

КРАТКИЕ СООБЩЕНИЯ

UDC 548.737:547.573

THE CRYSTAL STRUCTURE OF N₅O₃ CRYPTANDL.-X. Pan¹, B. Zhang², Y. Su², Z. Ma²

¹State Key Laboratory of Non-Food Biomass and Enzyme Technology, National Engineering Research Center for Non-Food Biorefinery, Guangxi Key Laboratory of Biorefinery, Guangxi Academy of Sciences, Nanning, Guangxi, P. R. China

²School of Chemistry and Chemical Engineering, Guangxi University, Guangxi, P. R. China
E-mail: mzmz2009@sohu.com

Received October, 7, 2015

Revised — November, 10, 2015

The title compound, 1,4,13,22,27-pentaaza-6,9:17,20:29,32-tribenzo-10,16,33-trioxabicyclo [11,11,11] pentatriacontane (C₃₃H₄₅N₅O₃), is synthesized by [1+1] tripodal condensation of trialdehyde (4,4',4''-triformyl-triphenoxytriethylamine) with tris(2-aminoethyl)amine (tren) in the presence of La(NO₃)₃·6H₂O as a template, followed by reduction with KBH₄. There are six unique molecules in the unit. The molecule has a threefold symmetry axis passing through the bridgehead nitrogen atoms in the structure. As a result, only one strand of the cryptand molecule is present in the asymmetric unit. The structure presents an *endo-endo* conformation, with the distance between the two bridgehead nitrogen atoms of 10.030(8) Å.

DOI: 10.15372/JSC20170325

Keywords: cryptand, crystal structure, condensation, rare earth, tris(2-aminoethyl)amine.

The design and synthesis of macrocyclic compounds as complexing agents for transition metal ions and as hosts for organic/inorganic cations, anions, and neutral molecules are subjects of considerable current interest [1—9]. The Schiff base and their relative reduced polyaza cryptands have been synthesized by facile routes of [2+3], [1+1] or [2+2] tripodal condensation of trialdehydes, dialdehydes with tris(2-aminoethyl)amine (tren), tris(3-aminopropyl)amine (trpn) or a diamine [10—12].

Our research team and other researchers have been involved in synthesizing heteroditopic cryptands through [1+1] Schiff-base condensation of tripodal triamines with tripodal trialdehydes and reduction with KBH₄ in or no presence of metal ions as templates for cyclization [13, 1a]. Herein we report the molecular and crystal structure of N₅O₃ cryptand, 1,4,13,22,27-pentaaza-6,9:17,20:29,32-tribenzo-10,16,33-trioxabicyclo [11,11,11] pentatriacontane prepared by [1+1] tripodal condensation of trialdehyde (4,4',4''-triformyl-triphenoxytriethylamine) with tris(2-aminoethyl)amine (tren) in the presence of La(NO₃)₃·6H₂O as a template for cyclization, followed by reduction with KBH₄.

The compound crystallizes in a hexagonal space group *R3c*. A perspective view of the molecule showing the atom numbering scheme is given in Fig. 1, while the crystal data are collected in Table 1.

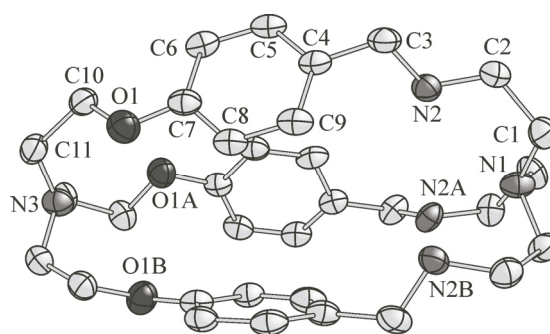


Fig. 1. A view of the title compound showing the atom labeling scheme with 30 % probability displacement ellipsoids. H atoms have been omitted for clarity

Table 1

Selected geometric parameters of the compound

Formula	C ₃₃ H ₄₅ N ₅ O ₃
Formula weight	559.74
Crystal system	Hexagonal
Crystal size, mm	0.35×0.25×0.21
Space group	R3c
<i>a</i> , <i>b</i> , <i>c</i> , Å	13.4796(19), 13.4796(19), 29.412(6)
α, β, γ, deg.	90, 90, 120
<i>V</i> , Å ³ ; <i>Z</i>	4628.2(13); 6
<i>D</i> _{calc} , g/cm ³	1.205
μ, mm ⁻¹	0.078
<i>F</i> (000)	1812
No. <i>R</i> fl. unique / observed	1187 / 958
<i>R</i> / <i>wR</i>	0.0544 / 0.1725
<i>R</i> / <i>wR</i> for all	0.0608 / 0.1783
GOOF	1.035
CCDC number	1422708

There are six unique molecules in the unit. The positions of the two bridgehead N atoms of L coincide with crystallographic threefold symmetry. As a result, only one strand of the cryptand molecule is present in the asymmetric unit. The average C—N bond length is 1.455 Å which is almost identical to that reported in an isomeric structure (1.452 Å) [1a].

