0.96 (3)	2.79 (3)	3.497 (3)	130 (2)
	1.08*	2.71*		129*
C(5)—H(4)···N(2^{iii})	0.94 (3)	2.78 (3)	3.504 (3)	134 (2)
	1.08*	2.69*		132*
C(9)—H(7)···O(3^{iv})	0.94 (3)	2.63 (2)	3.444 (3)	145 (2)
	1.08*	2.52*		144*
C(11)—H(8)···O(3^{iv})	0.89 (3)	2.45 (3)	3.238 (3)	146 (2)
	1.08*	2.30*		144*

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

* Normalized values (Jeffrey & Lewis, 1978; Taylor & Kennard, 1983).

All computations were performed on an IBM AT486 computer.

Data collection: *XSCANS* (Siemens, 1992). Cell refinement: *SHELXTL-Plus* (Sheldrick, 1987). Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXTL-Plus* (direct methods).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, torsion angles and complete geometry have been deposited with the IUCr (Reference: AB1126). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bartroli, R. (1985). PhD dissertation, Central University of VillaClara, Cuba.

Bartroli, R. & Lami, L. (1995). In preparation.

Bartroli, R., Lami, L., Quincoses, J. & Peseke, K. (1984). Certificado de autor de invención (Cuban Patent) No. 21789, La Habana, Cuba.

Clementi, S. (1984). *Drug Design: Fact or Fantasy?* edited by G. Jolles & K. R. H. Wooldridge, pp. 73–75. London: Academic Press.

Franke, R. (1984). *Theoretical Drugs Design Methods*, pp. 188–190. Amsterdam: Elsevier.

Jeffrey, G. A. & Lewis, L. (1978). *Carbohydr. Res.* **60**, 179–180.

Pomés Hernández, R., Duque Rodríguez, J., Villena Rodríguez, R. & Soriano Garcia, M. (1995). *Acta Cryst.* C**51**, 1575–1577.

Sheldrick, G. M. (1987). *SHELXTL-Plus*. PC Version. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1992). *XSCANS. X-ray Single Crystal Analysis System*. Version 2.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Taylor, R. & Kennard, O. (1983). *Acta Cryst.* B**39**, 133–134.

Acta Cryst. (1996). C**52**, 205–207

Pyo$_2$[18]diene-N$_6$.4HBr.H$_2$O

B. Nieslanik,[a] E. N. Duesler,[a] L. Miao,[a] S. C. Jackels[b] and R. T. Paine[a]

[a]*Department of Chemistry, University of New Mexico, Clark Hall 103, Albuquerque NM 87131-1096, USA, and* [b]*Department of Chemistry, Wake Forest University Winston-Salem, NC 27109, USA*

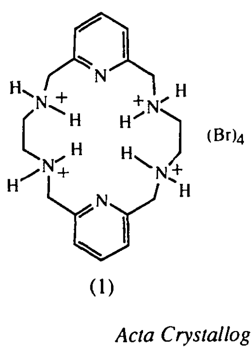
(*Received 27 September 1994; accepted 17 July 1995*)

Abstract

The X-ray crystal structure of 3,6,14,17,23,24-hexaazatricyclo[17.3.1.1^{8,12}]tetracosa-1(23),8,10,12(24),19,21-hexene tetrahydrobromide monohydrate, $C_{18}H_{30}N_6^{4+}$.-$4Br^-$.H_2O, was determined. The compound is monomeric and the 18-membered macrocyclic ring contains four saturated amine and two pyridine units. The pyridine rings are inclined so that the ring N atoms are pointed above and below the centroid of the macrocycle.

