Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Two macrocycles of different molecular topology obtained by the same synthetic procedure. Their crystal structures and ligational properties

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To cite this Article Bazzicalupi, Carla , Bencini, Andrea , Bianchi, Antonio , Ciampolini, Mario , Fusi, Vieri , Micheloni, Mauro , Nardi, Nicoletta , Paoli, Paola and Valtancoli, Barbara(1994) 'Two macrocycles of different molecular topology obtained by the same synthetic procedure. Their crystal structures and ligational properties', Supramolecular Chemistry, 3: 4, 279 — 290
To link to this Article: DOI: 10.1080/10610279408034927
URL: http://dx.doi.org/10.1080/10610279408034927

SUPRAMOLECULAR CHEMISTRY, Vol. 3, pp. 279–290
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Two macrocycles of different molecular topology obtained by the same synthetic procedure. Their crystal structures and ligational properties

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(Received August 3, 1993)

The synthesis and characterization of the two macrobicycles 10-methyl-4,15-dioxo-1,7,10-triaza[5.5.5]cycloheptadecane (1) and 27,32-dimethyl-4,10,16,22-tetraoxa-1,7,13,19,27,32-hexaazatricyclo-[17.5.5.5^{7,13}]tetratriacontane (2) is reported. The basicity behaviour in aqueous solution have been studied by potentiometry (25 °C, I = 0.15 mol dm^{-3}) and NMR spectroscopy (^{1}H and ^{13}C). Compound 1 behaves as diprotic base (log K_1 = 11.46(9), log K_2 = 5.40(9)), while compound 2 behaves as a pentaprotic base (log K_1 = 11.1(1), log K_2 = 10.85(9), log K_3 = 4.72(9), log K_4 = 2.76(9), log K_5 = 2.54(9)). NMR experiments indicate most of the stepwise protonation sites. Crystals of [H1][BPh$_4$] are monoclinic, space group $P2_1/n$, with a = 11.532(2), b = 20.538(2), c = 13.974(2) Å, β = 90.32(1)° and Z = 4; final R value of 0.085 (R_w = 0.080) for 1253 unique observed reflections with I > 4σ(I). The structure shows that the molecule adopts a fairly regular square pyramidal shape with N(1), N(2), O(1) and O(2) forming the basal plane and N(3) the vertex. Geometrical considerations indicate the methylated nitrogen N(3) as the protonation site. Crystals of [H$_2$2][BPh$_4$]$_2$ are triclinic, space group $P\bar{1}$, with a = 11.320(2), b = 12.576(3), c = 12.675(6) Å, α = 83.42(3), β = 73.61(2), γ = 75.68(2)° and Z = 1; final R value of 0.086 (R_w = 0.083) for 1058 unique observed reflections with I > 3σ(I). The macrotricycle has a cylindrical molecular shape, where the two bases are constituted by two N_3O macrocycles and the two O(CH$_2$-CH$_2$-)$_2$ chains representing the cylindrical wall.

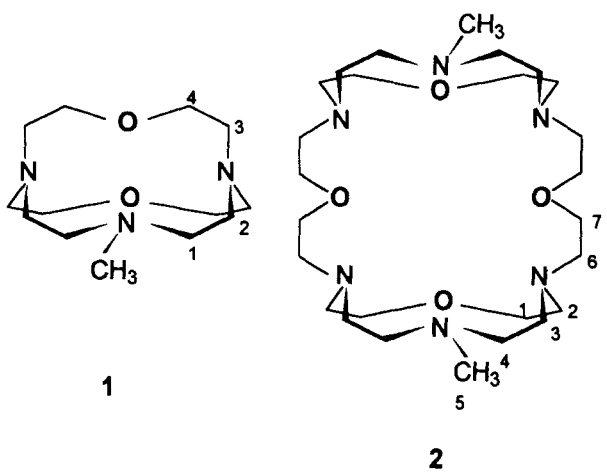

Figure 1 Molecular drawing of compounds **1** and **2**, with atoms labelling used in NMR experiments.

INTRODUCTION

An enormous amount of macrocyclic compounds have been investigated in the last few decades.[1–15] The interest about these compounds spans from fundamental academic research to specific industrial applications. Due to our continuing interest in small macrobicyclic cages behaving as 'proton sponge'[16] or able to selectively encapsulate Li^+ ion,[17–27] we report on the two new macrocyclic compounds: 10-methyl-4,15-dioxo-1,7,10-triaza[5.5.5]cycloheptadecane (**1**) and 27,32-dimethyl-4,10,16,22-tetraoxa-1,7,13,19,-27,32-hexaazatricyclo[17.5.5.5^{7,13}]tetratriacontane (**2**), depicted in Fig 1.

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EXPERIMENTAL SECTION

General methods

All melting points are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded at 200 and 50 MHz.

Dioxane was used as standard in ^{13}C NMR (δ = 67.4 ppm). In ^{1}H spectra in D_2O peak positions are reported relative to HOD at 4.75 ppm. When necessary pH was calculated as pH = pD − 0.40.[28]

Materials

Unless specified otherwise, reagent-grade reactants and solvents were used as received from chemical suppliers. Benzene was distilled over P_4O_{10}. Anhydrous DMF was obtained by distillation over CaH_2 of commercial DMF under reduced pressure and kept over molecular sieves.

The overall synthetic pathway for compounds **1** and **2** is reported in Fig 2.

4,10-Bis(p-tolylsulfonyl)-1-oxa-7-methyl-4,7,10-triazacyclododecane (5·Ts_2)

1,7-Bis(p-tolylsulfonyl)-4-methyl-1,4,7-triazaheptane (**3**) was synthesized as reported in Ref. 29. 1,7-bis(p-tolylsulfonyl)-1,4,7-trioxaheptane (**4**) was purchased