The distance between the ethereal O1 atom and the bridgehead N3 atom is 2.909(5) Å, which is in the range of 2.860(5)—2.919(7) Å reported for the aforementioned structure [1a]. In the crystal, the molecule has an *endo-endo* conformation with the distance of 10.020(8) Å between the two bridgehead nitrogen atoms, through which the threefold symmetry axis passes (Fig. 1). Both ¹H and ¹³C NMR data are also consistent with a 3-fold symmetry in the molecule in a chloroform solution [13]. Two atoms at the strand (C1 and N2) are disordered over two alternative sites with 59 % and 41 % occupancies, respectively.

The structure presents no intermolecular π—π interactions but two π-ring (X—H...Cg) interactions between two hydrogen atoms at two carbon atoms (C2 and C8) of the strand of the compound and one adjacent aryl ring constituted by C4—C5—C6—C7—C8—C9 with the atom-centroid distances (X...Cg) of 3.716 Å and 3.511(5) Å and the angles (X—H...Cg) of 149° and 130°, respectively. No classic hydrogen bond is present in the structure and unit cell contains no voids accessible for a residual solvent (Fig. 2).

Experimental. X-ray crystal structure determination. A single crystal of the compound was mounted on a glass fibre. Intensity data were collected using a Rigaku R-AXIS RAPID Weissenberg IP diffractometer with graphite monochromated MoK_α (λ = 0.71073) radiation by using the ω scan mode at room temperature. Data reduction was made. The ψ empirical absorption corrections were carried out [14]. Structures were solved by direct methods by using the SHELXS-97 package [15] and refined with SHELXL-97 [16]. The atomic positions of one methylene group (C1), and of N2 atom of the same strand of the compound, were disordered over two orientations and were refined following PART instruction. The occupancies of the two components on each atom were refined to a ratio of 59 % and 41 %. In spite of this, the carbon and nitrogen atoms had to be refined isotropically. The positions of the hydrogen atoms bonded to the disordered carbon atoms were inserted in the calculated positions by using the PART instructions in SHELXL and treated as riding atoms. The remaining hydrogen atoms were inserted in the calculated positions. Least squares refinement with anisotropic thermal motion parameters for all the non-hydrogen atoms, and isotropic refinement for the remaining

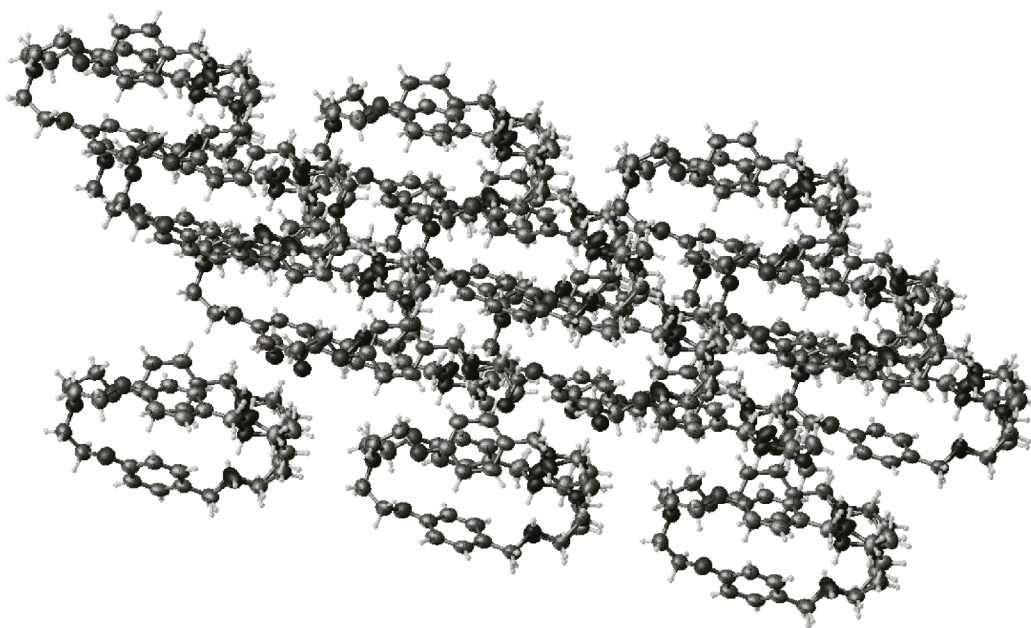


Fig. 2. An arbitrary view of the crystal packing

atoms were employed. CCDC 1422708 contains the supplementary crystallographic data of this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via w.ccdc.cam.ac.uk/data_request/cif. Crystal data are reported in Table 1.

Synthesis. The compound was prepared according to the reported procedure [13] by [1+1] Schiff-base condensation of tris(2-aminoethyl)amine (tren) with 4,4',4''-triformyl-triphenoxytriethylamine (trialdehyde) in the presence of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as a template and reduction with KBH_4 . Slow evaporation of a dichloromethane solution of the title compound led to the formation of colorless crystals suitable for X-ray characterization.

The authors are grateful for the financial support from the Science Foundation of China (21261002).

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