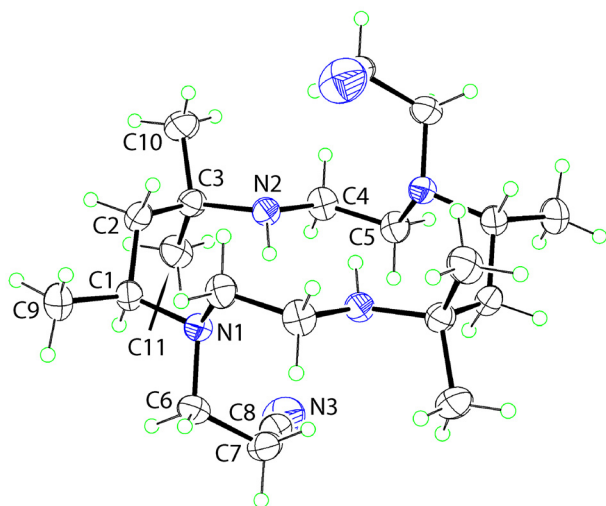


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# Crystal structure of *trans*- $N^1, N^8$ -bis(2-cyanoethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, $C_{22}H_{42}N_6$



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## Abstract

$C_{22}H_{42}N_6$ , triclinic,  $P\bar{1}$  (no. 2),  $a = 8.3115(2)$  Å,  $b = 8.8263(2)$  Å,  $c = 9.7688(2)$  Å,  $\alpha = 111.490(2)^\circ$ ,  $\beta = 115.056(2)^\circ$ ,  $\gamma = 93.681(2)^\circ$ ,  $V = 583.25(3)$  Å<sup>3</sup>,  $Z = 1$ ,  $R_{gt}(F) = 0.0465$ ,  $wR_{ref}(F^2) = 0.1351$ ,  $T = 294$  K.

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**Table 1:** Data collection and handling.

Crystal:	Colourless block
Size:	0.16 × 0.11 × 0.07 mm
Wavelength:	Cu K $\alpha$ radiation (1.54184 Å)
$\mu$ :	0.52 mm <sup>-1</sup>
Diffractometer, scan mode:	XtaLAB Synergy, $\omega$
$\theta_{max}$ , completeness:	67.1°, >99 %
$N(hkl)_{measured}$ , $N(hkl)_{unique}$ , $R_{int}$ :	13,649, 2075, 0.034
Criterion for $I_{obs}$ , $N(hkl)_{gt}$ :	$I_{obs} > 2\sigma(I_{obs})$ , 1928
$N(param)_{refined}$ :	130
Programs:	CrysAlis <sup>PRO</sup> [1], SHELX [2, 3], WinGX/ORTEP [4]

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

## 1 Source of material

The precursor molecule, tet-a, was prepared following a literature procedure [5]. Thus, the condensation of ethylenediamine with acetone in the presence of a quantitative amount of perchloric acid, yielded the hexamethyl derivative of the 14-membered tetraazamacrocycle, Me<sub>6</sub>[14] diene·2HClO<sub>4</sub>. The diene ligand, on reduction with NaBH<sub>4</sub>, followed by extraction with CHCl<sub>3</sub> at pH above 12, resulted in a mixture of isomeric macrocycles, the Me<sub>6</sub>[14]anes. These were separated by fractional crystallisation from xylene and designated as tet-a and tet-b. The reaction of tet-a with excess acrylonitrile was stereoselective and gave the N-pendent derivative, tet-ax, in which two ethylcyano groups are attached to less crowded nitrogen atom. **Elemental analysis (Leco CHNS-932 elemental analyzer; %)** for  $C_{22}H_{42}N_6$ : C, 67.65; H, 10.84; N, 21.51. Found: C, 67.82; H, 10.95; N, 21.35. **IR (Shimadzu IR 20 spectrophotometer, KBr, cm<sup>-1</sup>):** 3227 (w)  $\nu$ (N–H), 1361 (s)  $\nu$ (CH<sub>3</sub>), 2965 (m)  $\nu$ (C–H), 1141 (w)  $\nu$ (C–C), 1177 (m)  $\nu$ (N–C), 2241(s)  $\nu$ (C–N). **<sup>1</sup>H NMR (Bruker AVANCE 400 NMR spectrometer, DMSO-d<sub>6</sub>, ppm)  $\delta$ :** Mehtyl–H: 0.92 (d, e, 6H), 1.05 (s, e, 6H), 1.15 (s, a,

