

# Solution and solid-state structures of dibenzylamino calix[4]arene with complexed solvent molecules

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## Abstract

The solution and solid state structures of 1,3-dibenzylamino calix[4]arene were investigated via NMR and X-ray crystallography for MeCN, ethanol, hexane, THF, chloroform and toluene solvents. Analysis of the obtained structures show a symmetric flattening/pinching of the calixarene for solvents with a roughly cylindrical shape (MeCN, ethanol, hexane) and an asymmetrical flattening of the cone for more anisotropic, flat solvents, such as THF or toluene. Due to the deviation from planarity of the N<sub>2</sub>O<sub>2</sub> fragment in the latter case, these solvents might be best suited for the preparation of octahedral or tetrahedral metal complexes, while the former would be more suitable for the preparation of square-planar complexes.

## Keywords

calixarenes, calix[4]arenes, X-ray crystallography, calixarene deformations

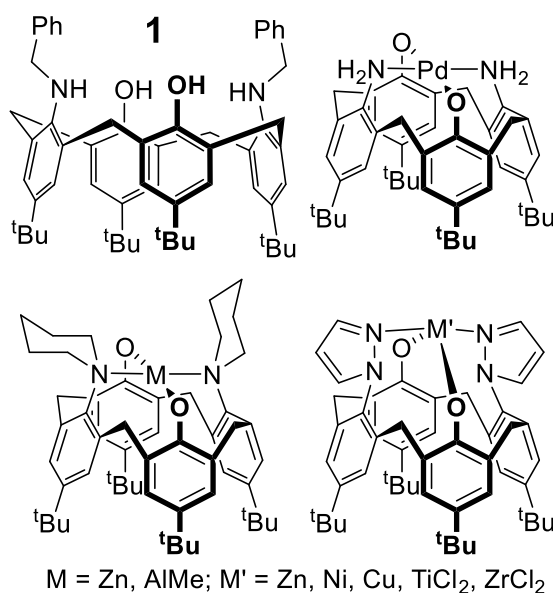
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## Introduction

Calixarenes (“calix”), in particular their calix[4]arene-derivatives have been widely studied, in part due to their ability to bind metal ions on the polar lower rim and neutral small guest in their hydrophobic cavity.<sup>1</sup> Unsurprisingly, the two binding sites influence each other: the type of metal coordinated to the lower rim was calculated to influence the binding strength of host-guest interactions in the hydrophobic cavity.<sup>2</sup> On the other hand, guest incorporation was shown to influence the photophysical properties of a coordinated metal.<sup>3</sup> Namor showed that incorporation of solvent in the cavity leads to different geometries (or distortions of geometry) of the calixarene ligand and determines the binding selectivity of the lower rim for metal cations.<sup>4,5</sup>

