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THE SYNTHESIS AND STRUCTURE OF MACROCYCLIC PYRIDINOPHANES - POTENTIAL ANION RECEPTORS*

Agnieszka Szumna,[a] Daniel T. Gryko,[a] and Janusz Jurczak[a,b,]*

[a] Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

[b] Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland

Abstract – The simple synthesis of eight di- and tetralactams possessing 2,6-dicarbamoylpyridine moieties linked by aliphatic units is reported. The X-Ray structures of two tetralactams having 22 and 26-membered rings are analyzed in terms of cavity size and potential anion binding ability.

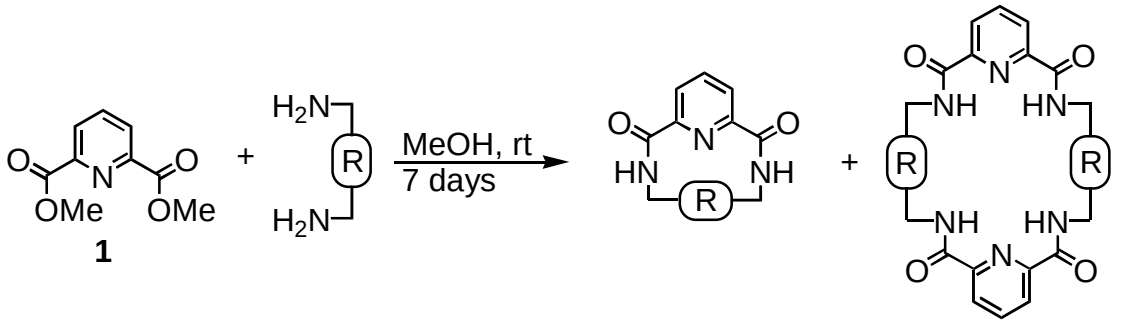
INTRODUCTION

Molecules containing 2,6-dicarbamoylpyridine moiety are of great interest due to their increasing role in the construction of cation[1,2] and anion receptors,[3,4] catenands,[5] dendrimers,[6] and helical structures.[7] Anion recognition, as compared with cation binding, is a relatively new and less explored area in the field of supramolecular chemistry.[8] Among receptors that employ hydrogen bond interactions for anion recognition examples involve: amides,[9] ureas,[10] alcohols,[11] and calix[4]pyrroles.[12] The design of macrocyclic receptors for this purpose is challenging since anions are relatively large and therefore require receptors of considerably greater size than cations (e.g. one of the smallest anions, F^-, is comparable in ionic radius to K^+). We have recently synthesized the 18-membered tetralactam, containing 2,6-dicarbamoylpyridine moieties, which proved to be an efficient anion receptor.[4] Currently, we aimed at the synthesis of bigger amide-based macrocycles with potential anion binding abilities. Our objectives in present study were: a) to synthesize a broad range of macrocyclic dilactams and tetralactams containing 2,6-dicarbamoylpyridine moieties joined by aliphatic spacers; b) to analyze results of the macrocyclization reaction; c) to study structures of macrocyclic products.

* Dedicated to Professor James P. Kutney on the occasion of his 70th birthday.

RESULTS AND DISCUSSION

In order to accomplish the first aim we decided to apply the method of macrocyclization consisting in the reaction of α,ω-diamines with dimethyl α,ω-dicarboxylates.[13] This simple approach was recently used for preparing several types of macrocyclic lactams.[14-16] Thus, we carried out reactions of dimethyl pyridine-2,6-dicarboxylate **(1)** with a broad set of aliphatic α,ω-diamines **(2-6)**, possessing even numbers of carbon atoms (Scheme 1, Table 1). During the investigation we found as follows: a) reactions with diamines **(2)** and **(3)** led only to the formation of tetralactams **(10)** and **(11)**; b) reactions with diamines **(4-6)** afforded dilactams **(7-9)** as well as tetralactams **(12-14)**; c) yields of tetralactams **(10-14)** are approximately the same (9-12%) independently of amine length and are substantially lower than that of analogous tetralactam derived from ethylenediamine.[4]