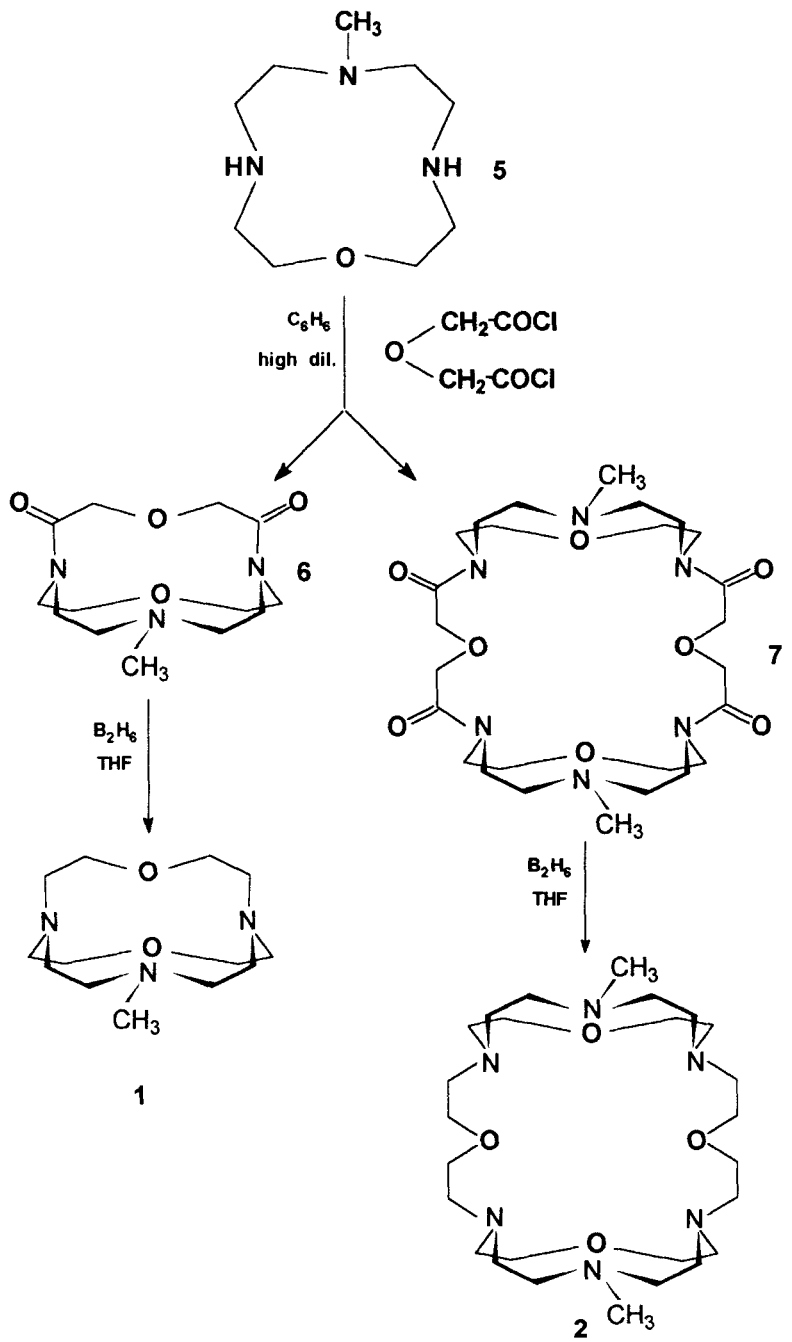

Figure 2 Reaction pathway for the synthesis of **1** and **2**.

from Aldrich Co. The disodium salt of **3** was obtained by dropwise adding 11.5 g (0.5 mol) of Na dissolved in 300 cm^3 of dry EtOH to 200 cm^3 of EtOH containing 106.25 g (0.25 mol) of **3**. After the addition was completed, the mixture was stirred and refluxed for 20 min. The white precipitate was dried under vacuum at 105 °C and used in the next step. The disodium salt was dissolved in DMF (1800 cm^3) at 110 °C. To this solution was added, over a period of 1 h, 300 cm^3 of DMF containing 103.6 g (0.25 mol) of **4**. After the addition the reaction was continued for 45 min then concentrated to 1/3 of its original volume. The reaction mixture was allowed to cool and then water was added (200 cm^3). The white precipitate was filtered and washed with a DMF/H_2O (1:3) mixture, and recrystallized from EtOH to give the ditosyl derivative of **5** (91 g, 73%) as a white solid with mp 137–138 °C. Anal. Calcd for $C_{23}H_{33}N_3O_5S_2$: C, 55.74; H, 6.71; N, 8.48. Found C, 55.7; H, 6.8; N, 8.7.

The removal of tosyl groups from **5**·Ts_2 was performed by the procedure previously described for other similar compounds.[30] A 25 g sample of the ditosyl derivative of **5** (0.05 mol) yielded 6 g of **5** (64%) as white solid with mp 35–36 °C. Anal. Calcd for $C_9H_{21}N_3O$: C, 57.72; H, 11.30; N, 22.44. Found: C, 57.6; H, 11.3; N, 22.3.

Bicyclic diamides 6 and 7

A 3.74 g (0.02 mol) of **5** and 5.5 cm^3 of triethylamine in 500 cm^3 of dry benzene and 3.4 g (0.02 mol) of 2,2′-oxydiacetyl dichloride in 500 cm^3 of dry benzene were added simultaneously to 1 dm^3 of dry benzene, under stirring, over a period of ca. 7 h at room temperature. The reaction mixture was then filtered and evaporated to dryness on a rotary evaporator. The crude yellowish product obtained was extracted with hot hexane and chromatographed over a Al_2O_3 (basic, 7-230 mesh, activity **II–III**) column with $CHCl_3$. The eluted solution was evaporated under reduced pressure, the colourless oil obtained on fractional crystallization with ethylacetate yielded two white solids: 1.43 g of **1** (25%) with mp 218–219 °C and 1.37 g of **2** (12%). Anal. Calcd for $C_{13}H_{23}N_3O_4$: C, 54.72; H, 8.12; N, 14.72. Found: C, 54.6; H, 8.1; N, 14.6.

1·3HCl and 2·6HCl

A sample of B_2H_6 (100 cm^3 of diborane 1 M in THF) was added dropwise, in a nitrogen atmosphere, to a solution containing 4 g of **6** (0.014 mol) in 50 cm^3 of THF. The addition was performed over a period of 30 min, then the reaction mixture refluxed for 5 h. The solution was then cooled and the excess of diborane was destroyed with water. The solution was evaporated to dryness, the white solid obtained was dissolved in an HCl/H_2O/MeOH mixture (2:3:10) and refluxed for 5 h; the resulting solution was evaporated to dryness and the residue was dissolved in 30 cm^3 of water. The solution was made alkaline by addition of a concentrated NaOH solution and extracted with $CHCl_3$ (5 × 50 cm^3), the combined extracts were dried over Na_2SO_4. The $CHCl_3$ was removed under reduced pressure and the yellowish oil residue was extracted with hexane (3 × 50 cm^3). The solvent was removed and the resulting colourless oil dissolved in 10 cm^3 of EtOH and treated with 2 cm^3 of concentrated HCl, yielded 3.3 g (60%) of **1**·3HCl. Anal. Calcd for $C_{13}H_{30}N_3O_2Cl_3$: C, 42.57; H, 8.25; N, 11.46. Found: C, 42.6; H, 8.2; N, 11.4. The free macrocycle **1** was obtained by treating aqueous solution of **1**·3HCl with NaOH and extracting with $CHCl_3$: ^{13}C NMR ($CDCl_3$) δ 40.7 (C5, 1C), 53.6 (C1, 2C), 54.8 (C3, 4C), 57.3 (C2, 2C), 69.0 (C4, 4C); ^1H NMR spectrum shows a ABC_2 spin system (ν_A = 3.62 ppm, ν_B = 3.57, ν_C = 2.65 ppm, $J_{AB} = -10.5$ Hz, $J_{AC} = J_{BC} = 4.6$ Hz), corresponding respectively to the hydrogens of C4 and C3 and a AA′BB′ subspectrum (ν_A = 2.54 ppm, ν_B = 2.48 ppm, $J_{AA'} = J_{BB'} = -2.2$ Hz, $J_{AB} = J_{A'B'} = 2.6$ Hz, $J_{AB'} = J_{A'B} = 6.7$ Hz) assigned to the hydrogen atom of C1 and C2. The methyl group gives rise to a singlet at 2.20 ppm.

