

## Synthesis and Characterization of the Aza-cage 4-Benzyl-10,15-dimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane (L). Its Proton Transfer Properties and Lithium Complex. The Crystal Structure of the Monoprotonated Salt [HL][BPh<sub>4</sub>]

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The synthesis and characterization of the small, new benzyl aza-cage 4-benzyl-10,15-dimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane (L) are reported. The basicity constants have been determined in aqueous solution by potentiometry (25 °C, [NaCl] 0.15 mol dm<sup>-3</sup>). L behaves as a biprotic base: log  $K_1 = 11.8$ , log  $K_2 = 8.3$ . The crystal structure of the monoprotonated salt [HL][BPh<sub>4</sub>] has been determined by single-crystal X-ray analysis. The compound crystallizes in an orthorhombic unit cell (space group  $Pc2_1n$ ,  $Z = 4$ ) with lattice constants  $a = 11.400(4)$ ,  $b = 16.893(3)$ ,  $c = 20.537(6)$  Å. Least-squares refinement converged at  $R = 0.078$  ( $R_w = 0.056$ ) for 1290 unique reflections with  $I > 3\sigma(I)$ . The structure of [HL]<sup>+</sup> shows the five nitrogens atoms in an *endo* configuration, indicating that the proton is inside the cage cavity. The cage L encapsulate Li<sup>+</sup> and the complex formation equilibrium for [LiL]<sup>+</sup> has been investigated by potentiometry [lg  $K = 3.0(1)$ ] and <sup>7</sup>Li NMR techniques.

A series of small synthetic aza-cages have been studied by us in the last few years.<sup>1-8</sup> Attention has been paid to the role played by molecular topology, cavity size and the nature of the donor atoms in determining the proton-transfer and metal-complex formation properties of these compounds. Some of these cages have been found to behave as 'fast proton sponges',<sup>1,2,4</sup> while most of them are good lithium binders. To continue this systematic investigation we have synthesized the benzyl derivative 4-benzyl-10,15-dimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane, hereafter abbreviated as L.

### Experimental

**Synthesis of the Aza-cage L.**—The title compound (Fig. 1) was obtained by benzylation of the macrobicyclic 10,15-dimethyl-1,4,7,10-pentaazabicyclo[5.5.5]heptadecane (LI), the preparation of which has been previously reported.<sup>7,8</sup> LI (0.68 g, 2.5 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.27 g, 2.5 mmol) and dried ethanol (25 cm<sup>3</sup>) were introduced into a conical flask. To the resulting suspension a sample of benzyl bromide (0.48 g, 2.8 mmol) was added. The reaction mixture was stirred at room temperature for 1.5 h, then refluxed for 1 h and left to stand overnight. The reaction mixture was filtered and then evaporated under reduced pressure to give a white solid. The crude product was washed twice with hot cyclohexane and recrystallized from ethanol–diethyl ether to yield L·HBr (1 g, 90%) (Found: C, 57.2; H, 8.9; N, 15.7. Calc. for C<sub>21</sub>H<sub>38</sub>BrN<sub>5</sub>: C, 57.26; H, 8.69; N, 15.89%;  $\delta_c(\text{CDCl}_3)$  43.3 (C-*l*), 50.6 (C-*i*), 52.7 (C-*h*), 53.0 (C-*g*), 60.4 (C-*e*), 128.0 (C-*a*), 128.5 (C-*b*), 129.9 (C-*c*), 135.9 (C-*d*). The <sup>1</sup>H NMR spectrum of [HL][Br] in CDCl<sub>3</sub> exhibits a broad signal at 10.1 ppm, integrating for one proton. The <sup>1</sup>H spectrum is completed by signals between 7.1 and 7.3 ppm, integrating for 5 protons, due to aromatic protons on carbons *a*, *b* and *c* (see Fig. 1), a sharp peak at 3.6 ppm attributable to protons on carbon *e*, and two complicated multiplet patterns, each one integrating for twelve protons, between 2.99 and 3.10 ppm and 2.51 and 2.63 ppm respectively. The low-field pattern is

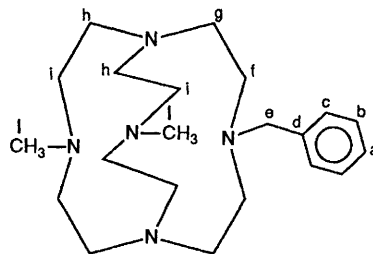


Fig. 1 Cage L drawing with labelling employed in <sup>13</sup>C NMR assignment

attributable to protons on carbons *h* and *g*, while the second pattern is attributable to protons on carbons *i* and *f*.