2. R = -$(CH_2)_4$-
3. R = -$(CH_2)_6$-
4. R = -$(CH_2)_8$-
5. R = -$(CH_2)_{10}$-
6. R = -$(CH_2)_{12}$-

7. R = -$(CH_2)_8$-
8. R = -$(CH_2)_{10}$-
9. R = -$(CH_2)_{12}$-

10. R = -$(CH_2)_4$-
11. R = -$(CH_2)_6$-
12. R = -$(CH_2)_8$-
13. R = -$(CH_2)_{10}$-
14. R = -$(CH_2)_{12}$-

Scheme 1

Table 1. Results of Reaction of Ester **(1)** with Diamines **(2-6)**

Amine	Yield of dilactam (%)		Yield of tetralactam (%)	
2	—		11	**10**
3	—		11	**11**
4	23	**7**	12	**12**
5	16	**8**	10	**13**
6	12	**9**	9	**14**

We compared present results with these obtained earlier for other α,ω-diamines under analogous conditions,[14,15,17] as well as with those obtained under high-dilution conditions.[18-20] Yields of dilactams **(7-9)** are much lower (around 3-4 times) than those observed for α,ω-diamino aliphatic ethers or polyamines of similar lenghts.[14,15,17] The difference is difficult to explain based solely on steric effects.

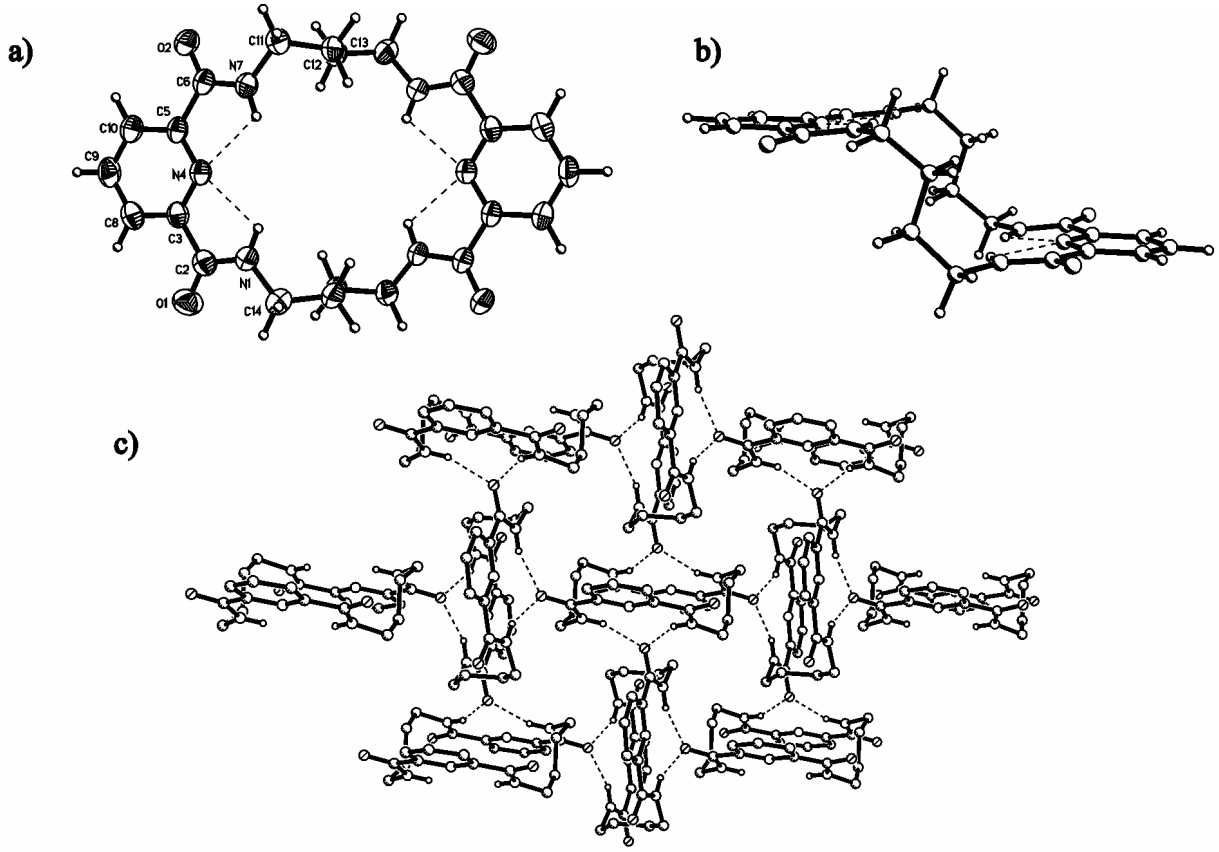


Figure 1. X-Ray structure of tetralactam (**10**): a) ORTEP projection; b) side view, c) packing mode: a layer of hydrogen bound molecules.