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	x	y	z	$U_{iso}^*/U_{eq}$
N1	0.25155 (14)	0.64361 (13)	0.78500 (12)	0.0392 (3)
N2	0.09668 (14)	0.63110 (13)	0.44208 (13)	0.0399 (3)
H2N	0.079 (2)	0.6321 (19)	0.5235 (15)	0.048*
N3	-0.0730 (3)	0.9230 (3)	0.7599 (2)	0.0890 (5)
C1	0.41794 (17)	0.74675 (17)	0.80962 (16)	0.0443 (3)
H1	0.414383	0.864536	0.857784	0.053*
C2	0.42117 (18)	0.71433 (18)	0.64616 (17)	0.0472 (3)
H2A	0.414904	0.595849	0.591858	0.057*
H2B	0.539675	0.777984	0.675326	0.057*
C3	0.27230 (18)	0.75613 (16)	0.51628 (16)	0.0438 (3)
C4	-0.06654 (19)	0.65103 (17)	0.31906 (18)	0.0486 (4)
H4A	-0.057710	0.625263	0.217452	0.058*
H4B	-0.071656	0.767527	0.362875	0.058*
C5	-0.24211 (18)	0.53737 (17)	0.27652 (18)	0.0466 (3)
H5A	-0.256766	0.573082	0.376085	0.056*
H5B	-0.345163	0.553591	0.191829	0.056*
C6	0.22886 (19)	0.71069 (19)	0.93481 (16)	0.0506 (4)
H6A	0.310087	0.823248	1.009622	0.061*
H6B	0.264383	0.640267	0.993298	0.061*
C7	0.0307 (2)	0.7179 (2)	0.89235 (19)	0.0553 (4)
H7A	-0.050866	0.605779	0.815547	0.066*
H7B	0.020344	0.754019	0.994125	0.066*
C8	-0.0271 (2)	0.8322 (2)	0.8169 (2)	0.0581 (4)
C9	0.5997 (2)	0.7334 (2)	0.9360 (2)	0.0609 (4)
H9A	0.701336	0.802967	0.945872	0.091*
H9B	0.604645	0.770563	1.043532	0.091*
H9C	0.606339	0.618284	0.897435	0.091*
C10	0.3248 (2)	0.7361 (2)	0.3789 (2)	0.0648 (5)
H10A	0.438823	0.817019	0.426245	0.097*
H10B	0.338405	0.624311	0.332689	0.097*
H10C	0.230010	0.754533	0.291709	0.097*
C11	0.2638 (2)	0.93911 (18)	0.5961 (2)	0.0567 (4)
H11A	0.381147	1.014363	0.642046	0.085*
H11B	0.171415	0.963152	0.512237	0.085*
H11C	0.233529	0.954165	0.684010	0.085*

6H). Methylene–H: 1.19 (m), 2.55 (m), 2.75 (m), 2.98 (m). Methine–H: 3.10 (m). Amine–H: 7.26 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (Bruker AVANCE 400 NMR spectrometer, DMSO-*d*<sub>6</sub>, ppm) δ: Methyl–C: 14.66, 18.69, 25.92. Ring–C: 28.73, 40.29, 45.64, 47.55, 49.55. Ethylcyano–C: 52.62, 54.31, 119.92.

## 2 Experimental details

The C–bond H atoms were geometrically placed (C–H = 0.93–0.98 Å) and refined as riding with  $U_{iso}(H) = 1.2\text{--}1.5U_{eq}(C)$ . The N–bond H atom was located in a difference map and refined with N–H = 0.86 ± 0.01 Å, and with  $U_{iso}(H) = 1.2U_{eq}(N)$ .

## 3 Comment

Cyclam (1,4,8,11-tetraazacyclotetradecane) is a 14-membered macrocycle, is classified as an aza-crown ether and its ability to complex metal ions is well known [6]. Being readily substituted at practically all positions in the ring and being flexible in its coordination potential, isomerism gives rise to fascinating structural chemistry, e.g. for 2,5,5,7,9,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradecane, 30 different configurations may be envisaged when this molecule is coordinated to nickel(II) [7]. The determination of pharmaceutical potential has motivated on-going interest in this area, such as the recent report of the evaluation of the antimicrobial activity of cadmium derivatives of the N-bond bis-cyanoethyl derivative of a related octa-methyl macrocycle [8]. In continuation of this work, herein the crystal structure determination of a related bis-cyanoethyl substituted macrocycle lacking methyl substituents in the ethylene link, (I), is described.

The molecular structure is shown in the figure (35 % probability ellipsoids). The unlabelled atoms in the figure are related by the symmetry operation  $-x, 1 - y, 1 - z$  as the molecule is disposed about an inversion centre. The four nitrogen atoms define a plane and participate in intramolecular secondary-amine–N–H···N (tertiary amine) hydrogen bonds [N2–H2n···N1: H2n···N1 = 2.298(13) Å, N2···N1 = 2.9916(15) Å with angle at H2n = 137.3 (15)°]; this interaction serves to close a slightly twisted, six-membered {···NC<sub>3</sub>NH} synthon. When viewed side-on through the N<sub>4</sub> plane, the ethylene bridges lie to either side of the plane as do the N–bond ethylcyano substituents. Further, the four N–bond carbon atoms of the propylene links are close to co-planar with the N<sub>4</sub> plane. This latter configuration is in stark contrast to that observed in the methanol solvate of the compound [9], where the C<sub>3</sub> links are kinked with respect to the N<sub>4</sub> plane. This change in conformation in the literature precedent is correlated with the influence of methanol–O–H···N (secondary amine) hydrogen bonding interactions.

In accord with an analysis of the molecular packing of (I), employing PLATON [10], the crystal is largely devoid of directional interactions between molecules, partially owing to the intramolecular N–H···N hydrogen bonds, precluding these atom from forming intermolecular contacts. This conclusion is confirmed by an analysis of the calculated Hirshfeld surfaces, employing CrystalExplorer [11] and standard procedures [12]. This analysis shows that 77.5 % of all surface contacts are H···H contacts. The other contributors are N···H/H···N [18.3 %] and N···C/C···N [3.6 %] contacts.

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