**Preparation of [LiL][Br].**—A sample of LiOH (0.055 g, 2.3 mmol) was added to a solution of hot methanol (30 cm<sup>3</sup>) containing [HL][Br] (0.1 g, 0.23 mmol). The resulting solution was refluxed for 15 min and then evaporated to dryness with a rotary evaporator. The white product was treated with CHCl<sub>3</sub> (50 cm<sup>3</sup>) and the resulting suspension filtered. The clear solution was concentrated to 10 cm<sup>3</sup>, and on addition of hexane (50 cm<sup>3</sup>) a white precipitate separated (Found: C, 56.4; H, 8.5; N, 15.5. Calc. for C<sub>21</sub>H<sub>37</sub>LiBrN<sub>5</sub>: C, 56.50; H, 8.35; N, 15.69%).

**Reagents.**—NaCl (Merck Suprapur) was used as ionic medium. Standardized CO<sub>2</sub>-free solutions of NaOH were prepared as reported in ref. 9.

**Potentiometric Measurements.**—The potentiometric titrations were carried out with a fully automatic apparatus, as described in ref. 10. Four titration curves (189 data points) were used to determine the protonation constants of L. A batchwise potentiometric procedure was used to determine the stability of the complex [LiL]<sup>+</sup>. This procedure and its application to macrocyclic complexes has been described in ref. 11. Ten aqueous solutions of the ionic medium (NaCl), containing

**Table 1** Crystal data and intensity collection parameters for [HL]-[BPh<sub>4</sub>]

Formula	C <sub>45</sub> H <sub>58</sub> N <sub>5</sub> B
<i>M</i>	679.8
Space group	<i>Pc</i> 2 <sub>1</sub> <i>n</i>
<i>a</i> /Å	11.400(4)
<i>b</i> /Å	16.893(3)
<i>c</i> /Å	20.537(6)
<i>U</i> /Å <sup>3</sup>	3955(2)
<i>Z</i>	4
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.14
<i>F</i> (000)	1472
μ(Mo-Kα)/cm <sup>-1</sup>	0.62
<i>T</i>	Ambient
Scan rate/° min <sup>-1</sup>	4.12
Scan mode	θ - 2θ
Scan width/°	0.80 + 0.35tanθ
2θ range/°	5-50
No. of reflections collected	3909
Unique obs. reflections	
[ <i>I</i> > 3.0σ( <i>I</i> )]	1290
Refined parameters	274
<i>R</i> <sup>a</sup>	0.078
<i>R</i> <sub>w</sub> <sup>b</sup>	0.056

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

different amounts of the complex [LiL][Br] (concentration range 1-3 × 10<sup>-3</sup> mol dm<sup>-3</sup>) and NaOH, were prepared in separate bottles. The solutions were maintained at 25 °C, and the value of pH for each solution was measured periodically until a constant value was reached. The computer program SUPERQUAD<sup>12</sup> was used to process the potentiometric data and calculate the protonation and stability constants.

**NMR Spectroscopy.**—A 300 MHz Varian VXR-300 instrument was used to record the <sup>13</sup>C spectra at an operating frequency of 75.43 MHz and <sup>7</sup>Li spectra at 116.59 MHz.

**Preparation of [HL][BPh<sub>4</sub>].**—Crystals of [HL][BPh<sub>4</sub>] suitable for X-ray analysis were obtained by evaporating at room temperature a solution containing L·HBr (30 mg, 0.068 mmol) in methanol (10 cm<sup>3</sup>), NaBPh<sub>4</sub> (23 mg, 0.068 mmol) and a few drops of butanol.