In much the same way as with **6**, the reduction of 4 g (0.007 mol) of **7** yielded 6.3 (58%) of **2**·6HCl·H_2O Anal. Calcd for $C_{26}H_{62}N_6O_5Cl_6$: C, 41.56; H, 8.31; N, 11.18. Found: C, 41.7; H, 8.3; N, 11.1.

Determination of pK_a values

Potentiometric titrations were carried out at constant ionic strength (0.15 M NaCl or Et_4NCl). Standardized CO_2-free solutions of NaOH were prepared according to the literature procedure.[31] The computer program SUPERQUAD[32] was used to process the potentiometric data and calculate the protonation constants. Two titrations curves have been used for each compounds: 67 data points for **1** and 80 data points for **2**.

X-ray structure analysis

Analyses on single crystals of [H**1**][BPh_4] and [H_2**2**][BPh_4]$_2$ were carried out with an Enraf-Nonius CAD4 X-ray diffractometer; a summary of the crystallographic data of both compounds is reported in Table 1. Colourless crystals of approximate dimensions 0.3 × 0.2 × 0.1 mm and 0.2 × 0.1 × 0.1 mm of [H**1**][BPh_4] and [H_2**2**][BPh_4]$_2$ respectively, were mounted on the diffractometer and used for data collection at room temperature with graphite-monochromatized Mo-Kα radiation. Cell parameters of both compounds were determined by least-squares refinement of diffractometer setting angles for 25 carefully centred reflections. The intensities of two

Table 1 Crystallographic data for [H1][BPh_4] and [$H_2$2][BPh_4]$_2$

	[H1][BPh$_4$]	*[H$_2$2][BPh$_4$]$_2$*
Formula	$C_{37}H_{48}BN_3O_2$	$C_{74}H_{96}B_2N_6O_4$
M	577.61	1155.22
Space group	$P2_1/n$	$P\bar{1}$
a/Å	11.532(2)	11.320(2)
b/Å	20.538(2)	12.576(3)
c/Å	13.974(2)	12.675(6)
α/deg	90	83.42(3)
β/deg	90.32(1)	73.61(2)
γ/deg	90	75.68(2)
U/Å^3	3309.6(8)	1675(1)
Z	4	1
D_c/g cm^{-3}	1.16	1.14
F(000)	1248	624
μ(Mo-Kα)cm^{-1}	0.66	0.65
T	ambient	ambient
Scan rate/deg min^{-1}	4.1	variable
Scan mode	θ–2θ	θ–2θ
Scan width/deg	0.7 + 0.35 tgθ	0.8 + 0.35 tgθ
2θ range/deg	5–50	5–40
No of reflections collected	5876	3292
Unique obs. reflections	1253	1058
	[$I > 4.0\,\sigma(I)$]	[$I > 3.0\,\sigma(I)$]
Refined parameters	220	150
R[a]	0.085	0.086
R_w[b]	0.080	0.083

[a] $R = \Sigma \cdot |F_o| - |F_c| / \Sigma |F_o|$.
[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$.

standard reflections were monitored periodically during data collection. Intensities data were corrected for Lorentz and polarization effects. Once the structures were solved, an absorption correction was applied by using the Walker and Stuart method.[33] The structures were solved by direct methods using the SIR88 program,[34] for [H1][BPh_4], and the MULTAN80 program,[35] for [$H_2$2][BPh_4]$_2$, and subsequently refined by the full-matrix least-squares technique. In both cases the function minimized was $\Sigma w(|Fo| - |Fc|)^2$, with $w = a/[\sigma^2(F) + 0.0002\ F^2]$ and $w = a/[\sigma^2(F) + 0.0003\ F^2]$, where a is an adjustable parameter, for [H1][BPh_4] and [$H_2$2][BPh_4]$_2$ respectively.

[H1][BPh_4]

The crystals of the compound belong to the monoclinic family, space group $P2_1/n$, $Z = 4$, with $a = 11.532(2)$, $b = 20.538(2)$, $c = 13.974(2)$ Å, $\beta = 90.32(1)°$. All the hydrogen atoms, bound to the carbon atoms of the ligand, were introduced in calculated positions and their coordinates refined in agreement with those of the linked atoms, with a temperature factor U of 0.05 Å^2. Anisotropic thermal parameters were used for all the other non-hydrogen atoms of the macrobicycle and for the boron atoms of the counterion. The phenyl groups of the anion were refined like rigid groups using isotropic thermal parameters for the carbon atoms and fixing those of the hydrogen atoms at U = 0.05 Å^2. The ΔF map did not allow us to localize the acidic hydrogen atom of the [H1]$^+$ cation. The final agreement factors were R = 0.085 and Rw = 0.080. Table 2 shows the final coordinates with estimated standard deviations.

[$H_2$2][BPh_4]$_2$

The compound crystallizes in the triclinic crystal family, space group $P\bar{1}$, $Z = 1$, with $a = 11.320(2)$, $b = 12.576(3)$, $c = 12.675(6)$ Å, $\alpha = 83.42(3)$, $\beta = 73.61(2)$,

Table 2 Atomic coordinates ($\times 10^4$) of [H1][BPh_4], with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
N(1)	5367(9)	820(6)	7988(9)
C(1)	4893(11)	387(7)	7255(11)
C(2)	5098(12)	644(7)	6267(11)
O(1)	6281(9)	818(4)	6074(6)
C(3)	7053(13)	298(7)	5999(10)
C(4)	8268(13)	559(7)	6207(9)
N(2)	8356(9)	757(6)	7205(8)
C(5)	8801(10)	239(7)	7838(11)
C(6)	8598(12)	384(7)	8884(10)
O(2)	7456(9)	601(4)	9092(6)
C(7)	6573(13)	124(7)	8988(10)
C(8)	5430(11)	464(7)	8914(10)
C(9)	4918(11)	1471(7)	8038(10)
C(10)	5799(15)	1940(7)	7560(15)
N(3)	6951(11)	1750(5)	7816(9)
C(11)	7890(15)	1907(8)	7156(12)
C(12)	8874(11)	1389(8)	7351(11)
C(13)	7247(14)	2026(8)	8754(13)
B	7923(12)	1233(7)	2579(10)
C(15)	8154(5)	2069(4)	4009(6)
C(16)	8783(5)	2358(4)	4751(6)
C(17)	9875(5)	2118(4)	5000(6)
C(18)	10339(5)	1589(4)	4507(6)
C(19)	9711(5)	1300(4)	3765(6)
C(14)	8618(5)	1539(4)	3516(6)
C(21)	5903(7)	1274(3)	3465(5)
C(22)	4694(7)	1296(3)	3490(5)
C(23)	4061(7)	1364(3)	2643(5)
C(24)	4636(7)	1409(3)	1770(5)
C(25)	5845(7)	1388(3)	1745(5)
C(20)	6478(7)	1320(3)	2592(5)
C(27)	8224(6)	27(4)	3300(4)
C(28)	8254(6)	−649(4)	3211(4)
C(29)	8146(6)	−937(4)	2310(4)
C(30)	8008(6)	−548(4)	1499(4)
C(31)	7978(6)	128(4)	1588(4)
C(26)	8086(6)	416(4)	2489(4)
C(33)	8127(5)	2242(4)	1394(5)
C(34)	8706(5)	2609(4)	705(5)
C(35)	9704(5)	2362(4)	277(5)
C(36)	10122(5)	1750(4)	538(5)
C(37)	9543(5)	1384(4)	1227(5)
C(32)	8545(5)	1630(4)	1655(5)