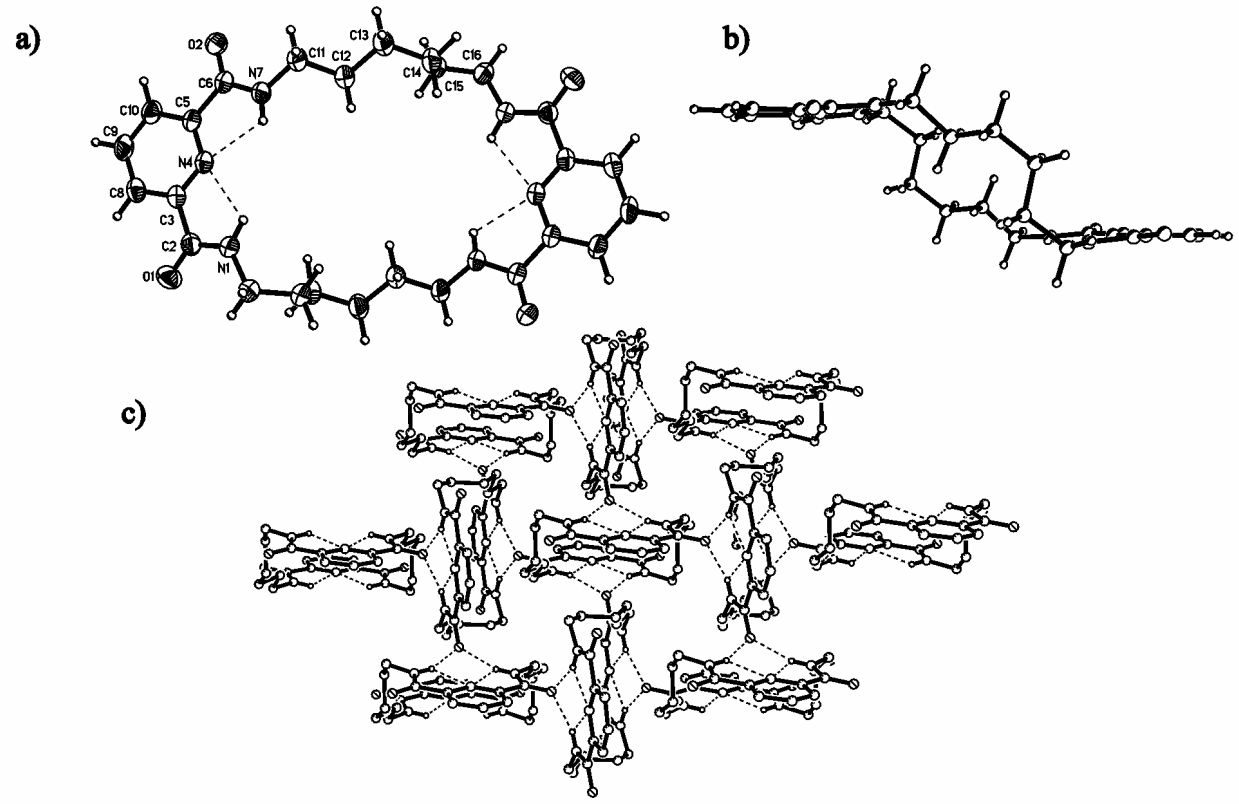


Figure 2. X-Ray structure of tetralactam (**11**): a) ORTEP projection; b) side view, c) packing mode: a layer of hydrogen bound molecules.

Contrarily, under high-dilution conditions this difference is less pronounced.[19,20] To explain these results we carefully assume that ethereal oxygen atoms (from the amine molecule) promote conformation that increases probability of formation of cyclic products, although it is hard to say what kind of interactions could be involved. In the present study this promoting factor is absent.

It is clear that ethylenediamine is too short to form an appropriate dilactam in the reaction with diester **(1)**, and the smallest macrocyclic product is the corresponding tetralactam, prepared by us earlier.[4] We also have not observed formation of dilactam products from diamines **(2)** and **(3)**. It is substantially different from high-dilution results reported by Krakowiak,[20] who has observed the formation of dilactams in analogous reactions.