**X-Ray Structure Analysis.**—Crystal data and other crystallographic details are reported in Table 1. A colourless crystal of approximate dimensions 0.2 × 0.2 × 0.1 mm was mounted on an Enraf-Nonius CAD4 automatic diffractometer and used for data collection at room temperature with graphite-monochromatized Mo-Kα radiation. Cell constants were determined by least-squares fitting of 25 accurately centred reflections. The intensities of three standard reflections were monitored periodically during data collection. Intensity data were corrected for Lorentz and polarization effects. The structure was solved by direct methods of SIR88<sup>13</sup> and subsequently refined by a full-matrix least-squares technique. The function minimized was Σw(|F<sub>o</sub>| - |F<sub>c</sub>|)<sup>2</sup>, with w = a/σ<sup>2</sup>(F), where a is an adjustable parameter. The phenyl rings of the [BPh<sub>4</sub>]<sup>-</sup> anion were processed as regular hexagons. Hydrogen atoms were introduced in calculated positions and not refined, with a temperature factor *U* of 0.05 Å<sup>2</sup>. Anisotropic thermal parameters were used for carbon and nitrogen atoms of the macrobicyclic ligand, the non-hydrogen atoms of the tetraphenylborate anion were treated isotropically. A Fourier difference map performed in the last refinement cycle did not allow us to localize the hydrogen ion of the monoprotonated cation [HL]<sup>+</sup>. All calculations, carried out on an IBM PS/2 computer model 80, were performed with the SHELX-76<sup>14</sup> set of programs which use the analytical approximation for the

**Table 2** Atomic co-ordinates (× 10<sup>4</sup>) of [HL][BPh<sub>4</sub>], with estimated standard deviations in parentheses

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
N(1)	7 386(15)	10 352	925(7)
C(1)	6 178(14)	10 422(16)	1 148(9)
C(2)	5 782(15)	9 672(14)	1 478(8)
N(2)	6 217(12)	8 982(12)	1 161(7)
C(3)	5 740(14)	8 259(14)	1 532(9)
C(4)	6 097(15)	8 227(14)	2 218(10)
N(3)	7 261(14)	8 544(11)	2 340(7)
C(5)	8 192(14)	8 032(12)	2 107(8)
C(6)	9 166(12)	8 530(13)	1 839(8)
N(4)	8 833(10)	8 905(11)	1 227(7)
C(7)	92 34(12)	9 756(12)	1 213(7)
C(8)	8 217(13)	10 257(12)	1 442(8)
C(9)	7 711(17)	10 995(10)	518(8)
C(10)	7 383(16)	8 751(13)	3 017(7)
C(11)	9 279(13)	8 477(13)	667(8)
C(12)	8 324(13)	8 466(13)	137(7)
N(5)	7 400(12)	7 936(11)	349(5)
C(13)	6 232(13)	8 200(12)	143(8)
C(14)	5 832(13)	8 919(12)	483(9)
C(15)	7 585(15)	7 063(10)	211(6)
C(16)	7 720(9)	6 836(10)	-484(7)
C(17)	6 727(9)	6 630(10)	-843(7)
C(18)	6 840(9)	6 395(10)	-1 491(7)
C(19)	7 947(9)	6 367(10)	-1 780(7)
C(20)	8 940(9)	6 572(10)	-1 421(7)
C(21)	8 827(9)	6 807(10)	-773(7)
B(1)	7 321(15)	4 355(12)	1 001(7)
C(30)	7 364(6)	4 056(9)	210(4)
C(31)	7 221(6)	3 254(9)	69(4)
C(32)	7 278(6)	2 991(9)	-574(4)
C(33)	7 479(6)	3 530(9)	-1 077(4)
C(34)	7 622(39)	4 332(9)	-936(4)
C(35)	7 564(6)	4 595(9)	-293(4)
C(36)	7 248(7)	3 610(10)	1 490(4)
C(37)	8 255(7)	3 303(10)	1 782(4)
C(38)	8 181(7)	2 625(10)	2 168(4)
C(39)	7 101(7)	2 253(10)	2 260(4)
C(40)	6 094(7)	2 560(10)	1 968(4)
C(41)	6 168(7)	3 239(10)	1 583(4)
C(42)	8 542(9)	4 918(10)	1 140(4)
C(43)	9 580(9)	4 680(10)	837(4)
C(44)	10 611(9)	5 108(10)	937(4)
C(45)	10 605(9)	5 773(10)	1 339(4)
C(46)	9 568(9)	6 011(10)	1 642(4)
C(47)	8 536(9)	5 583(10)	1 542(4)
C(48)	6 136(8)	4 946(10)	1 131(4)
C(49)	5 634(8)	5 402(10)	638(4)
C(50)	4 762(8)	5 952(10)	788(4)
C(51)	4 393(8)	6 046(10)	1 431(4)
C(52)	4 895(8)	5 590(10)	1 924(4)
C(53)	5 766(8)	5 040(10)	1 774(4)

