Structure of *C-meso*-2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene Monohydrate

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Abstract. $C_{15}H_{26}N_4.H_2O$, $M_r = 280.4$, orthorhombic, *Pbca*, $a = 17.715$ (3), $b = 14.342$ (4), $c = 13.385$ (5) Å, $V = 3400.7$ Å^3, $Z = 8$, $D_x = 1.095$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.66$ cm^{-1}, $F(000) = 1232$, $T = 298$ K, $R = 0.060$ for 1528 independent observed reflections. The 14-membered tetraaza macrocycle adopts a puckered rectangular conformation in order to minimize lone-pair interactions. Deviations of −0.30, +0.21, −0.31 and +0.39 Å from the best least-squares tetraaza plane are observed for N(3), N(7), N(11) and N(17), with the pyridyl ring making an angle of 65.6° to this plane. The structure confirms the *C-meso* geometry with the two methyl groups mutually *syn*. These methyl groups are *syn* to the protons on N(3) and N(11), but *anti* to the proton on N(7). Transannular donor N−N distances of 4.024 (4) and 4.895 (4) Å are observed for the N(7)−N(17) and N(3)−N(11) distances respectively. The water molecule associated with this structure forms hydrogen bonds to N(3) and N(11), but not N(7).

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Table 1. *Fractional coordinates and equivalent isotropic thermal parameters with e.s.d.'s*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}(Å^2)
C(1)	0.43300 (16)	0.78496 (21)	0.02535 (23)	0.0469 (20)
C(2)	0.50185 (19)	0.7618 (3)	−0.0382 (3)	0.0588 (23)
C(2A)	0.50889 (21)	0.65675 (24)	−0.0508 (3)	0.076 (3)
N(3)	0.49994 (16)	0.80642 (21)	−0.13831 (22)	0.0600 (20)
C(4)	0.50311 (20)	0.9089 (3)	−0.1341 (3)	0.070 (3)
C(5)	0.49753 (24)	0.9522 (3)	−0.2379 (3)	0.083 (3)
C(6)	0.42417 (24)	0.9360 (3)	−0.2921 (3)	0.077 (3)
N(7)	0.36020 (20)	0.9672 (3)	−0.2322 (3)	0.0804 (24)
C(8)	0.28823 (25)	0.9443 (3)	−0.2796 (3)	0.087 (3)
C(9)	0.22210 (25)	0.9628 (3)	−0.2128 (3)	0.087 (3)
C(10)	0.22544 (21)	0.9155 (3)	−0.1110 (3)	0.071 (3)
N(11)	0.22613 (16)	0.81322 (22)	−0.11856 (23)	0.0599 (20)
C(12)	0.22970 (17)	0.76766 (24)	−0.01926 (25)	0.0534 (21)
C(12A)	0.21822 (21)	0.66382 (24)	−0.0307 (3)	0.073 (3)
C(13)	0.30348 (17)	0.78704 (21)	0.03478 (23)	0.0464 (20)
C(14)	0.30525 (18)	0.81839 (22)	0.13346 (24)	0.0504 (20)
C(15)	0.37482 (19)	0.83285 (22)	0.17795 (25)	0.0566 (22)
C(16)	0.43966 (19)	0.81589 (22)	0.1240 (3)	0.0545 (21)
N(17)	0.36612 (14)	0.77034 (18)	−0.01818 (18)	0.0481 (16)
O(1W)	0.37981 (16)	0.28958 (23)	0.2520 (3)	0.0846 (22)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°)