Parent calix[4]arenes are tetraphenols with limited binding ability to transition metals, most of which have oxidation states lower than IV. Even for metals in the +IV oxidation state, the planar arrangement of the four oxygen atoms is often incompatible with the tetrahedral or octahedral coordination environment expected for these weak-field ligands. The Ti(*tert*-butylcalix[4]arene) complex, for example, one of the first structurally characterized calixarene metal complexes, dimerizes to coordinate three phenolic groups from one and one phenolic group of another calixarene ligand to enable a tetrahedral coordination environment around titanium.<sup>6</sup> A common derivatization is thus alkylation or acylation of the phenolic groups, resulting in most cases in neutral or dianionic ligands. Recently, a new class of calix[4]arene derivatives emerged in which two of the phenolic groups are replaced by amines, of which benzyl amine-derivatized calixarene **1** is an example (Chart 1).<sup>7-9</sup> This affords dianionic, tetradentate ONON-calix[4]arenes as potential ligands, the coordination chemistry of which is somewhat underdeveloped. Of the small number of metal complexes reported (Chart 1),<sup>9-12</sup> structurally characterized complexes are limited to bis(pyrazolyl) ONON-calix[4]arenes, where the nitrogen atom coordinated to the metal is not part of the lower rim. The only structurally characterized coordination complex with the metal actually coordinated to the N<sub>2</sub>O<sub>2</sub> binding site is the square-planar Pd complex of NH<sub>2</sub>-derivatized calix[4]arene, (ONON<sup>H2</sup>)Pd (Chart 1).<sup>11</sup> In this complex, the calixarene adopts a symmetrical cone shape with nitrogen and oxygen atoms in the same plane and with similar O-O and N-N distances (4.0 and 4.1 Å, respectively). This planar arrangement of the donor atoms is detrimental in octahedral coordination geometry. In complexes of the related dialkylated calixarene ligands, e. g. in (O,O'-dimethylcalixarene)TiCl<sub>2</sub>,<sup>13</sup> the calixarene deforms into a “pinched/flattened cone” conformation to adopt to the octahedral coordination environment of titanium. This deformation typical involves a flattening of the phenol substituents (increase of the angle between the aryl and the O<sub>4</sub> mean plane), while the aryl ether moieties become more coplanar (decrease of the aryl-O<sub>4</sub> angle). This decreases the distances between the phenoxide oxygen atoms, which were found in

*cis*-position, and increases the distance between the ether oxygen atoms, which were found in *trans*-position of a distorted octahedral coordination environment.<sup>13</sup>



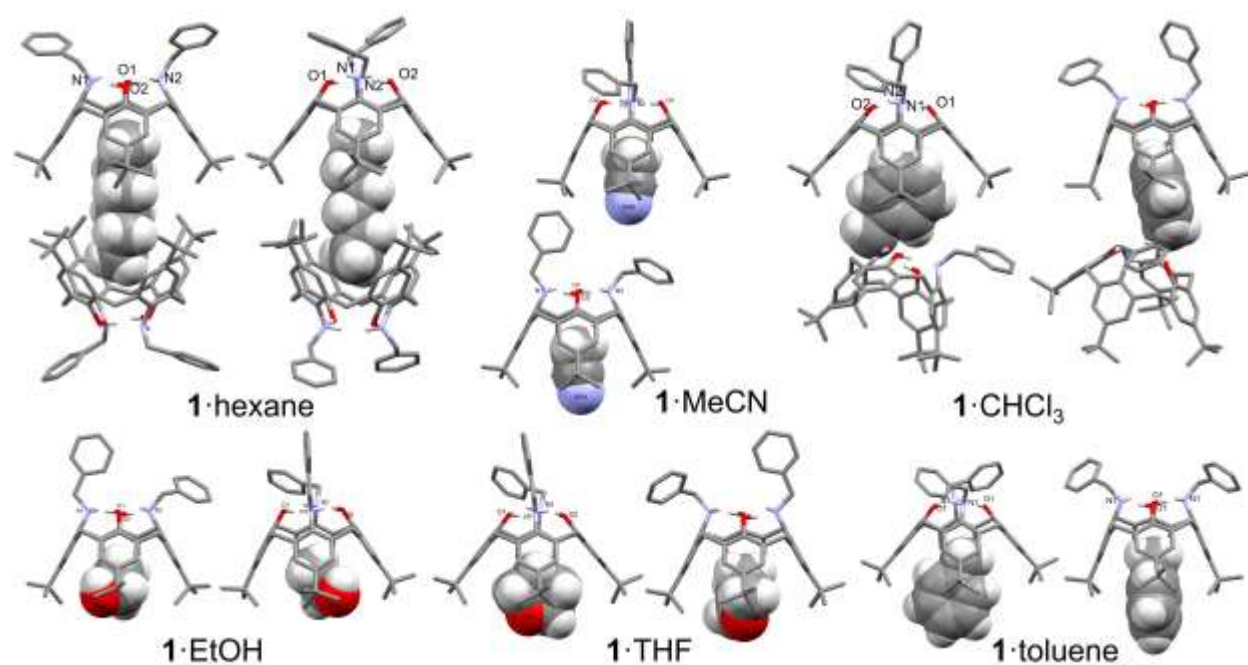
**Chart 1.** Dibenzyl amine-derivatized calix[4]arene, **1**,<sup>8</sup> and literature reported metal complexes with ONON-calix[4]arene ligands.<sup>9-12</sup>