Comment

The title compound (1) was prepared as described in the literature (Rothermel, Miao, Hill & Jackels, 1992) and its structure was determined in order to compare its features with those found for various metal complexes of the ligand (Bryant, Lachgar, Coates & Jackels, 1994). The compound crystallized in a monoclinic space group with four molecules per unit cell. Each molecule consists of a macrocyclic tetracation, pyo$_2$[18]-diene-N$_6$H$_4^{4+}$, four Br$^-$ anions, and a water molecule. The macrocyclic ring sits on a crystallographic center of symmetry (1/4,1/4,0), the water molecule resides on a crystallographic twofold axis and the two distinct Br$^-$ atoms are in general positions. The macrocyclic ring is puckered with N(1) (−0.043 Å), C(9) (−0.236 Å), N(2) (−0.612 Å) and C(6) (−0.510 Å) lying below the best plane through the macrocyclic backbone and C(1) (0.432 Å), N(3) (0.165 Å), C(8) (0.476 Å), C(7) (0.685 Å), and C(5) (0.110 Å) lying above that plane. The symmetry and puckering result in the N-atom lone pair on each pyridine ring being tipped out of the macrocycle cavity in directions opposite to each other.



(1)

Each amine H atom is hydrogen bonded to a Br^- ion and the unique distances are shown in the molecular view. The H atoms on the water molecule could not be located in the pyo[18] difference map; however, in calculated positions, they appear to be hydrogen bonded to Br^- ions. The C—C and C—N bond distances and the various bond angles in the macrocycle show no unusual features.

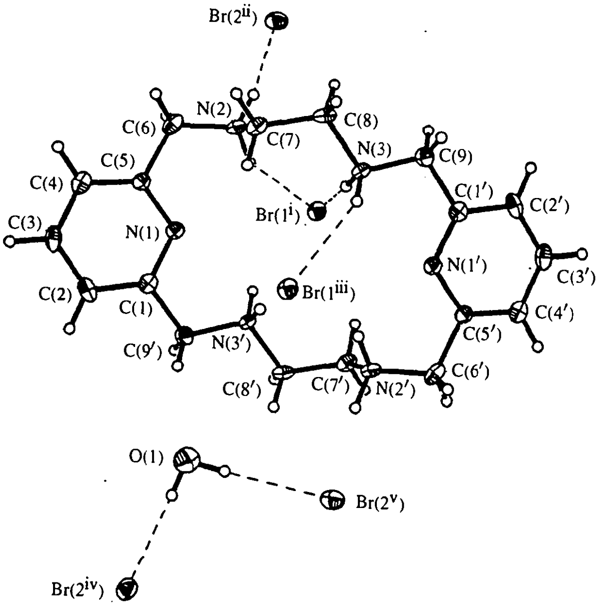


Fig. 1. View of $Pyo_2[18]dieneN_6.4HBr.H_2O$. Displacement ellipsoids are plotted at the 20% probability level.

Experimental

Prepared by the method of Rothermel, Miao, Hill & Jackels (1992).

Crystal data

$C_{18}H_{30}N_6^{4+}.4Br^-.H_2O$
$M_r = 668.1$
Monoclinic
$C2/c$
$a = 20.480\ (4)$ Å
$b = 10.952\ (2)$ Å
$c = 12.931\ (3)$ Å
$\beta = 117.58\ (3)°$
$V = 2570.6\ (9)$ Å^3
$Z = 4$
$D_x = 1.726$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 4–20°$
$\mu = 6.223$ mm^{-1}
$T = 293$ K
Prism
0.230 × 0.207 × 0.207 mm
Colorless

Data collection

Siemens *R3m/V* diffractometer
ω scans
Absorption correction: empirical, *SHELXTL-Plus* (Sheldrick, 1991)
$T_{\min} = 0.6459$, $T_{\max} = 0.9634$
6185 measured reflections
2942 independent reflections
1265 observed reflections $[F > 2\sigma(F)]$

$R_{\rm int} = 0.0225$
$\theta_{\max} = 22.5°$
$h = -26 \rightarrow 26$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$
3 standard reflections monitored every 97 reflections
intensity decay: 0.93–1.03%

Refinement

Refinement on F
$R = 0.0596$
$wR = 0.0582$
$S = 0.99$
2942 reflections
132 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.001F^2]$