C(1)−C(2)	1.524 (5)	C(8)−C(9)	1.498 (6)
C(1)−C(16)	1.397 (5)	C(9)−C(10)	1.522 (6)
C(1)−N(17)	1.337 (4)	C(10)−N(11)	1.471 (5)
C(2)−C(2A)	1.521 (5)	N(11)−C(12)	1.482 (5)
C(2)−N(3)	1.486 (5)	C(12)−C(12A)	1.511 (5)
N(3)−C(4)	1.472 (5)	C(12)−C(13)	1.519 (5)
C(4)−C(5)	1.525 (6)	C(13)−C(14)	1.396 (4)
C(5)−C(6)	1.507 (6)	C(13)−N(17)	1.338 (4)
C(6)−N(7)	1.458 (5)	C(14)−C(15)	1.384 (5)
N(7)−C(8)	1.462 (6)	C(15)−C(16)	1.379 (5)
C(2)−C(1)−C(16)	121.9 (3)	C(9)−C(10)−N(11)	112.5 (3)
C(2)−C(1)−N(17)	115.6 (3)	C(10)−N(11)−C(12)	112.2 (3)
C(16)−C(1)−N(17)	122.4 (3)	N(11)−C(12)−C(12A)	109.8 (3)
C(1)−C(2)−C(2A)	110.1 (3)	N(11)−C(12)−C(13)	112.5 (3)
C(1)−C(2)−N(3)	113.0 (3)	C(12A)−C(12)−C(13)	110.1 (3)
C(2A)−C(2)−N(3)	109.2 (3)	C(12)−C(13)−C(14)	121.9 (3)
C(2)−N(3)−C(4)	113.3 (3)	C(12)−C(13)−N(17)	115.4 (3)
N(3)−C(4)−C(5)	111.7 (3)	C(14)−C(13)−N(17)	122.7 (3)
C(4)−C(5)−C(6)	115.6 (3)	C(13)−C(14)−C(15)	118.4 (3)
C(5)−C(6)−N(7)	111.0 (3)	C(14)−C(15)−C(16)	119.3 (3)
C(6)−N(7)−C(8)	111.7 (3)	C(1)−C(16)−C(15)	118.7 (3)
N(7)−C(8)−C(9)	112.5 (4)	C(1)−N(17)−C(13)	118.4 (3)
C(8)−C(9)−C(10)	115.2 (4)		
C(16)−C(1)−C(2)−C(2A)	106.8 (4)	N(7)−C(8)−C(9)−C(10)	−54.5 (5)
C(16)−C(1)−C(2)−N(3)	−130.8 (3)	C(8)−C(9)−C(10)−N(11)	−62.4 (5)
N(17)−C(1)−C(2)−C(2A)	−70.7 (4)	C(9)−C(10)−N(11)−C(12)	179.8 (3)
N(17)−C(1)−C(2)−N(3)	51.7 (4)	C(10)−N(11)−C(12)−C(12A)	171.4 (3)
C(2)−C(1)−C(16)−C(15)	−178.0 (3)	C(10)−N(11)−C(12)−C(13)	−65.6 (4)
N(17)−C(1)−C(16)−C(15)	−0.7 (5)	N(11)−C(12)−C(13)−C(14)	130.1 (3)
C(2)−C(1)−N(17)−C(13)	178.2 (3)	N(11)−C(12)−C(13)−N(17)	−51.1 (4)
C(16)−C(1)−N(17)−C(13)	0.7 (4)	C(12A)−C(12)−C(13)−C(14)	−107.1 (3)
C(1)−C(2)−N(3)−C(4)	64.5 (4)	C(12A)−C(12)−C(13)−N(17)	71.7 (4)
C(2A)−C(2)−N(3)−C(4)	−172.5 (3)	C(12)−C(13)−C(14)−C(15)	178.9 (3)
C(2)−N(3)−C(4)−C(5)	−177.5 (3)	N(17)−C(13)−C(14)−C(15)	0.1 (5)
N(3)−C(4)−C(5)−C(6)	64.2 (4)	C(12)−C(13)−N(17)−C(1)	−179.3 (3)
C(4)−C(5)−C(6)−N(7)	55.3 (5)	C(14)−C(13)−N(17)−C(1)	−0.4 (4)
C(5)−C(6)−N(7)−C(8)	−174.8 (3)	C(13)−C(14)−C(15)−C(16)	−0.1 (5)
C(6)−N(7)−C(8)−C(9)	171.4 (3)	C(14)−C(15)−C(16)−C(1)	0.3 (5)

Experimental. The compound was prepared by the literature method (Karn & Busch, 1969). A crystal of size $0.6 \times 0.6 \times 0.5$ mm suitable for X-ray analysis was obtained on slow evaporation of a diethyl ether solution. A crystal was mounted about the *c* axis on a STADI-2 diffractometer. Unit-cell dimensions were obtained from accurate 2θ values on 13 *hk*0 and two 00*l* reflections with $10 < \theta < 20°$ using graphite-monochromated Mo $K\alpha$ radiation. 2853 data were measured to $\theta = 25°$ $(0 \le h \le 19,\ 0 \le k \le 16,\ 0 \le l \le 15)$ of which 1333 were classed as unobserved $[F \le 6\sigma(F)]$. No significant drift was observed. No absorption