Solvents are often incorporated in the hydrophobic cavity of calixarene ligands. Since the conformation of calixarene ligands is clearly different in square-planar and octahedral/tetrahedral complexes, we studied the geometries adopted by benzyl amine-derivatized *tert*-butyl calix[4]arene, ONON<sup>Bn</sup>H<sub>2</sub>, **1**,<sup>8</sup> with the aim to determine if choice of the optimal solvent can prearrange the calixarene geometry for the targeted coordination environment.

## Results and discussion

**Single-crystal diffraction studies.** Single crystals of compound **1** were grown from acetonitrile, chloroform, ethanol, hexane, THF and toluene solution. All structures showed the all-*syn* cone conformation (Fig. 1). In all cases but **1**·CHCl<sub>3</sub>, a solvent molecule was complexed in the calixarene cavity. While **1**·CHCl<sub>3</sub> did contain a co-crystallized chloroform, the cavity was filled by the N-benzyl moiety of a neighbouring calixarene. With regard to the influence of the host molecule on the deformation of the cavity, **1**·CHCl<sub>3</sub> is thus expected to give results similar to **1**·toluene. In **1**·(hexane)<sub>1/2</sub>, two calixarene units complexed one hexane molecule. For the polar solvents MeCN, EtOH and THF, the heteroatoms were oriented towards the cavity opening (Fig. 1). Apart from **1**·CHCl<sub>3</sub>, all complexes have molecular C<sub>2</sub> symmetry. However, only **1**·toluene shows C<sub>2</sub> symmetry in the solid state (Table 1). While it is tempting to correlate this to the C<sub>2v</sub> symmetry of the toluene guest (ignoring hydrogen atoms), all guests are highly disordered and

**1**·MeCN with the most symmetric guest shows only crystallographic  $C_1$  symmetry in the solid state. There is thus no evidence for any correlation between molecular symmetry of the guest and crystallographic symmetry of the **1**·solvent host-guest complexes. Hydroxy and amine groups in the lower rim form an 8-membered, hydrogen-bonded ring, often described as “circular hydrogen bonding”. Hydrogen atoms on N and O could usually be located on the electron density map (with the exception of **1**·CHCl<sub>3</sub>) and were refined with a minimum of restraints. OH-distances refined to the range of 0.95-0.98 Å, NH distances to 0.89-0.93 Å. Even considering the uncertainties in determining hydrogen atom positions from X-ray crystallography, this indicates strong hydrogen bonding from OH to N and slightly less from NH to O (Table S1).



**Figure 1.** X-ray structures of **1** with different solvent guests in projections along the O-O and the N-N axis. Additional molecules in the asymmetric unit, co-crystallized solvent outside the cavity, minor fractions of disordered solvent or tert-butyl groups, and most hydrogen atoms were omitted for clarity.

**Table 1.** Observed point group symmetries of **1**·solvent host-guest complexes

	<b>1</b> ·MeCN	<b>1</b> ·EtOH	<b>1</b> ·(hexane) <sub>1/2</sub>	<b>1</b> ·THF	<b>1</b> ·toluene	<b>1</b> ·CHCl <sub>3</sub>
Space group	<i>P2</i> <sub>1</sub> / <i>c</i>	<i>P2</i> <sub>1</sub> / <i>c</i>	<i>Pbcn</i>	<i>Cc</i>	<i>C2</i> / <i>c</i>	<i>C2</i> / <i>c</i>
Z; Z'	4; 1	4; 1	8; 1	8; 2	8; ½	8; 1
molecular symmetry	<i>C</i> <sub>2</sub>	<i>C</i> <sub>2</sub>	<i>C</i> <sub>2</sub>	<i>C</i> <sub>2</sub>	<i>C</i> <sub>2</sub>	<i>C</i> <sub>1</sub>

crystallographic symmetry	$C_1$	$C_1$	$C_1$	$C_1$	$C_2$	$C_1$
apparent symmetry in $^1\text{H-NMR}$	$C_{2v}$	$C_{2v}$	$C_{2v}$	$C_{2v}$	$C_{2v}$	$C_{2v}$