$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.88$ e Å^{-3}
$\Delta\rho_{\min} = -0.95$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Br(1)	0.1902 (1)	0.2064 (1)	0.7862 (1)	0.045 (1)
Br(2)	0.3685 (1)	0.2958 (1)	0.7352 (1)	0.055 (1)
N(1)	0.3792 (5)	0.1022 (9)	0.0180 (8)	0.037 (5)
N(2)	0.2549 (5)	−0.0337 (8)	−0.0419 (8)	0.037 (4)
N(3)	0.1532 (5)	0.1596 (7)	0.0041 (8)	0.035 (4)
C(1)	0.4386 (7)	0.1743 (10)	0.0635 (9)	0.037 (6)
C(2)	0.5104 (6)	0.1310 (13)	0.1264 (9)	0.046 (6)
C(3)	0.5197 (7)	0.0066 (12)	0.1412 (10)	0.049 (6)
C(4)	0.4596 (7)	−0.0694 (12)	0.0988 (9)	0.044 (6)
C(5)	0.3907 (7)	−0.0183 (11)	0.0362 (9)	0.036 (5)
C(6)	0.3229 (6)	−0.0972 (12)	−0.0224 (10)	0.048 (7)
C(7)	0.2459 (7)	−0.0153 (10)	0.0655 (10)	0.045 (6)
C(8)	0.1681 (7)	0.0255 (10)	0.0365 (11)	0.045 (6)
C(9)	0.0737 (6)	0.1919 (11)	−0.0411 (10)	0.043 (6)
O(1)	1/2	0.5137 (12)	1/4	0.094 (9)

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

N(1)—C(1)	1.337 (15)	N(1)—C(5)	1.343 (15)
N(2)—C(6)	1.469 (16)	N(2)—C(7)	1.497 (18)
N(3)—C(8)	1.518 (13)	N(3)—C(9)	1.494 (14)
C(1)—C(2)	1.395 (16)	C(1)—C(9^{i})	1.492 (16)
C(5)—C(6)	1.508 (16)	C(2)—C(3)	1.38 (2)
C(3)—C(4)	1.373 (18)	C(7)—C(8)	1.525 (19)
C(4)—C(5)	1.379 (16)		
C(1)—N(1)—C(5)	117.0 (9)	N(1)—C(1)—C(2)	123.7 (11)
C(6)—N(2)—C(7)	114.7 (8)	C(2)—C(1)—C(9^{i})	119.0 (11)
C(8)—N(3)—C(9)	112.4 (9)	C(1)—C(2)—C(3)	117.3 (11)
N(1)—C(1)—C(9^{i})	117.2 (10)	C(3)—C(4)—C(5)	118.2 (12)
C(2)—C(3)—C(4)	120.3 (12)	N(1)—C(5)—C(4)	123.4 (11)
N(1)—C(5)—C(6)	115.4 (10)	C(4)—C(5)—C(6)	121.1 (11)
N(2)—C(6)—C(5)	113.2 (10)	N(2)—C(7)—C(8)	112.0 (9)
N(3)—C(8)—C(7)	113.9 (11)	N(3)—C(9)—C(1^{i})	111.3 (8)
H(1)—O(1)—H(1^{ii})	99.5 (13)		

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

Table 3. *Contact distances (Å)*

Br(1^{i})···H(3B)	2.325	Br(1^{iii})···H(3C)	2.581
Br(1^{i})···H(2B)	2.429	Br(2^{iv})···H(1)	2.465
Br(2^{ii})···H(2C)	2.256	Br(2^{v})···H(1^{vi})	2.465

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

The structure was solved by direct methods and all non-H atoms were located and refined anisotropically. The H atoms on the amine N atoms and methylene C atoms were refined in idealized positions (riding model) with $U_{\rm iso}$ set at $1.25U_{\rm eq}$ of the parent atom. Difference Fourier maps did not show the sites for the water H atoms. The water H atoms were placed along the Br(2)—O(1) vector and the O(1)—H(1) length fixed at 0.86 Å. The twofold axis generates the other water H atom such that the H—O—H angle is 102.7°.

Data collection: Siemens *R3m/V* software. Data reduction: *SHELXTL-Plus* (VMS) (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus* (VMS). Program(s) used to refine structure: *SHELXTL-Plus* (VMS).

RTP recognizes financial support for this study from US Department of Energy, Office of Basic Energy Sciences Grant No. DE-FG03-94ER14446 and Los Alamos National Laboratory.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PT1017). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bryant, L. H. Jr, Lachgar, A., Coates, K. S. & Jackels, S. C. (1994). *Inorg. Chem.* **33**, 2219–2226.