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corrections were applied. The structure was solved using *SHELX*84 (Sheldrick, 1984). All non-H atoms were refined anisotropically. H atoms were fixed in calculated positions (C—H = 1·08 Å) and not refined except for torsion of methyl groups. At convergence (max. $\Delta/\sigma = 0·14$), a final electron density synthesis gave max. peak and trough at 0·23 and $-0·20$ e Å^{-3}. $R = 0·060$, $wR = 0·076$. The weighting scheme in the final cycles of refinement, which showed no variation with $\sin\theta$ or $|F|$, was $w^{-1} = \sigma^2(F) + 0·0005|F^2|$. Structure refinement used *SHELX*76 (Sheldrick, 1976) including supplied atom scattering factors. Atomic coordinates are given in Table 1 while bond lengths, angles and torsion angles appear in Table 2.* The

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* Lists of structure factors, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44719 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
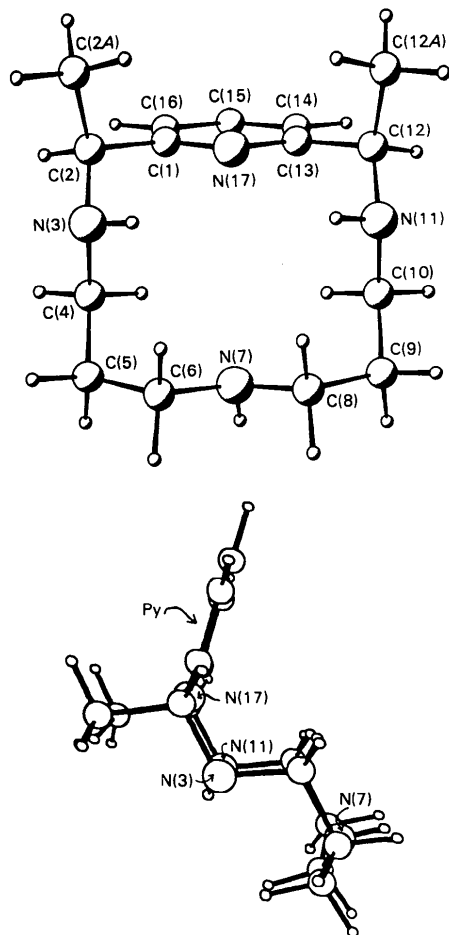

Fig. 1. Two views of the structure of $L^1.H_2O$.

atom-numbering scheme for the structure is shown in Fig. 1 together with two views of the molecule.

Related literature. The structure of the unsolvated ligand L^1 shows all three secondary amine protons lying *syn* to the *meso* methyl groups (Drew, Rice, Silong & Yates, 1986). Torsion angles around N(7), therefore, differ from those for the hydrated structure; the torsion angles C(4)C(5)C(6)N(7) and C(6)N(7)C(8)C(9) are $-60·2$ and $-68·7°$ respectively for L^1, compared with values of $+55·3$ and $+171·4°$ for $L^1.H_2O$. The unsolvated ligand is considerably more planar with a maximum deviation of $\pm0·08$ Å for an N donor group from the best least-squares tetraaza plane; the pyridine ring makes a dihedral angle of 49·2° to this plane. The folded conformation observed for $L^1.H_2O$ is similar to the conformation of the coordinated ligands in the complexes *cis*-[RuCl(CO)L^2]$^+$ (Blake, Hyde, Smith & Schröder, 1986) and *cis*-[IrCl(H)L^3]$^+$ (Blake, Hyde & Schröder, 1988). It has also been noted that benzylation of macrocycles related to L^1 occurs preferentially at N(3) and N(11) (Alcock, Balakrishnan, Moore & Pike, 1987). This may be rationalized by the relative steric hindrance at N(7) in $L^1.H_2O$ due to the propyl chains C(4)—C(6) and C(8)—C(10) of the macrocycle.

L^1 $R^1 = Me, R^2 = R^3 = H$
L^2 $R^1 = R^3 = Me, R^2 = H$
L^3 $R^1 = R^2 = H, R^3 = Me$
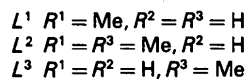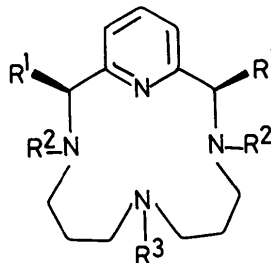
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