We were able to obtain compounds **(10)** and **(11)** as monocrystals suitable for X-Ray analysis. In both cases crystals were obtained directly from reaction mixtures. Figures 1 and 2 show conformations of ligands **(10)** and **(11)** in the solid state and packing of molecules in the crystal lattices.

The macrorings of ligands **(10)** and **(11)** have symmetrical, expanded, stair-like conformations (Figures 1a and 2a). Two pyridine rings are arranged in antiparallel relations. Both ligands possess amide hydrogen atoms directed into the cavity. It is thanks to the presence in each molecule of four $NH_{amide}\cdots N_{py}$ interactions, which are known to stabilize a flat *syn-syn* conformation for compounds containing 2,6-dicarbamoylpyridine moieties.[21,22] We can suppose that as a result, the macrorings do not adopt collapsed conformations and have amide hydrogen atoms arranged in a convergent manner, and thereby are preorganized for anion binding. The most important distances, characterizing cavity sizes, are summarized in Table 2.

Table 2. Distances characterizing cavity sizes of **(10)** and **(11)**

Tetralactam	$d_{Py\text{-}Py}$ (Å)	d_1 (Å)	d_2 (Å)
10	2.8	2.93	4.57
11	3.7	2.91	7.02

$d_{Py\text{-}Py}$ – distance between parallel pyridine rings
d_1 - distance between H atoms (ester linker)
d_2 - distance between H atoms (amine linker)

The interesting observation is that the packing patterns of those ligands in the crystal lattices are very similar (Figures 1c and 2c). In both cases molecules form hydrogen bound layers. Within the layer, each molecule is surrounded by four symmetry related ones, forming tetrameric assemblies. The very similar pattern was also observed for the earlier reported 18-membered tetralactam derived from 1,2-diaminoethane.[4] Even the presence of methanol molecules in the structure (as in the latter case) does not change this pattern.

EXPERIMENTAL

General methods: Melting points were taken on a Köfler type (Boetius) hot stage apparatus and are not corrected. ^{1}H NMR spectra were recorded with a Varian Gemini (200 MHz) and/or a Bruker AM500 (500

MHz) spectrometers in $CDCl_3$, CF_3COOD or CD_3CN using TMS as an internal standard. ^{13}C NMR spectra were recorded using also a Varian Gemini (50 MHz) and/or a Bruker AM500 (125 MHz) spectrometers. All chemical shifts are quoted in parts per million relative to tetramethylsilane (δ, 0.00 ppm), and coupling constants (J) are measured in Hertz. High-resolution mass spectrometry (HRMS) experiments were performed on an AMD-604 Intectra instrument using the electron impact (EI) or LSIMS techniques. Column chromatography was carried out on silica gel (Kieselgel-60, 200-400 mesh).

General procedures for the synthesis of macrocyclic lactams: An equimolar 0.1 M methanolic solution (1.5 mmol) of α,ω-diamine and ester **(1)** was left at ambient temperature over a period of 7 days. Then the solvent was evaporated and the residue was chromatographed on a silica gel column using 0.5-10% mixtures of methanol in methylene chloride.

3,12,18-Triazabicyclo[12.3.1]octadeca-1(17),14(18),15-triene-2,13-dione (7): This dilactam was prepared as a colorless crystals in 22.7 % yield. mp 158-160°C (CH_2Cl_2); IR (KBr): ν = 3371, 3332, 2933, 2875, 1693, 1656, 1527, 1447 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 8.4-8.0 (m, 3H), 7.98 (br t, 2H), 3.49 (m, 4H), 1.9-1.5 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 163.1, 148.5, 139.4, 123.8, 39.4, 28.4, 27.3, 25.6; HREI: calcd for $C_{15}H_{21}N_3O_2$ $(M)^+$ 275.1634; found 275.1639; Anal. Calcd for $C_{15}H_{21}N_3O_2$: C, 65.43; H, 7.69; N, 15.26. Found: C, 65.42; H, 7.78; N, 15.22.