We were particularly interested in the deformation of the calixarene cavity (or as Gutsche expressed it “the shaping of the basket”)<sup>14</sup> by the complexed solvent guest and how the latter influenced the relative geometry of the N and O atoms in the lower rim. Table 2 characterizes the shape of the cavity by the aryl plane angle  $\alpha$  of phenol and aniline rings, respectively, calculated from the virtual trapezoid formed by the *ipso* and *para* carbon atoms of opposing aryl rings (see Sup. Information and Fig. S1). This angle is practically identical to the angle between the aryl mean planes and the mean plane of the lower rim  $\text{N}_2\text{O}_2$  fragment. As an alternative evaluation, the angle between opposing aryl planes  $\beta = 2\alpha - 180^\circ$  is also provided (Fig. S1, Table S2). There is no established nomenclature to describe calixarene deformations, but we will refer in the following to “flattening” when we observe an increase in the  $\alpha$  (or  $\beta$ ) angle and to “pinching” when we observe a decrease of the  $\alpha$  (or  $\beta$ ) angle. “Pinching” the cone, i.e. increasing the coplanarity of two opposing aryl rings, leads to an increased X-X distance in the lower rim and places these heteroatoms above their neighbours in the lower rim. “Flattening” on the other hand, increases the planarity of the two opposite aryl rings and moves the heteroatoms below their neighbours. Table 2 characterizes the geometry of the lower rim by the asymmetry of the O-O and N-N distances, as well as the O-N-N-O dihedral angle. The larger the deviation of the latter from  $180^\circ$ , the larger the deviation of the  $\text{N}_2\text{O}_2$  fragment from planar geometry.

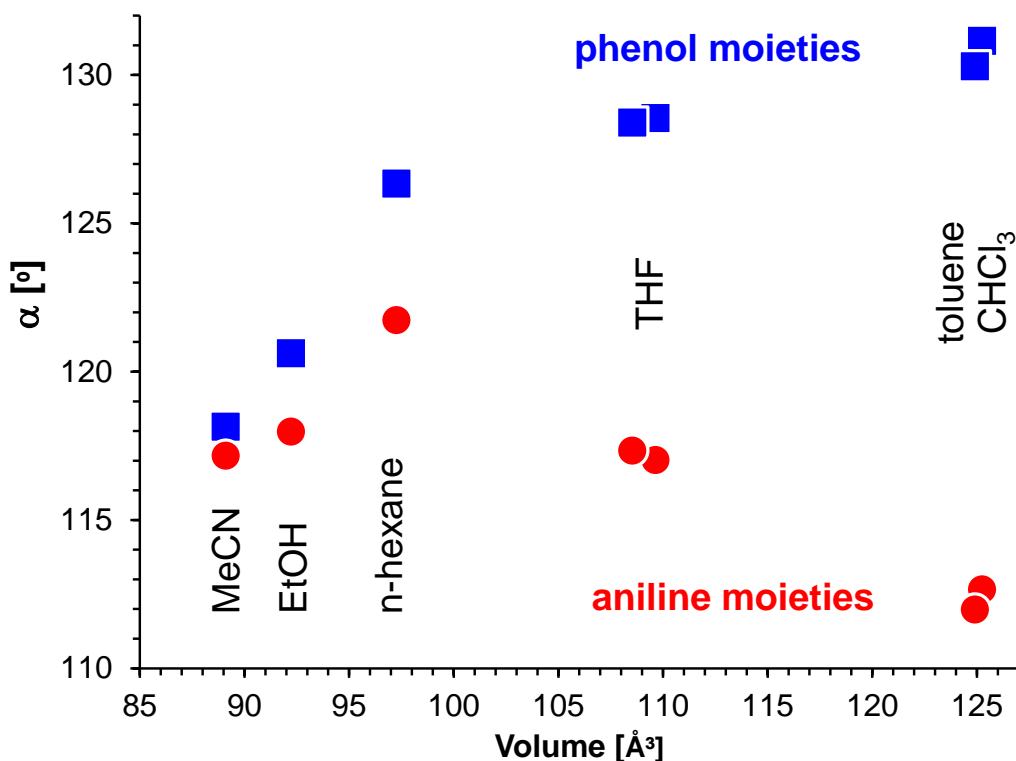
**Table 2.** Characteristic distances [ $\text{\AA}$ ] and angles [ $^\circ$ ] in the X-ray structures of **1** with solvent guest molecules.

