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Structure of 1,4,7,10,13,16-Hexaazapentacyclo[11.5.1.1.^{4,10}0.^{7,20}0.^{16,19}]icosane, $C_{14}H_{26}N_6$

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Abstract. $M_r = 278{\cdot}40$, $C2/c$, $a = 15{\cdot}024\ (5)$, $b = 6{\cdot}275\ (2)$, $c = 15{\cdot}100\ (4)$ Å, $\beta = 91{\cdot}79\ (2)°$, $V = 1422{\cdot}9\ (7)$ Å^3, $Z = 4$, $D_x(140\ \mathrm{K}) = 1{\cdot}30$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}90$ cm^{-1}, $F(000) = 1216$, $T = 140$ K, $R = 0{\cdot}040$, 1191 unique observed reflections. The structure incorporates a tetraazacyclodecane ring, which results from a simple condensation of 1,4,7,10,13,16-hexaazacyclooctadecane with *N,N*-dimethylformamide dimethyl acetal. The methine carbons, bridging three nitrogens, have a considerably distorted geometry. The endocyclic angles of the five-membered rings are normal but the exocyclic angles are larger. There are no short intermolecular contacts.

Introduction. Recent investigations in this laboratory have shown that aliphatic tetraazamacrocycles can coordinate early transition metals such as titanium and vanadium (Olmstead, Power & Viggiano, 1983). The complexes are unique in the sense that all the nitrogens are bound to the metal as amido ligands, *i.e.* $M{-}\ddot{\mathrm{N}}{<}$, rather than as classical two-electron ammine donors, *i.e.* $M{\leftarrow}{:}\mathrm{N}{<}$. As part of our continuing investigations we are extending this work using the hexaazamacrocycles and their derivatives. Our objective is the synthesis of ligands based on N_6[18]ane and its derivatives (Atkins, Richman & Oettle, 1978) incorporating other potential donor ligands. One of the ligand combinations in which we are interested is a macrocyclic ligand system involving carbene and amido groups (Hitchcock, Lappert, Terreros & Wainwright, 1980). A synthetic route we investigated was a condensation between N_6[18]ane and *N,N*-dimethylformamide dimethyl acetal. This reaction is closely related to the synthesis of electron-rich olefins which have been extensively investigated as precursors to numerous transition-metal carbene complexes (Lappert, 1975). The major product isolated from the above condensation was the macropolycyclic title compound rather than a macrocyclic system involving the electron-rich olefinic moiety $({>}N)_2C{=}C(N{<})_2$.

Experimental. Title compound synthesized by addition of *N,N*-dimethylformamide dimethyl acetal (0·77 ml, 5·8 mmol) in toluene (5 ml) to N_6[18]ane (0·5 g, 1·9 mmol) in toluene (25 ml) and heating the mixture to 333 K for 2 h. Volume was reduced to *ca* 10 ml; filtration and slow cooling to 278 K yielded colorless needles of the product, m.p. 427–433 K, 0·52 g. Crystal dimensions 0·25 × 0·25 × 0·08 mm; Syntex $P2_1$ diffractometer, graphite monochromator, space group $C2/c$ or Cc based on conditions hkl, $h + k = 2n$; $h0l$, $l = 2n$ and confirmed as former by successful solution and refinement; unit-cell dimensions from least-squares fit of fourteen reflections having $30 < 2\theta < 40°$; absorption correction factors 1·01–1·04; absorption ignored; ω scan (8° min^{-1}), 1·0° range, 1·0° offset for background, $2\theta_{\max} = 55°$ with hkl ranges from 0 to 20, 0 to 9 and −20 to 20, respectively, two check reflections < 2% average fluctuation; direct methods, 1847 reflections measured, $R_{\mathrm{int}} = 0{\cdot}010$, 1640 unique reflections, 1191 $[I > 2{\cdot}5\sigma(I)]$ observed used in solution and refinement (based on F); full-matrix least-squares refinement, anisotropic thermal parameters for non-hydrogen atoms, isotropic thermal parameter of $U = 0{\cdot}03$ Å^2 fixed for hydrogen atoms, $R_w = 0{\cdot}040$, $w = [\sigma^2(F_o) + 0{\cdot}00032F_o^2]^{-1}$, $S = 1{\cdot}31$, $(\Delta/\sigma)_{\max} = 0{\cdot}091$ for overall scale, $(\Delta/\sigma)_{\mathrm{av}} = 0{\cdot}018$, max. and min. $\Delta\rho = 0{\cdot}21$ and $-0{\cdot}18$ e Å^{-3}, respectively, atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); computer programs from *SHELXTL* (version 3) package (Sheldrick, 1981).

Discussion. The final atomic fractional coordinates and equivalent isotropic thermal parameters are given in Table 1. Bond distances and angles are listed in Table 2.*

The numbering scheme of the title compound is presented in Fig. 1. The structure results in well separated molecules with no short intermolecular contacts. The compound, which has overall $\bar{1}$ symmetry, contains two methine groups, each bridging three nitrogens of the 18-membered ring. This results in a central ten-membered ring system involving four