Table 3 Atomic coordinates ($\times 10^4$) of $[H_2\mathbf{2}][BPh_4]_2$ with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
N(1)	189(10)	2839(9)	2276(9)
C(1)	−452(12)	2822(12)	1429(12)
C(2)	−1860(14)	2883(13)	1998(12)
N(2)	−2005(10)	2131(8)	2984(9)
C(3)	−3335(13)	2474(12)	3718(12)
C(4)	−3541(15)	1719(13)	4741(13)
N(3)	−2549(12)	1672(9)	5297(9)
C(5)	−2396(15)	666(14)	6017(14)
C(6)	−1332(17)	371(15)	6428(14)
O(1)	1049(10)	778(8)	3222(9)
C(7)	1702(14)	1027(11)	2130(13)
C(8)	1518(13)	2262(11)	1996(12)
C(9)	−10(14)	3934(12)	2659(12)
C(10)	−275(14)	3888(12)	3891(12)
O(2)	−1376(8)	3464(7)	4365(8)
C(11)	−1562(14)	3162(12)	5519(13)
C(12)	−2690(13)	2672(12)	5886(12)
C(13)	−1666(13)	982(12)	2664(12)
B(1)	2539(14)	2261(12)	7813(13)
C(21)	2498(8)	2267(7)	5777(9)
C(22)	2725(8)	2659(7)	4680(9)
C(23)	3282(8)	3557(7)	4347(9)
C(24)	3612(8)	4064(7)	5110(9)
C(25)	3385(8)	3672(7)	6207(9)
C(20)	2828(8)	2774(7)	6540(9)
C(27)	4166(9)	423(8)	7028(7)
C(28)	4889(9)	−634(8)	7150(7)
C(29)	4881(9)	−1112(8)	8199(7)
C(30)	4151(9)	−534(8)	9128(7)
C(31)	3428(9)	523(8)	9006(7)
C(26)	3435(9)	1001(8)	7956(7)
C(33)	4083(8)	2927(7)	8680(8)
C(34)	4389(8)	3616(7)	9299(8)
C(35)	3451(8)	4461(7)	9857(8)
C(36)	2208(8)	4616(7)	9796(8)
C(37)	1903(8)	3926(7)	9177(8)
C(32)	2840(8)	3081(7)	8619(8)
C(39)	557(8)	1358(6)	8886(7)
C(40)	−732(8)	1375(6)	9222(7)
C(41)	−1594(8)	2259(6)	8894(7)
C(42)	−1168(8)	3125(6)	8231(7)
C(43)	121(8)	3107(6)	7896(7)
C(38)	984(8)	2224(6)	8224(7)

$\gamma = 75.68(2)°$. The $[H_2\mathbf{2}]^{2+}$ cation is localized around the crystallographic inversion centre, so only the non-hydrogen atoms belonging to the asymmetric unit of the cation and one of the counterions had been found by the direct method. Anisotropic temperature factors were used for the nitrogen and the oxygen atoms, while isotropic thermal parameters were used with all the carbon and the boron atoms. The phenyl groups were refined like rigid groups. The hydrogen atoms were introduced in calculated position, with an overall temperature factor of 0.05 Å^2, and their positional parameters varied accordingly to those of the linked carbon atoms. The difference Fourier map did not show the position of the acidic hydrogen atom in the asymmetric part of the $[H_2\mathbf{2}]^{2+}$ cation. The convergence factors were R = 0.086 and Rw = 0.083. The final atomic coordinates are reported in Table 3. All calculations, carried out on an IBM PS/2 computer model 80, were performed with the SHELX-76[36] set of programs which use the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all the atoms from the International Table for X-ray Crystallography.[37]

The molecular plots were produced by means of the ORTEP program.[38]

RESULTS AND DISCUSSION

Solution studies

Compound **1** behaves as a diprotic base in the employed experimental conditions, although the triprotonated species $[H_3\mathbf{1}]^{3+}$ can be isolated in strong acidic condition as the solid **1**·3HCl (see experimental part). Compound **1** is a relatively strong base in the first protonation step ($\log K_1 = 11.46(9)$) and is a weak base in the second protonation step ($\log K_2 = 5.40(9)$). The sharp decrease in basicity, six log units, going from the first to the second protonation step indicates a rather strong repulsion between the two positive charges forced by the molecular topology to stay close each other. Compound **2** behaves, at most, as a pentaprotic base: $\log K_1 = 11.1(1)$, $\log K_2 = 10.85(9)$, $\log K_3 = 4.72(9)$, $\log K_4 = 2.76(9)$, $\log K_5 = 2.54(9)$. It can be noted that the first two protonation constants are rather similar to each other and also comparable with the first basicity constant of **1**. The molecular topology of **2**, with two identical subunits, separated by a rather long $(\text{-}CH_2\text{-}CH_2)_2\text{-}O$ chain, can explain such a protonation behaviour. Very likely the first two protons localize in different subunits, which are able to provide similar chemical environment and feel each other very little. Only in the third step of protonation two protons must stay in the same subunit, thus experiencing charge repulsion, and explaining the marked reduction in basicity going from second to third protonation step. The latter situation is very similar to that found for **1** between the first and second protonation step.

Neither compounds **1** nor **2** behave as proton sponges,[39,40] indicating that the peculiar hydrogen-bond arrangement, responsible for the very high basicity of some aza-cages, is not working here.[17,18,27]

The NMR spectral features of **1** in $CDCl_3$ (see Fig 3a and Fig 4a) indicate a C_{2v} time averaged symmetry. The ^1H and ^{13}C spectra obtained after the addition of 0.5 equivalent of CF_3COOH to a chloroform