Rothermel, G. L., Miao, L., Hill, A. L. & Jackels, S. C. (1992). *Inorg. Chem.* **31**, 4854–4859.

Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1996). C**52**, 207–210

Two *cis* Ring-Fused *exo* *N*-Aryl Heterocycles: 1-Phenyl-2-(2,4,6-trimethylphenyl)decahydroquinolin-4-one and 1-(4-Trifluoromethylphenyl)-2-phenyldecahydroquinolin-4-one

Denise Nogue,[a] Renée Paugam,[a] Lya Wartski,[a] Martine Nierlich,[b] Daniel Vigner[b] and Monique Lance[b]

[a]*ICMO Laboratoire des Carbocycles, CNRS-URA 478, Bâtiment 420, 91405 Orsay CEDEX, France, and* [b]*CEA, DRECAM, SCM, Saclay, Bâtiment 125, 91191 Gif sur Yvette CEDEX, France*

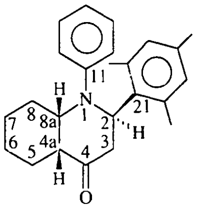
(*Received 12 April 1995; accepted 3 July 1995*)

Abstract

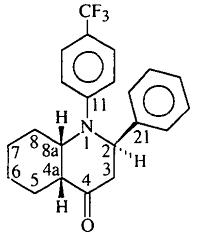
For the title compounds, $C_{24}H_{29}NO$ (I) and $C_{22}H_{22}F_3NO$ (II), the cyclohexane ring adopts a chair conformation. Both compounds exhibit a *cis* ring-fused *exo* configuration. When the N atom bears a phenyl ring and the C(2) atom is substituted by a 2,4,6-trimethylphenyl group (I) ring *B* lies in a chair conformation, the N atom being tetrahedral. When the N atom is substituted by a 4-trifluoromethyl group and the C(2) atom by a phenyl moiety as in (II), however, the *B* ring adopts a quasi-boat conformation, the N atom being planar.

Comment

1-Phenyl-2-(2,4,6-trimethylphenyl)decahydroquinolin-4-one (I) and 1-(4-trifluoromethylphenyl)-2-phenyldecahydroquinolin-4-one (II), are obtained by stereospecific hydrolysis of the cycloadducts formed by imino Diels–Alder reaction between substituted imines and the trimethylsilylenol ether of 1-acetylcyclohexene (Nogue, Paugam & Wartski, 1992). The determination of the structure of these heterocycles is necessary to understand their reactivity and to assign the configuration of the starting cycloadducts.



(I)



(II)

For both compounds, the ^{1}H-NMR data allow the determination of the *cis* relationship between C(4a)—H(4a) and C(8a)—H(8a) bonds and the axial and equatorial position of the H(8a) and H(4a) atoms in the cyclohexane ring. However, no information is given about the relationship between C(2)—H(2) and C(8a)—H(8a) bonds. Moreover, the N-atom geometry as well as the conformation of the *A* and *B* rings is unknown. Unambiguous assignment of these structures has to be obtained by single-crystal X-ray structure analysis.

In both compounds, the value of the torsion angle H(8a)—C(8a)—C(4a)—H(4a) of 57.8 (6) (I) and 56.4 (8)° (II) confirms the *cis* relationship between the

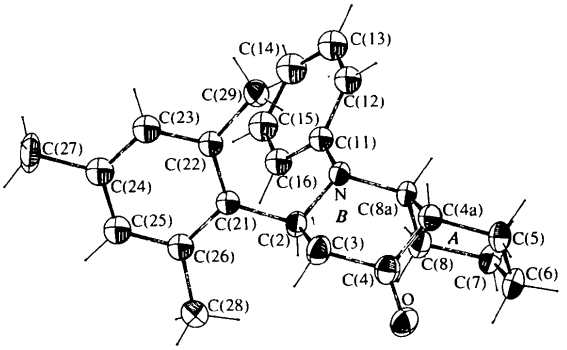


Fig. 1. Drawing of the molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level.