atomic scattering factors and anomalous dispersion corrections for all the atoms from the International Tables.<sup>15</sup> The molecular plot was produced by ORTEP<sup>16</sup> program. Table 2 shows the final co-ordinates with estimated standard deviations.

Tables of thermal parameters and hydrogen atom co-ordinates, have been deposited at the Cambridge Crystallographic Data Centre.

## Results and Discussion

**Crystal Structure of [HL][BPh<sub>4</sub>].**—The structure of the compound consists of discrete [HL]<sup>+</sup> cations and [BPh<sub>4</sub>]<sup>-</sup> anions. Fig. 2 shows an ORTEP drawing of the [HL]<sup>+</sup> cation with the atom labelling. Selected bond lengths and angles are reported in Table 3.

**Protonation.**—The cage L behaves as a biprotic base in aqueous solution, further protonation steps being inappreciable

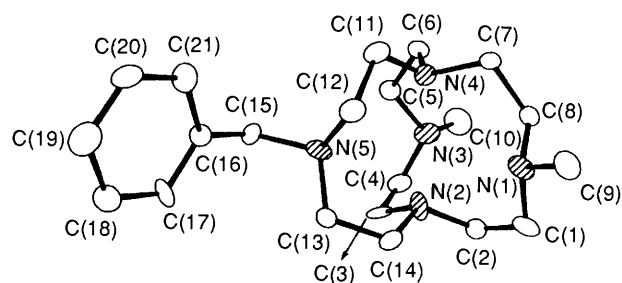


Fig. 2 ORTEP drawing of the cation  $[\text{HL}]^+$

under the experimental conditions employed in the potentiometric measurements. In the first protonation step **L**, and its methylated analogue 4,10,15-trimethyl-1,4,7,10,15-penta-azabicyclo[5.5.5]heptadecane<sup>5</sup> (**L2**) (see Table 4), show moderately strong basicity for tertiary amines [ $\log K_1 = 11.8(1)$  for both cages]. They do not behave, however, as proton sponges, indicating that the peculiar hydrogen-bond arrangement, responsible for the high basicity of 12,17-dimethyl-1,5,9,12,17-pentaazabicyclo[7.5.5]nonadecane<sup>1,2</sup> (**L3**) and 12,17-dimethyl-5-oxa-1,9,12,17-tetraazabicyclo[7.5.5]nonadecane<sup>4</sup> (**L4**), is not working here. The <sup>1</sup>H NMR spectrum of  $[\text{HL}][\text{Br}]$  in deuteriated  $\text{CDCl}_3$  exhibits a broad signal at 10.1 ppm, integrating for one proton, attributable to one encapsulated, deshielded hydrogen-bonded  $-\text{NH}^+$  proton.<sup>1,4</sup> This signal disappears upon adding water, due to excessive linewidth,

Table 3 Selected bond distances/Å and angles/° of  $[\text{HL}][\text{BPh}_4]$ , with estimated standard deviations in parentheses