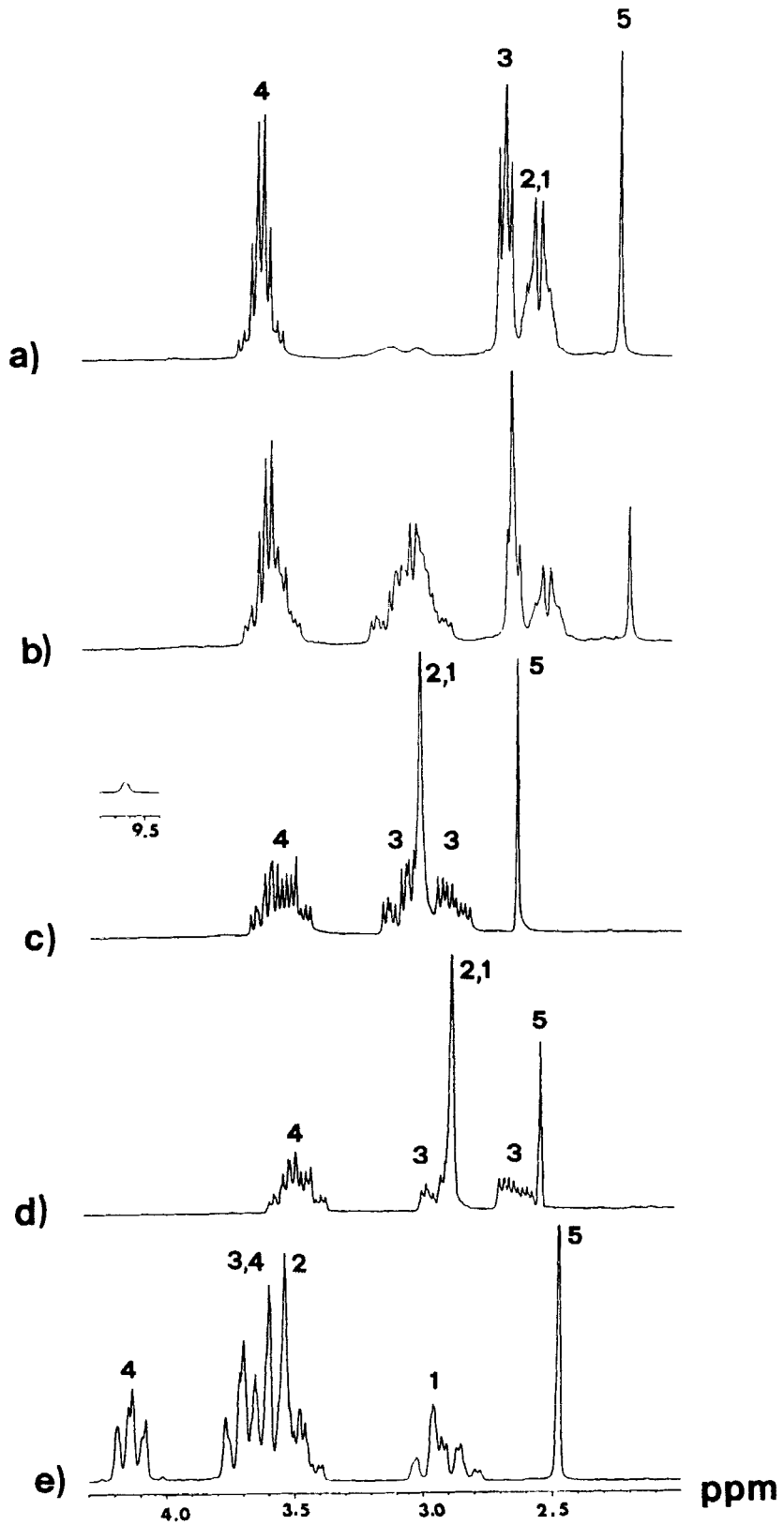

Figure 3 ^1H NMR spectrum of 1 in $CDCl_3$ (a); after addition of 0.5 mol of CF_3COOH (b); after addition of 1 mol of CF_3COOH (c); ^1H NMR spectrum of 1 in D_2O at pH = 10 (d); ^1H NMR spectrum of 1 in D_2O at pH = 2 (E).

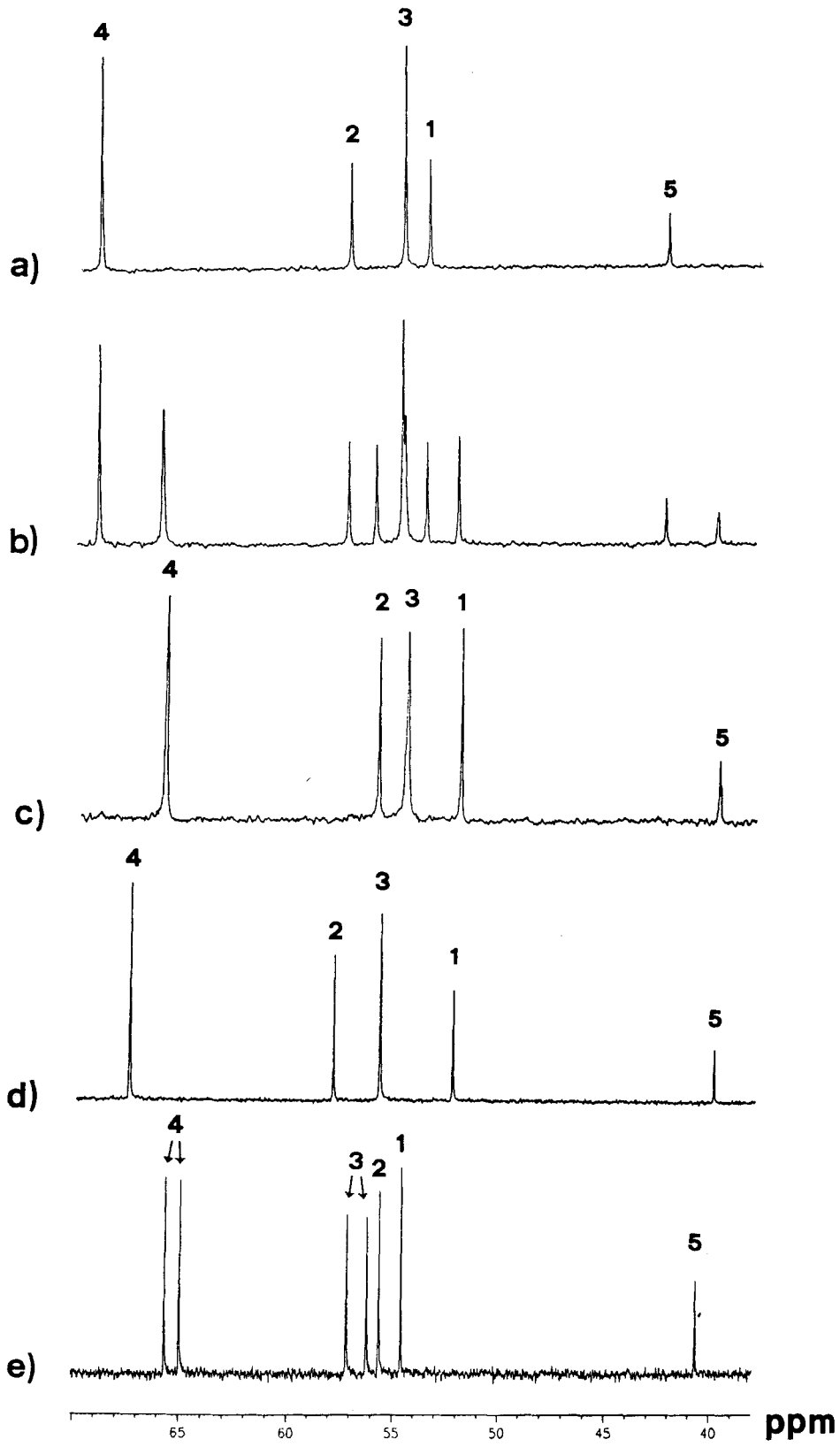

Figure 4 ^{13}C NMR spectrum of **1** in $CDCl_3$ (a); after addition of 0.5 mol of CF_3COOH (b); after addition of 1 mol of CF_3COOH (c); ^{13}C NMR spectrum of **1** in D_2O at pH = 10 (d); ^{13}C NMR spectrum of **1** in D_2O at pH = 2 (E).

