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Key indicators

Single-crystal X-ray study
T = 150 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.064
wR factor = 0.131
Data-to-parameter ratio = 14.6

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

A tetraazamacrocycle with benzyl substituents

The molecule of the title compound, 2,13-dibenzyl-5,16-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0^{1,18}.0^{7,12}]docosane, C₃₄H₅₂N₄, is centrosymmetric. The 14-membered macrocycle adopts the stable *trans*-III (*RRSS*) configuration, with one benzyl group above and the other below the macrocycle mean plane. The crystal structure is stabilized by N—H···N hydrogen bonds. There is no intermolecular π – π interaction between benzyl planes, which are almost 6 Å apart.

Comment

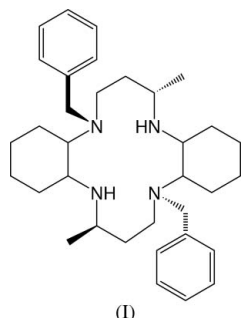
The 14-membered cyclam (1,4,8,11-tetraazacyclotetradecane) ligand and its substituted derivatives are involved in diverse application fields, such as catalysis, enzyme mimics, chemical sensors, selective metal ion recovery, pharmacology and therapy (Meyer *et al.*, 1998, and references therein). Metal–cyclam adducts have a moderately flexible structure, and can adopt both planar (*trans*) and folded (*cis*) configurations (Poon *et al.*, 1980). There are five configurational *trans* isomers for the N₄-donor set of cyclam which differ in the chirality of the *sec*-NH centres. The *trans*-V configuration can fold to form a *cis*-V isomer. We previously described the spectroscopic and ligand-field properties based on the emission, far-IR and electronic spectroscopy of chromium(III) complexes with 14-membered cyclam derivatives and two auxiliary ligands (Choi, 2000*a,b*; Choi, Oh, Suzuki & Kaizaki, 2004; Choi, Oh, Linder & Schönherr, 2004; Choi, Oh, Lim & Park, 2004). The modification of C- and/or N-configurational isomers of polyaza macrocyclic ligands to control the chemical and physical properties of metal complexes has been of considerable interest (Dong & Lindoy, 2001). The 14-membered cyclam containing two 1,2-diaminocyclohexanediamine subunits occurs in both *cis*- and *trans*-configurations (Kang & Jeong, 2003).

Octahedral transition metal complexes with cyclam derivatives display UV–visible electronic absorption bands. The *d*–*d* transitions are symmetry forbidden, so extinction coefficients are relatively small. Thus, it is necessary to prepare new systems with ligand-based chromophores with higher extinction coefficients (Bernhardt & Riley, 2002). Benzyl groups are introduced as possible internal sensitizers of the macrocyclic ligand and its metal complexes. Recently, the synthesis and chemical properties of tetraaza macrocycles containing two pendant arms and their nickel(II) and copper(II) complexes have been reported (Kang & Kim, 2003). However, the structures of (I) and its complexes have not previously been determined by X-ray crystallography. We report here the crystal structure of the title macrocycle, (I), with the aim of confirming the stereochemistry of the attached groups and

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gaining further insight into its coordination properties for various transition metal ions.



Selected bond lengths and angles are listed in Table 1. A perspective drawing of the centrosymmetric molecular structure is depicted in Fig. 1. Bond distances and angles are in normal ranges. The crystal structure of (I) shows a configuration with one benzyl group above and the other below the macrocycle mean plane, this being the sterically least-hindered configuration. The cyclam ligand has the *trans*-III (*RRSS*) form, consistent with a crystallographic centre of symmetry. The four N atoms are exactly coplanar as a result of the centrosymmetry of the molecule. The $(\text{CH}_2)_4$ part of the cyclohexane subunit is *anti* with respect to the macrocycle plane. The intramolecular hydrogen bond between secondary N2—H₂N and tertiary N1 lends some rigidity to the cyclam ring. The closest intermolecular distance between benzyl rings is $>5.8\text{\AA}$, which is not within the range associated with π - π interactions (Munakata *et al.*, 1994). We can anticipate that a related new macrocycle, containing two naphthylmethyl pendant arms, will adopt the most stable *trans*-III configuration, in which the two H atoms on the secondary amines and the two naphthylmethyl groups are likewise oriented on opposite sides of the macrocycle plane. The crystal structure of a copper(II) complex with the title ligand will be reported later (Choi *et al.*, 2006).