3,14,20-Triazabicyclo[14.3.1]eicosa-1(19),16(20),17-triene-2,15 -dione (8): This dilactam was prepared as a colorless crystals in 16.3 % yield. mp 168-170°C (CH_2Cl_2); IR (KBr): ν = 3368, 3305, 2927, 2852, 1681, 1655, 1542, 1447 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 8.34 (d, *J* = 7.8 Hz, 2H), 8.1-7.9 (m, 1H), 7.80 (br t, 2H), 3.6-3.5 (m, 4H), 1.8-1.3 (m, 16H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 163.3, 148.8, 139.1, 124.6, 38.6, 27.6, 27.5, 26.9, 25.9; HREI: calcd for $C_{17}H_{25}N_3O_2$ $(M)^+$ 303.1947; found 303.1942.

3,6,22-Triazabicyclo[16.3.1]docosa-1(21),17(22),19-triene-2,17-dione (9): This dilactam was prepared as a colorless crystals in 12.1 % yield. mp 247-250°C (CH_2Cl_2); ^1H NMR (500 MHz, CD_3CN): δ = 8.36 (br s, 2H), 8.24 (d, J = 7.5 Hz, 2H), 8.05 (t, J = 7.5Hz, 1H), 3.5-3.4 (m, 4H), 1.7-1.6 (m, 4H), 1.5-1.2 (m, 16H); ^{13}C NMR (125 MHz, CD_3CN): δ = 164.2, 149.8, 139.8, 125.0, 39.7, 29.4, 28.9, 28.5, 28.0, 26.8; HREI: calcd for $C_{19}H_{29}N_3O_2$ $(M)^+$ 331.2260; found 331.2258; Anal. Calcd for $C_{19}H_{29}N_3O_2$: C, 68.85; H, 8.82; N, 12.68. Found: C, 68.91; H, 9.02; N, 12.68.

3,8,16,21,27,28-Hexaazatricyclo[33.3.1.1.^{10,14}]octacosa-1(26),10,12,14(28),23(27),24-hexaene-2,9,15,22-tetraone (10) This tetralactam was prepared as a colorless crystals (which partially precipitate directly from reaction mixture) in 10.8 % yield. mp 340-350 °C (sublime); ^1H NMR (200 MHz, CF_3COOD): δ = 8.51 (d, J = 7.8 Hz, 4H), 8.34 (t, J = 7.8 Hz, 2H), 3.8-3.4 (m, 4H), 1.9-1.4 (m, 4H); ^{13}C NMR (50 MHz, CF_3COOD): δ = 167.7, 149.2, 143.7, 128.6, 42.9, 29.4.

3,10,18,25,31,31-Hexaazatricyclo[25.3.1.1^{12,16}]dotriaconta-1(30),12,14,16(32),27(31),28-hexaene-2,11,17,26-tetraone (11): This tetralactam was prepared as a colorless crystals (which partially precipitate directly from reaction mixture) in 11.1 % yield. mp 340-350°C (sublime); IR (KBr): ν = 3325, 3283, 2931, 286, 1679, 1660, 1652, 1448 cm^{-1}; ^{1}H NMR (200 MHz, CF_3COOH): δ = 8.41 (d, J = 8 Hz, 4H), 8.30 (t, J = 8 Hz, 2H), 3.8-3.4 (m, 4H), 1.9-1.4 (m, 16H); ^{13}C NMR (50 MHz, CF_3COOH): δ = 166.9, 148.8, 144.9, 128.7, 42.9, 30.7, 28.3; HREI: calcd for $C_{26}H_{34}N_6O_4$ $(M)^+$ 494.2642; found 494.2637.

3,12,20,29,35,36-Hexaazatricyclo[29.3.1.1^{14,18}]hexatriaconta-1(34),14,16,18(36),31(35),32-hexaene-2,13,19,30-tetraone (12): This tetralactam was prepared as a colorless crystals (which partially precipitate directly from reaction mixture) in 12.1 % yield. mp 340-350°C (sublime); IR (KBr): ν = 3330, 3287, 2917, 2850, 1679, 1536, 1447) cm^{-1}; ^{1}H NMR (200 MHz, CF_3COOH): δ = 8.35-8.25 (m, 4H), 8.25-8.18 (m, 2H); 3.38 (br s, 8H), 1.49 (br s, 8H), 1.18 (br s, 16H); ^{13}C NMR (50 MHz, CF_3COOH): δ = 165.6, 147.9, 146.0, 128.7, 43.2, 30.7, 30.5, 28.4; HREI: calcd for $C_{30}H_{42}N_6O_4$ $(M)^+$ 550.3268; found 550.3269; Anal. Calcd for $C_{30}H_{42}N_6O_4$: C, 65.43; H, 7.69; N, 15.26. Found: C, 64.99; H, 7.94; N, 15.06.