N(1)–C(1)	1.46(2)	N(1)–C(8)	1.43(2)
N(1)–C(9)	1.42(2)	C(1)–C(2)	1.51(3)
N(2)–C(2)	1.42(3)	N(2)–C(3)	1.54(3)
N(2)–C(14)	1.46(2)	C(3)–C(4)	1.47(3)
N(3)–C(4)	1.45(3)	N(3)–C(5)	1.45(3)
N(3)–C(10)	1.44(2)	C(5)–C(6)	1.50(2)
N(4)–C(6)	1.46(2)	N(4)–C(7)	1.51(3)
N(4)–C(11)	1.45(2)	C(7)–C(8)	1.51(2)
C(11)–C(12)	1.54(2)	N(5)–C(12)	1.45(2)
N(5)–C(13)	1.47(2)	N(5)–C(15)	1.52(3)
C(13)–C(14)	1.47(3)	C(15)–C(16)	1.49(2)
C(8)–N(1)–C(9)	111(1)	C(1)–N(1)–C(9)	112(1)
C(1)–N(1)–C(8)	114(1)	N(1)–C(1)–C(2)	111(1)
C(1)–C(2)–N(2)	112(2)	C(2)–N(2)–C(14)	113(2)
C(2)–N(2)–C(3)	107(1)	C(3)–N(2)–C(14)	108(1)
N(2)–C(3)–C(4)	114(2)	C(3)–C(4)–N(3)	114(2)
C(4)–N(3)–C(10)	110(1)	C(4)–N(3)–C(5)	113(2)
C(5)–N(3)–C(10)	113(1)	N(3)–C(5)–C(6)	109(2)
C(5)–C(6)–N(4)	112(1)	C(6)–N(4)–C(11)	112(1)
C(6)–N(4)–C(7)	111(1)	C(7)–N(4)–C(11)	111(1)
N(4)–C(7)–C(8)	107(1)	N(1)–C(7)–C(8)	110(1)
N(4)–C(11)–C(12)	109(1)	C(11)–C(12)–N(5)	108(1)
C(12)–N(5)–C(15)	116(1)	C(12)–N(5)–C(13)	113(1)
C(13)–N(5)–C(15)	112(1)	N(5)–C(13)–C(14)	113(1)
N(2)–C(14)–C(13)	115(2)	N(5)–C(15)–C(16)	116(1)
C(15)–C(16)–C(21)	121(1)	C(15)–C(16)–C(17)	119(1)

Table 4 Basicity and lithium complex formation constants (logarithms) of three similar cages (C) in water, at 25 °C,  $I = 0.15 \text{ mol dm}^{-3}$  NaCl. Chemical shifts of lithium complexes.

Reaction <sup>a</sup>	Cages (bridging unit)		
	L $[-\text{CH}_2-\text{CH}_2]_2-\text{N}-\text{Bz}$	L1 $[-\text{CH}_2-\text{CH}_2]_2-\text{NH}$	L2 $[-\text{CH}_2-\text{CH}_2]_2-\text{N}-\text{CH}_3$
$\text{H} + \text{C} \longrightarrow \text{HC}$	11.8(1) <sup>b</sup>	12.48 <sup>c</sup>	11.8 <sup>d</sup>
$\text{HC} + \text{H} \longrightarrow \text{H}_2\text{C}$	8.3(1) <sup>b</sup>	9.05 <sup>c</sup>	10.0 <sup>d</sup>
$\text{Li} + \text{C} \longrightarrow \text{LiC}$	3.0(1) <sup>b</sup>	4.8 <sup>c</sup>	5.5 <sup>d</sup>
$\delta_{\text{Li}}^e$	2.47 <sup>b</sup>	2.85 <sup>c</sup>	2.88 <sup>d</sup>

<sup>a</sup> Charges omitted for clarity. <sup>b</sup> This work, the last digit in parentheses are the standard deviations on the last significant figure. <sup>c</sup> Taken from refs. 7, 8.

<sup>d</sup> Taken from ref. 5. <sup>e</sup> <sup>7</sup>Li NMR spectra in aqueous solution.