solution of **1** show the presence in solution of two species, the free amine and the monoprotonated ligand slowly interchanging on the NMR time scale (see Fig 3b and Fig 4b). The ^1H spectrum displays also a broad signal at 9.6 ppm, that can be assigned to the N-H^+ proton. These spectral features suggest that the N-H^+ proton is located inside the macrobicyclic cavity. Adding 1 equivalent of CF_3COOH the resonances of the free amine disappear and the spectrum exhibits (Fig 3c) a multiplet at 3.66-3.44 ppm (integrating for 8 protons, assigned to the hydrogens of C4), a complex multiplet at 3.16-2.63 ppm (16 protons, corresponding to the hydrogens of C1, C2, and C3), a singlet at 2.62 ppm (the hydrogens of the methyl group) and a signal at 9.6 ppm (integrating 1 proton, due to the ammonium proton). The signals of the hydrogens of C1, C2, C3 and C5 bear a remarkable downfield shift with respect to the spectrum of the unprotonated amine, suggesting that all the nitrogens are involved in the first protonation step, at least in $CDCl_3$ solution. This hypothesis is confirmed by a 2D ^1H-^1H homonuclear correlation, displaying a coupling between the resonance of the N-H^+ proton and both the signal of the methyl group and the multiplet at 3.16-2.63 ppm. With respect to the unprotonated macrocycle, the ^{13}C spectrum of the monoprotonated species shows an upfield shift of the resonances of C1, C2 and C4 (see Fig 4c) in agreement with the β-shift reported for the protonation of the polyamines.[41] Furthermore, these ^1H and ^{13}C spectral features indicate that the C_{2v} time averaged symmetry is also maintained by this monoprotonated species. By addition of H_2O or MeOH to this chloroform solution, the signal at 9.6 ppm does not disappear, indicating a slow exchange on the NMR time scale with the mobile protons of the solvent. Instead, this resonance disappears when D_2O or MeOD are added. The ^{13}C and ^1H NMR spectra of **1** in D_2O (at pH = 10, where the monoprotonated form of the macrobicycle is prevalent) are reported in Figs 4d and 3d, respectively; the assignment of the signals was made by using ^1H-^1H homonuclear and ^1H-^{13}C heteronuclear correlations. In the ^1H spectrum the ethylenic chains bridging the nitrogen atoms give rise to a signal at 2.66 ppm, while the hydrogens of C4 and C3 exhibit an ABCD subspectrum ($\nu_A = 3.53$, $\nu_B = 3.43$, $\nu_C = 2.94$, $\nu_D = 2.65$ ppm, $J_{AB} = 11.2$, $J_{AC} = 3.3$, $J_{AD} = 6.2$, $J_{BC} = 7.6$, $J_{BD} = 4.1$, $J_{CD} = 14.5$ Hz). The ^{13}C spectrum of a D_2O solution at pH = 2, where the $[H_2\mathbf{1}]^{2+}$ species predominates, shows seven signals as reported in Fig 4e. With respect to the $[H\mathbf{1}]^+$ species the loss of the time averaged symmetry is evident: in fact the ethylenic chains connecting the oxygen atoms and the bridgehead nitrogens give rise to four signals, while again two resonances are exhibited by the carbon atoms C1 and C2. In other words, the $[H_2\mathbf{1}]^{2+}$ form loses the C_2 axis together with the symmetry plane through the three nitrogens atom. The plane through the two oxygens and the nitrogen atom bearing the methyl group is maintained, originating a C_S symmetry, averaged on the NMR time scale. This behaviour can be explained taking into account the stiffening of the

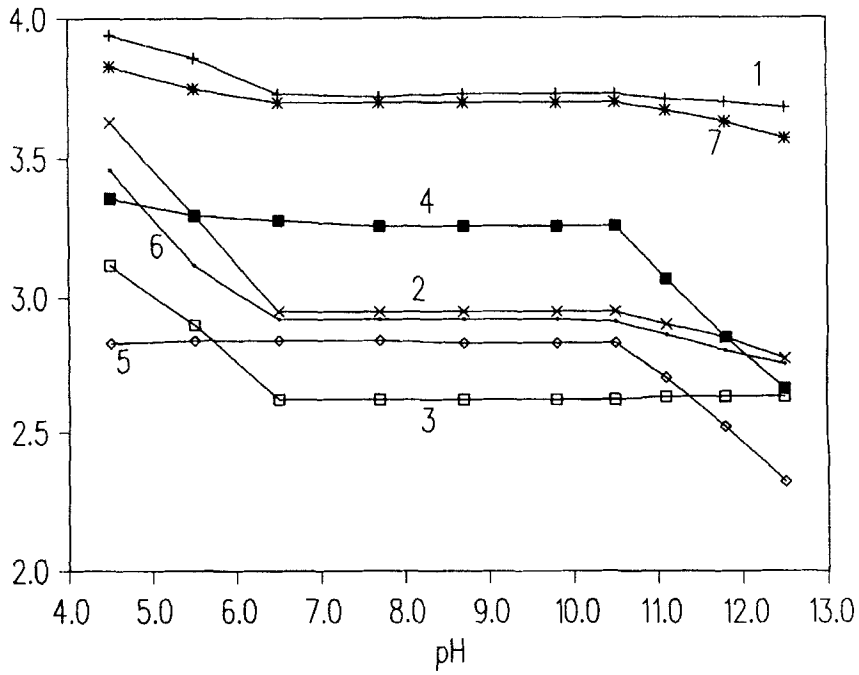

Figure 5 Experimental ^1H NMR chemical shifts of **2** as a function of pH. Labels refer to the carbon atoms as reported in Fig 1.

structure, due to the increased positive charge in the $[H_2\mathbf{1}]^{2+}$ species. The ^1H spectrum recorded at pH = 2 displays a complex pattern of signals, which has been assigned (see Fig 3e). With respect to the $[H\mathbf{1}]^+$ spectrum, the resonances of the hydrogens of C2, C3 and C3', in α-position with respect to the bridgehead nitrogens, experience a remarkable downfield shift, while the hydrogen atoms of the methyl group as well as those of C1 do not shift appreciably. This suggests that the second protonation step involves mainly the bridgehead nitrogen atoms. The ^{13}C spectrum at this pH, in which the resonances of C1 and C4, in β-position with respect to the bridgehead nitrogens, bear an upfield shift (ca. 3 ppm), supports this hypothesis.