Experimental

The title macrocycle was prepared according to a published procedure (Kang *et al.*, 1991). To a solution of 5,16-dimethyl-2,6,13,17-tetraazatricyclo[14.4.0^{1.18}.0^{7.12}]docosane (8.814 g, 2.42 mmol) in methanol (10 ml) were added benzyl bromide (0.838 g, 4.90 mmol) and a solution containing Na_2CO_3 (0.520 g, 4.90 mmol) in water (4 ml). The solution was refluxed for 24 h and cooled to room temperature, and the resultant white solid was filtered off and washed with cold water. The crude compound was recrystallized from tetrahydrofuran to give colourless crystals suitable for X-ray analysis (yield 0.828 g, 66.3%). The IR spectrum (KBr) showed peaks at 3264 (N—H), 3063 and 3027 (aromatic C—H), 1603 and 1484 cm^{-1} (aromatic C=C). Analysis found: C 79.71, H 10.48, N 10.99%; $\text{C}_{34}\text{H}_{52}\text{N}_4$ requires: C 79.02, H 10.14, N 10.84%. The new macrocycle containing two naphthylmethyl pendant arms was also prepared by a similar method, except that 1-chloromethylnaphthalene was used instead of benzyl bromide.

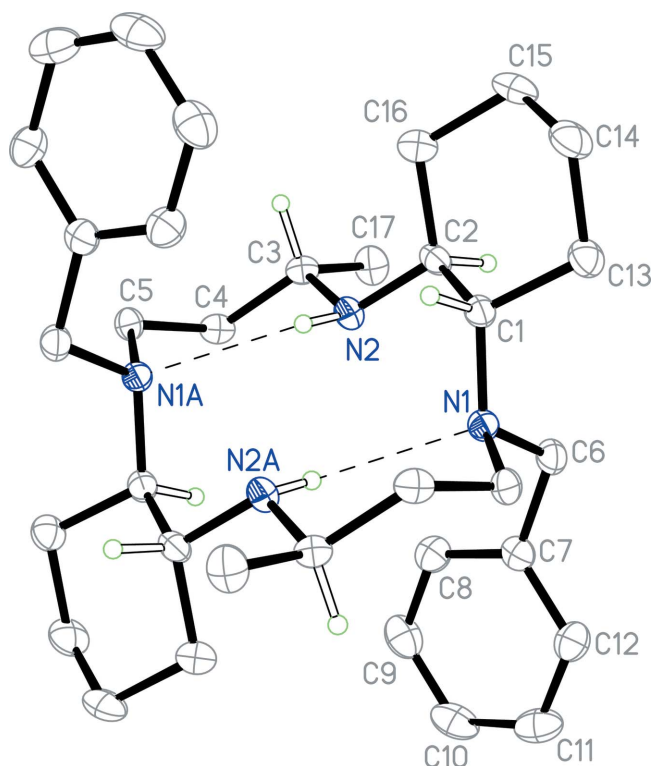


Figure 1

The molecular structure with 50% probability displacement ellipsoids. H atoms have been omitted, except for those on N atoms and major asymmetric centres. The dashed lines represent N—H...N hydrogen bonds. The suffix A corresponds to symmetry code (i) in Tables 1 and 2.

Crystal data

$\text{C}_{34}\text{H}_{52}\text{N}_4$
 $M_r = 516.80$
 Triclinic, $P\bar{1}$
 $a = 8.8976$ (12) \AA
 $b = 9.2438$ (12) \AA
 $c = 9.2535$ (12) \AA
 $\alpha = 82.467$ (2) $^\circ$
 $\beta = 87.605$ (2) $^\circ$
 $\gamma = 79.982$ (2) $^\circ$
 $V = 742.87$ (17) \AA^3

$Z = 1$
 $D_x = 1.155$ Mg m^{-3}
 Mo $K\alpha$ radiation
 Cell parameters from 5357 reflections
 $\theta = 2.3$ – 28.7 $^\circ$
 $\mu = 0.07$ mm^{-1}
 $T = 150$ (2) K
 Block, colourless
 $0.56 \times 0.55 \times 0.50$ mm

Data collection

Bruker SMART 1K CCD diffractometer
 ω scans
 Absorption correction: none
 5375 measured reflections
 2590 independent reflections

2363 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\text{max}} = 25.0$ $^\circ$
 $h = -10 \rightarrow 10$
 $k = -10 \rightarrow 10$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.064$
 $wR(F^2) = 0.131$
 $S = 1.27$
 2590 reflections
 178 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0312P)^2 + 0.5246P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.27$ e \AA^{-3}
 $\Delta\rho_{\text{min}} = -0.19$ e \AA^{-3}
 Extinction correction: *SHELXTL*
 Extinction coefficient: 0.015 (4)

Table 1Selected geometric parameters (\AA , $^\circ$).

N1—C5 ⁱ	1.463 (3)	N2—C2	1.463 (3)
N1—C6	1.468 (3)	N2—C3	1.466 (3)
N1—C1	1.474 (3)		
C5 ⁱ —N1—C6	110.47 (15)	C6—N1—C1	113.44 (15)
C5 ⁱ —N1—C1	113.92 (15)	C2—N2—C3	116.53 (16)

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.**Table 2**Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2N \cdots N1 ⁱ	0.86 (2)	2.32 (2)	3.025 (2)	139.9 (19)

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

The H atom bonded to N2 was located in a difference map and refined freely. Other H atoms were positioned geometrically, with C—H distances of 0.95–1.00 \AA , and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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