indicating intermediate or fast proton exchange on the NMR time-scale. Actually, the X-ray crystal structure of  $[\text{HL}][\text{BPh}_4]$  (see Fig. 2) shows that the five nitrogen atoms of  $[\text{HL}]^+$  are in the *endo* configuration, thus encapsulating  $\text{H}^+$ . They are at the vertices of a distorted trigonal bipyramid with a very short distance [2.99(2) Å] between the two apical bridgehead nitrogens. This distance compares well with that found for  $[\text{HL1}]^+$  (3.03 Å)<sup>8</sup> and is much shorter than that found for  $[\text{H}(111)]^+$  (3.60 Å).<sup>17</sup> It must be noted that the average distances between each of the two bridgehead nitrogens and the other three nitrogens N(1), N(3) and N(5) are not equal [N(2)⋯N(1), 2.71(2) Å; N(2)⋯N(3), 2.80(2) Å; N(2)⋯N(5), 2.78(2) Å; N(4)⋯N(1), 3.01(2) Å; N(4)⋯N(3), 2.97(2) Å; N(4)⋯N(5), 2.93(2) Å], evidence which suggests that the proton is bound to N(2) and interacts with N(1), N(3) and N(5) *via* hydrogen bonds. A similar situation was found with  $[\text{HL1}]^+$ .<sup>8</sup> The relatively high values of  $K_1$  for both monoprotonated ions may suggest the occurrence of the X-ray ascertained structures of them even in aqueous solution. The second protonation constant of **L** [ $\log K_2 = 8.3(1)$ ] is significantly lower than that of **L1** [ $\log K_2 = 10.0(1)$ ].<sup>7,8</sup> This comparison suggests that the second protonation involves the benzylamine group which is presumably less basic than the other alkylamine groups (Note:  $\log K_1$  for amines  $\text{BzEt}_2\text{N}$  and  $\text{Et}_3\text{N}$  are 9.44 and 10.75, respectively).<sup>18</sup>

*Lithium Complex.*—Like the other members of the azacage series **L** also binds the lithium ion in aqueous solution fairly strongly. However, the equilibrium constant [ $\log K = 3.0(1)$ ] for the reaction (1) is *ca.* 300 times lower than that with the



$[\text{LiL1}]^+$  complex [ $\log K = 5.5(1)$ ]. The lithium encapsulation by **L** is unambiguously shown by the <sup>13</sup>C and <sup>7</sup>Li NMR spectra of the complex. The <sup>13</sup>C NMR spectrum of a solution containing the preformed  $[\text{LiL}][\text{Br}]$  salt in strongly alkaline aqueous solution consists of twelve sharp signals at room temperature ( $\delta_{\text{C}}$ , 40.3, 50.1, 53.4, 54.1, 55.1, 55.3, 59.2, 59.6, 129.1, 129.6, 132.8 and 133.7). The spectrum shows six resonances for the methylene carbons of ethylenic bridges, whereas the two methyl carbons give rise to one single signal (40.3 ppm). The spectrum is completed by four aromatic signals and one signal (50.1 ppm) attributable to the methylenic carbon of the benzyl group. In chloroform the <sup>13</sup>C NMR spectrum shows the same pattern as in aqueous solution with the signals of the methyl groups resolved ( $\delta_{\text{C}}$ , 40.1, 40.2, 50.2, 52.8, 53.6, 54.4, 54.5, 58.6, 58.8, 128.1, 128.5, 131.3 and 131.5). These spectra are typical of a time-averaged  $C_v$  symmetry for the complex with the lithium atom and the two nitrogens of the  $\text{N}-\text{CH}_3$  groups lying in the symmetry plane. The <sup>7</sup>Li NMR spectrum of an aqueous solution containing a mixture of  $[\text{LiL}][\text{ClO}_4]$  and  $\text{LiCl}$  exhibits two sharp peaks, one for the complexed and shielded lithium ( $\delta = 2.47 \text{ ppm}$ ) and one for the free lithium, indicating a slow exchange between the two species, on the NMR time-scale. This

chemical shift is indicative of a highly deshielded cation and typical of encapsulated lithium.<sup>5,7,8</sup> The value of 2.47 ppm is in agreement with those found for related cages (see Table 4). The lower value of the formation constant for the  $[\text{LiL}]^+$  complex, with respect to that for  $[\text{LiL1}]^+$  may be due to lower hydration of the lipophilic benzyl derivative, as well as to the higher steric hindrance of the N-Bz group.

### Conclusions

The benzylation of the secondary nitrogen atom of the cage 10,15-dimethyl-1,4,7,10,15-pentaazabicyclo[5.5.5]heptadecane (L1) produces the cage L which shows both a lower overall basicity and a reduced ability to encapsulate  $\text{Li}^+$  with respect to L1, although the cavity size is unchanged.

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