	<b>1</b> ·MeCN	<b>1</b> ·EtOH	<b>1</b> ·(hexane) <sub>1/2</sub>	<b>1</b> ·THF	<b>1</b> ·toluene	<b>1</b> ·CHCl <sub>3</sub>
Phenol : $\alpha$	118	121	126	128 & 129	130	131
Aniline : $\alpha$	117	118	122	117 & 117	112	113
Phenol : $\beta$	56	61	73	77 & 77	81	82
Aniline : $\beta$	54	56	63	54 & 55	44	45
$d_{\text{O-O}}$ <sup>a</sup>	3.9	3.9	3.7	3.6 & 3.6	3.6	3.6
$d_{\text{N-N}}$ <sup>a</sup>	4.0	4.0	4.0	4.1 & 4.1	4.2	4.1
$\Delta(d_{\text{O-O}}, d_{\text{N-N}})$ <sup>a</sup>	0.1	0.2	0.3	0.5 & 0.5	0.6	0.6

Dihedral O,N,N,O	171	170	166	162 & 163	161	160
Cavity volume [ $\text{\AA}^3$ ] <sup>a</sup>	89	92	92	109 & 110	125	125

The cavity volume is represented by the volume of the truncated cone defined by the *ipso* and *para* carbon atoms (Fig. S1, supporting information). <sup>a</sup> The  $3\sigma$  confidence interval for O-O and N-N distances is  $<0.01$   $\text{\AA}$ .