3,14,22,33,39,40-Hexaazatricyclo[33.3.1.1^{16,20}]tetraconta-1(38),16,18,20(40),35(39),36-hexaene-2,15,21,34-tetraone (13): This tetralactam was prepared as a colorless crystals (which partially precipitate directly from reaction mixture) in 9.8 % yield. mp 320-324°C; IR (KBr): ν = 3330, 3287, 2917, 2850, 1679, 1536, 1447 cm^{-1}; ^{1}H NMR (200 MHz, CF_3COOH): δ = 8.40 (d, J = 7.5 Hz, 4H), 8.31 (t, J = 7.5 Hz, 2H), 3.6-3.4 (m, 8H), 1.9-1.2 (m, 32H); ^{13}C NMR (50 MHz, CF_3COOH): δ = 166.1, 148.3, 145.5, 128.6, 43.3, 31.2, 31.0, 30.6, 28.7; HREI: calcd for $C_{34}H_{50}N_6O_4$ $(M)^+$ 606.3894; found 606.3892; Anal. Calcd for $C_{34}H_{50}N_6O_4$: C, 67.30; H, 8.31; N, 13.85. Found: C, 66.99; H, 8.33; N, 13.60.

3,16,24,37,43,44-Hexaazatricyclo[37.3.1.1^{18,22}]tetratetraconta-1(42),18,20,22(44),39(43),40-hexaene-2,17,23,38-tetraone (14): This tetralactam was prepared as a colorless crystals (which partially precipitate directly from reaction mixture) in 9.4 % yield. mp 305-309°C; IR (KBr): ν = 3456, 3329, 3285, 2925, 2849, 1679, 1538 cm^{-1}; ^{1}H NMR (200 MHz, CF_3COOH): δ = 8.4-8.2 (m, 6H), 3.6-3.4 (m, 8H), 1.6-1.0 (m, 40H); ^{13}C NMR (50 MHz, CF_3COOH): δ = 165.6, 147.9, 146.1, 128.6, 43.4, 31.3, 31.3, 31.0, 30.5, 28.6; HRMS calcd for $C_{38}H_{58}N_6O_4$ $(M)^+$ 662.4520; found 662.4515; Anal. Calcd for $C_{38}H_{58}N_6O_4$: C, 68.85; H, 8.82; N, 12.68. Found: C, 68.64; H, 8.72; N, 12.52.

X-Ray analyses of (10) and (11). Crystals suitable for X-Ray analysis were obtained from the reaction mixtures. X-Ray single-crystal diffraction experiments were carried out on Enraf-Nonius CAD4 diffractometer (CAD4-EXPRESS program[23]) using CuK_α radiation (1.54178 Å) The program used to solve and refine was SHELX97[24]. All non-H atoms were refined with anisotropic displacement parameters. H atoms were refined in isotropic approximation. Amide H atoms were located from Fourier map and refined freely.

$C_{22}H_{26}N_6O_4$ (**10**), M=438.49, monoclinic, *a*=11.5684(4), *b*=9.4780(5), *c*=9.8725(8)Å, β=97.280(5)°, V=1073.7(1)Å^{-3}, space group $P2_1/c$, *Z*=2, D_x=1.356 Mg m^{-3}, μ(Cu-K_α)=0.791 mm^{-1}, 1419 reflections measured, 1334 unique reflections (R_{int}=0.0331), which were used in all calculations. Data/restraints/ parameters 1332/0/154. The final R1=0.0405 (all data), *s*=1.084. Residual electron density 0.147 and -0.190e Å^{-3}.

$C_{26}H_{34}N_6O_4$ (**11**), M=494.60, monoclinic, *a*=14.2536(9), *b*=9.4304(9), *c*=9.7507(5)Å, β=100.01(5)°, V=1290.7(1)Å^{-3}, space group $P2_1/c$, *Z*=2, D_x=1.273 Mg m^{-3}, μ(Cu-K_α)=0.715 mm^{-1}, 2365 reflections measured, 2222 unique reflections (R_{int}=0.0287), which were used in all calculations. Data/restraints/ parameters 2222/0/219. The final R1=0.0457 (all data), *s*=1.020. Residual electron density 0.254 and -0.264e Å^{-3}.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

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