The ^{13}C NMR spectrum of a D_2O solution of **2** at pH = 12.5, where the unprotonated molecule is prevalent, shows seven peaks at 72.0, 69.5 (assigned to C1 and C7), 57.4, 55.2 (C2 and C6) 50.5, 50.0 (C3 and C4) and 43.6 ppm (C5). The ^1H spectrum at this pH displays several multiplets at 3.68-3.61 and 3.60-3.55 (each integrating 8 protons, assigned to the hydrogens of C1 and C7), at 2.89-2.83 (16 protons, corresponding to the hydrogens of C3 and C4), at 2.78-2.73 (16 protons, due to the hydrogens of C2 and C6) and a sharp singlet at 2.32 ppm (6 protons, assigned to the hydrogens of the methyl group C5). In order to get further information on the protonation mechanism of such a macrocyclic polyamine, ^1H NMR spectra at different pH valued were recorded. The ^1H NMR chemical shift as a function of pH are reported in Fig 5. In the pH range 13-10.5 the signals of the hydrogens of C4 as well as those of the methyl group C5 bear a remarkable downfield shift, while the other resonances do not shift appreciably. This suggests that the first two protonation steps involve mainly the nitrogen atoms bearing the methyl group. In the pH range 10.5-6.5, where the diprotonated $[H_2\mathbf{2}]^{2+}$ species predominates in solution, no resonances bear significative shifts. Instead, in the pH region 6.5-4.5, where the species $[H_3\mathbf{2}]^{3+}$ becomes prevalent, the signals of the hydrogens of C2, C3 and C6 shift downfield remarkably, indicating that the bridgehead nitrogens are involved in the further protonation step. Below pH = 4.5, where the species $[H_4\mathbf{2}]^{4+}$ and $[H_5\mathbf{2}]^{5+}$ are present in solution, the ^1H resonances are much broader, most likely due to the formation of slowly-interchanging, on the NMR time scale, conformers and do not allow a detailed characterization.

Lithium complexes

The ^7Li NMR spectrum of an aqueous solution (pH = 12) of $[Li\mathbf{1}]ClO_4$ shows only one sharp signal at 3.91 ppm, suggesting the presence of a complexed, highly deshielded Li^+ ion. The recorded chemical shift is independent of the solvent; this can be explained assuming that the Li^+ ion is encapsulated inside the macrocyclic cavity.[22,24,25] Furthermore, the ^7Li spectrum of an aqueous solution of $[Li\mathbf{1}]ClO_4$ and LiCl exhibits two sharp peaks, one for the free lithium and one for the coordinated metal ion, indicating a slow exchange between the two species on the NMR time scale. The encapsulation of the Li^+ is confirmed by the ^{13}C NMR spectrum of $[Li\mathbf{1}]^+$ (aqueous solution, pH = 12), that shows seven sharp signal: δ 69.2, 68.6(C4); 57.8(C1); 53.8, 53.3(C3); 52.2(C2); 38.8(C7), indicative of a time averaged C_s symmetry, with the two oxygens, the nitrogen N1 and the lithium atom lying in the symmetry plane. This loss of symmetry, with respect to the free macrocycle **1**, could be ascribed to an increase in the molecular rigidity due to the encapsulation of the Li^+.

The ^7Li NMR spectrum of a solution of $[Li_2\mathbf{2}](BPh_4)_2$ in MeOD exhibits two peaks at 1.92 and 1.85 ppm. This can be due to the presence of two lithium ions complexed by the macrocyclic ligand, but characterized by different coordination environments. Furthermore, the two metal ions slowly interchange each other on the NMR time scale. Addition of an excess of Li^+ to a solution of **2** in MeOD gives rise to a sharp signal, due to solvated lithium, together with the signals above described, suggesting a slow exchange between complexed and free Li^+ ion. A similar behaviour is observed in CD_3CN. No interaction between the macrocycle and this metal ion is detected in aqueous solution (pH = 12).

Crystal structure of $[H\mathbf{1}][BPh_4]$

The crystal structure consists of $[H\mathbf{1}]^+$ cations and $[BPh_4]^-$ anions. Figure 6 reports an ORTEP drawing of the $[H\mathbf{1}]^+$ cation. In Table 4 selected bond distances and angles have been reported. The five donor atoms of $[H\mathbf{1}]^+$ are in the *endo* configuration and lie at the vertices of a fairly regular square pyramid, N1, N2, O1 and O2 forming the basal plane (max. deviation from the least-square plane 0.11(1) Å) and N3 the vertex. The comparison between the present structure with those obtained by structural studies on analogous monoprotonated cages, already reported,[18,22,25,26] could be useful to individuate the protonation site in **1**. In all these compounds two different set of donor atoms can be distinct to which the proton can bound: bridgehead donors (2 atoms) and lateral chain donors (3 atoms). The previous results seem to indicate a correlation between the resulting geometrical arrangement of the five donor atoms and the type of donor atom involved in the protonation. Particularly, when the protonation occurs on one of the donors

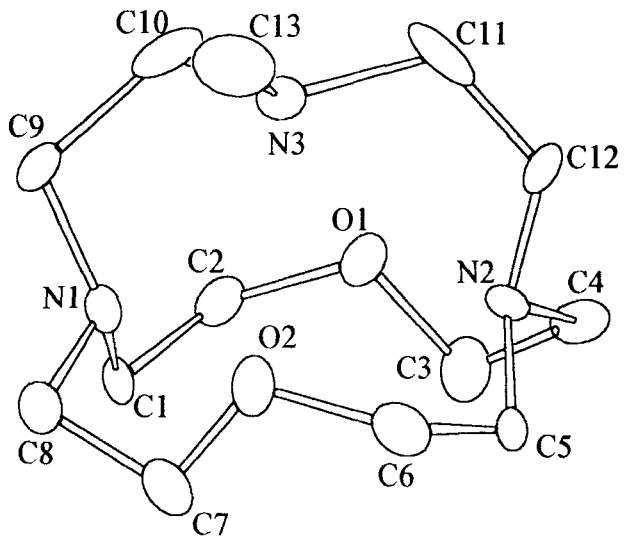

Figure 6 ORTEP drawing of the $[H1]^+$ cation.

Table 4 Selected bond distances/Å and angles/° of $[H1]^+$, with estimated standard deviations in parentheses

N(1)-C(1)	1.46(2)	C(5)-C(6)	1.51(2)
N(1)-C(8)	1.49(2)	C(6)-O(2)	1.42(2)
N(1)-C(9)	1.44(2)	O(2)-C(7)	1.42(2)
C(1)-C(2)	1.50(2)	C(7)-C(8)	1.50(2)
C(2)-O(1)	1.44(2)	C(9)-C(10)	1.55(2)
O(1)-C(3)	1.39(2)	C(10)-N(3)	1.43(2)
C(3)-C(4)	1.53(2)	N(3)-C(11)	1.46(2)
C(4)-N(2)	1.46(2)	N(3)-C(13)	1.47(2)
N(2)-C(5)	1.47(2)	C(11)-C(12)	1.58(2)
N(2)-C(12)	1.44(2)		
C(8)-N(1)-C(9)	116(1)	C(5)-C(6)-O(2)	114(1)
C(1)-N(1)-C(9)	118(1)	C(6)-O(2)-C(7)	115(1)
C(1)-N(1)-C(8)	109(1)	O(2)-C(7)-C(8)	108(1)
N(1)-C(1)-C(2)	112(1)	N(1)-C(8)-C(7)	109(1)
C(1)-C(2)-O(1)	115(1)	N(1)-C(9)-C(10)	109(1)
C(2)-O(1)-C(3)	116(1)	C(9)-C(10)-N(3)	109(1)
O(1)-C(3)-C(4)	108(1)	C(10)-N(3)-C(13)	109(1)
C(3)-C(4)-N(2)	110(1)	C(10)-N(3)-C(11)	118(1)
C(4)-N(2)-C(12)	114(1)	C(11)-N(3)-C(13)	108(1)
C(4)-N(2)-C(5)	113(1)	N(3)-C(11)-C(12)	106(1)
C(5)-N(2)-C(12)	115(1)	N(2)-C(12)-C(11)	107(1)
N(2)-C(5)-C(6)	113(1)		

located on lateral chains the resulting geometrical arrangement of the donor atoms is a square pyramid, where the protonated atom occupies the apical position.[18,22] Trigonal bipyramidal is the donor atoms disposition when the protonatoon interests one of the bridgehead nitrogen atoms, both of them being in axial positions.[25,26] In both cases the resulting geometry is that allowing the shortest distances between the protonated atom and the remaining donors, and thus the strongest hydrogen bonds. It is noteworthy that the acidic hydrogen was experimentally found from the X-ray analysis in all the monoprotonated species, except the present one, having a square pyramidal geometry for the donor atoms, while the Fourier difference map did not allow us to localize the hydrogen in structures with a trigonal bipyramidal arrangement. Perhaps this happens because in the trigonal bipyramidal geometry there are two equivalent axial positions which can share hydrogen atom, making more difficult its X-ray localization.