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* Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving hydrogen, torsion angles for the ten-membered ring portion and a packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39386 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atom coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (Å² ×10³)

	x	y	z	U_{eq}
N(1)	3392 (1)	2645 (2)	9668 (1)	17 (1)
N(2)	4082 (1)	−349 (2)	8977 (1)	19 (1)
N(3)	2563 (1)	246 (2)	8681 (1)	18 (1)
C(1)	3678 (1)	2831 (3)	10611 (1)	19 (1)
C(2)	4077 (1)	3419 (3)	9068 (1)	21 (1)
C(3)	4693 (1)	1500 (3)	8969 (1)	22 (1)
C(4)	3247 (1)	441 (2)	9386 (1)	17 (1)
C(5)	3824 (1)	−1180 (3)	8093 (1)	23 (1)
C(6)	2837 (1)	−1622 (3)	8176 (1)	23 (1)
C(7)	1644 (1)	110 (3)	8975 (1)	20 (1)
H(1*a*)	3419 (12)	1623 (30)	10936 (12)	
H(1*b*)	4350 (13)	2722 (30)	10689 (12)	
H(2*a*)	4369 (12)	4686 (31)	9307 (12)	
H(2*b*)	3784 (12)	3775 (28)	8472 (12)	
H(3*a*)	5024 (12)	1545 (28)	8392 (12)	
H(3*b*)	5122 (13)	1424 (29)	9464 (12)	
H(4)	3099 (12)	−436 (30)	9910 (11)	
H(5*a*)	3919 (11)	−94 (29)	7608 (11)	
H(5*b*)	4194 (12)	−2498 (31)	7949 (12)	
H(6*a*)	2724 (12)	−3005 (29)	8512 (12)	
H(6*b*)	2517 (12)	−1700 (28)	7592 (12)	
H(7*a*)	1565 (12)	−1095 (31)	9386 (12)	
H(7*b*)	1253 (11)	−178 (29)	8423 (11)	

* $U_{eq} = (U_{11} + U_{22} + U_{33})/3$. Hydrogen thermal parameters were fixed at $U = 0{\cdot}03$ Å².

Table 2. *Interatomic distances* (Å) *and angles* (°)

N(1)—C(1)	1·479 (2)	N(3)—C(4)	1·461 (2)
N(1)—C(2)	1·474 (2)	N(3)—C(6)	1·464 (2)
N(1)—C(4)	1·461 (2)	N(3)—C(7)	1·466 (2)
N(2)—C(3)	1·480 (2)	C(2)—C(3)	1·529 (2)
N(2)—C(4)	1·499 (2)	C(5)—C(6)	1·517 (2)
N(2)—C(5)	1·474 (2)	C(7)—C(1ⁱ)	1·521 (2)
C(1)—N(1)—C(2)	112·2 (1)	C(1)—N(1)—C(4)	113·1 (1)
C(2)—N(1)—C(4)	103·5 (1)	C(3)—N(2)—C(4)	105·7 (1)
C(3)—N(2)—C(5)	114·5 (1)	C(4)—N(2)—C(5)	106·9 (1)
C(4)—N(3)—C(6)	104·1 (1)	C(4)—N(3)—C(7)	115·6 (1)
C(6)—N(3)—C(7)	113·2 (1)	N(1)—C(1)—C(7ⁱ)	112·1 (1)
N(1)—C(2)—C(3)	103·7 (1)	N(2)—C(3)—C(2)	103·8 (1)
N(1)—C(4)—N(2)	108·3 (1)	N(1)—C(4)—N(3)	112·8 (1)
N(2)—C(4)—N(3)	104·5 (1)	N(2)—C(5)—C(6)	102·7 (1)
N(3)—C(6)—C(5)	100·8 (1)	N(3)—C(7)—C(1ⁱ)	112·9 (1)

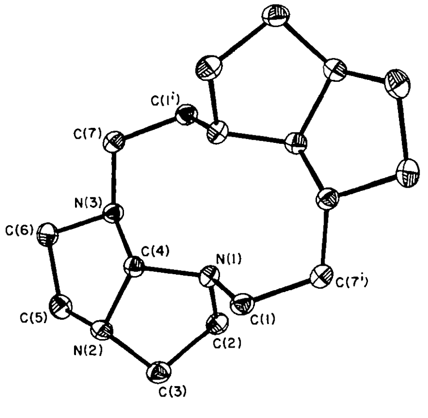

Fig. 1. A perspective drawing of $C_{14}H_{26}N_6$ showing the atom labeling scheme and anisotropic thermal ellipsoids at the 50% probability level. Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}-y, 2-z$.

nitrogen donors. Although tetraazamacrocycles are well known, they generally involve larger ring sizes having, most commonly, 14 members. It is possible that the molecule, donating through the four central nitrogens, will coordinate Li^+, forming a sandwich complex similar to $[Li(12\text{-crown-}4)_2]^+$ (Hope, Olmstead, Power & Xiaojie, 1984). The shortest transannular contact for non-hydrogen atoms (separated by more than one atom) is 2·897 (5) Å between N(1) and N(1ⁱ). Owing to the orientation of the other two nitrogens [N(2) and its inverse] it is doubtful that these would interact with any ion coordinated in the central cavity.

The carbon–carbon and carbon–nitrogen distances are generally close to those found in the compound N_6[18]ane.4HNO$_3$.2HCl (Margulis & Zompa, 1981). There are some significant differences owing to the presence of two bridgehead carbons. For example, the geometry at the methine carbon shows considerable distortion with the angles at C(4) being 104·5 (1), 108·3 (1) and 112·8 (1)° and the N(2)—C(4) distance, 1·499 (2) Å, being lengthened compared to the N(3)—C(4) and N(1)—C(4) distances, both 1·461 (2) Å. All the endocyclic angles in the five-membered rings are within *ca* 2° of the values expected at pyramidal nitrogen or tetrahedral carbon. However, the exocyclic angles (relative to the five-membered rings) are much larger, having the values 113·2 (1), 115·6 (1)° at N(3), 112·8 (1)° at C(4) and 112·2 (1) and 113·1 (1)° at N(1). These variations are no doubt due to the greater flexibility permitted the central ten-membered macrocycle compared to the more rigid five-membered ring systems.

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