As a result of the above discussion, in spite of the impossibility to '*see*' the acidic hydrogen atom by X-ray analysis in the case of $[H1]^+$, the square pyramidal geometry of the five donor atoms suggests that the protonation site is the methylated nitrogen atom N3, which lies on the apex of the pyramid. This allows a hydrogen bonds network as can be provided by the distances involving N3 and the remaining donor atoms: N3...N1 2.66(2), N3...O1 3.19(2), N3...N2 2.74(2), N3...O2 3.01(1) Å.

Crystal structure of $[H_2 2][BPh_4]_2$

The structure is made up by discrete $[H_2 2]^{2+}$ cations and $[BPh_4]^-$ anions. Figure 7 shows an ORTEP drawing of the $[H_2 2]^{2+}$ cation with the atom labelling. Selected bond lengths and angles are reported in Table 5. The macrotricycle has a cylindrical molecular shape, where the two bases are constituted by two N_3O

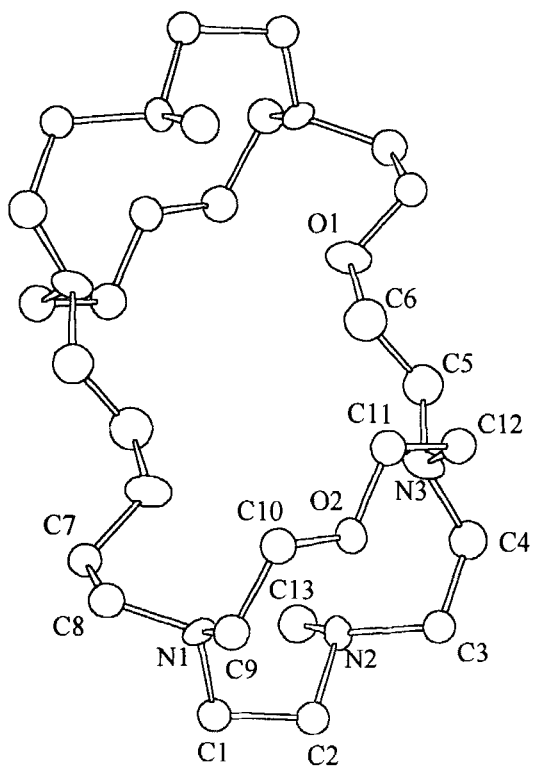

Figure 7 ORTEP drawing of the $[H_2 2]^{2+}$ cation.

Table 5 Selected bond distances/Å and angles/° of $[H_2\mathbf{2}]^{2+}$, with estimated standard deviations in parentheses

N(1)-C(1)	1.46(2)	N(3)-C(12)	1.49(2)
N(1)-C(8)	1.46(2)	C(5)-C(6)	1.40(3)
N(1)-C(9)	1.46(2)	C(6)-O(1)	1.45(2)
C(1)-C(2)	1.54(2)	O(1)-C(7)′	1.41(2)
C(2)-N(2)	1.47(2)	C(7)-C(8)	1.51(2)
N(2)-C(13)	1.52(2)	C(9)-C(10)	1.50(2)
C(3)-C(4)	1.52(2)	O(2)-C(11)	1.44(2)
C(4)-N(3)	1.47(2)	C(11)-C(12)	1.49(2)
N(3)-C(5)	1.48(2)	N(2)-C(3)	1.52(2)
C(8)-N(1)-C(9)	113(1)	C(5)-N(3)-C(12)	112(1)
C(1)-N(1)-C(9)	113(1)	N(3)-C(5)-C(6)	118(2)
C(1)-N(1)-C(8)	114(1)	C(5)-C(6)-O(1)	113(2)
N(1)-C(1)-C(2)	108(1)	C(6)-O(1)-C(7)′	115(1)
C(1)-C(2)-N(2)	110(1)	O(1)′-C(7)-C(8)	107(1)
C(2)-N(2)-C(13)	110(1)	N(1)-C(8)-C(7)	113(1)
C(2)-N(2)-C(3)	109(1)	N(1)-C(9)-C(10)	110(1)
C(3)-N(2)-C(13)	114(1)	C(9)-C(10)-O(2)	109(1)
N(2)-C(3)-C(4)	111(1)	C(10)-O(2)-C(11)	114(1)
C(3)-C(4)-N(3)	109(1)	O(2)-C(11)-C(12)	108(1)
C(4)-N(3)-C(12)	115(1)	N(3)-C(12)-C(11)	113(1)
C(4)-N(3)-C(5)	111(1)		

macrocycles, while the two $O(CH_2\text{-}CH_2\text{-})_2$ chains, which are in trans-gauche conformation, represent the cylindrical wall. The least square line passing through N1′, O1 and N3 forms an angle of 65(3)° with the mean basal plane described by N1, N2, N3 and O2. A very similar overall arrangement of atoms was already found in the analogous ligand 10,22,28,32-tetraoxa-1,4,7,13,16,18-hexaazatricyclo[17.5.5.5]tetratriacontane.[30] In that case, however, the four heteroatoms of the macrocyclic subunit better fitted the mean plane than in the present one. In **2** the distances from this least-square plane span from 0.26(1) to 0.47(1) Å for O2 and N3 respectively, being the two atom pairs N1, N3 and N2, O2 located on opposite sides in respect to their mean plane. Considering that the lone pairs of all the donor atoms point towards the macrotricyclic cavity, we can suppose that the two acidic hydrogens of the $[H_2\mathbf{2}]^{2+}$ cation are encapsulated within the macrotricyclic cavity and involved in intramolecular contacts via hydrogen bonds. In order to make a hypothesis about the protonation sites an analysis of the relative distances between each nitrogen atom and the remaining donor atoms of the asymmetric unit was undertaken. Because the averaged distance of the methylated nitrogen N2 from the donors N1, N3, O1 and O2 resulted the smallest one (3.00 Å vs 3.22 Å for N1 and 3.60 Å for N3) we can infer that the two protons are located on N2 and N2′ accordingly to the results of the ^1H and ^{13}C NMR spectra recorded at pH = 2.

ACKNOWLEDGEMENTS

We thank Dr. Palma Mariani for her technical help. We also thank the Italian Ministero dell'Università e della Ricerca Scientifica (MURST) and Progetto Finalizzato of the Italian Research National Council (CNR) for financial support.

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