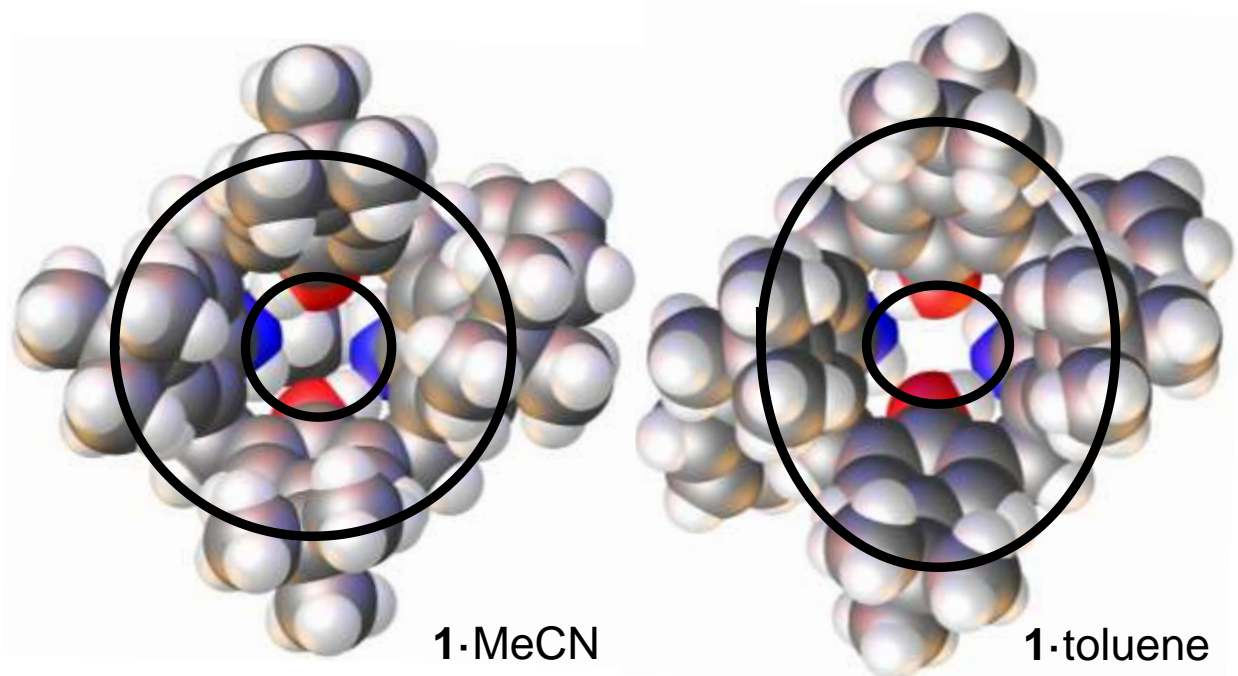
Deviations from  $C_{4v}$  symmetry to  $C_{2v}$  symmetry in the conformations of parent calixarenes are often described as “flattened cone” or “pinched cone” conformations, in which two aryl rings become more coplanar while the two other rings “flatten out”. While **1** showed the same “flattened cone” geometry, its reaction to the size of the guest was slightly more subtle. Of the characterized derivatives, **1**·MeCN displays a nearly symmetric cavity with essentially identical  $\alpha$  angles for phenol and aniline moieties (Table 2, Figs. 1-3). Consequently, the  $\text{N}_2\text{O}_2$  fragment is close to square-planar geometry, with the O-N-N-O angle close to  $180^\circ$  and very small differences in the O-O and N-N distances. The O-O and N-N distances in **1**·MeCN (3.9 and 4.0  $\text{\AA}$ , Table 2) resemble strongly those observed in the square-planar complex  $(\text{ONON}^{\text{H}_2})\text{Pd}$  (4.0 and 4.1  $\text{\AA}$ , Chart 1).<sup>11</sup> Complexation of the sterically more demanding, but still essentially cylindrical ethanol and hexane guests leads to a flattening of both phenol and aniline rings in the cone, although the flattening is slightly more pronounced in the phenol rings. Flattening of the aryl rings decreases the heteroatom-heteroatom distance of the two opposite moieties in the lower rim. The preference to flatten the phenol moieties instead of the N-benzyl anilines is thus likely purely sterically motivated. Dialkylated calixarenes likewise show preferably a flattening of the non-alkylated rings (see sup. information).



**Figure 2.** Angle  $\alpha$  of the phenol (blue squares) and then aniline moieties (red circles) in dependence of the volume of the cavity (as calculated in Table 2) of **1**-solvent adducts.

Introduction of the more anisotropic, flat THF solvent introduces strong asymmetry in the cavity: the phenol rings flatten out while the aniline rings retain the same geometry as in **1**-MeCN (Fig. 2). The asymmetry of the cavity now leads to notable differences of 0.5 Å in O-O and N-N distances (Table 2). Introduction of a toluene guest finally leads to the “pinched cone” conformation and the aniline rings become more coplanar, most likely to due to attractive  $\pi$ - $\pi$  interactions with the toluene guest. At the same time, the flattening of the phenol rings becomes even more pronounced. The pinched/flattened cone conformation of **1**-toluene consequently results in a large asymmetry in the N<sub>2</sub>O<sub>2</sub> fragment, with a notable difference of 0.6 Å between the O-O and N-N distances and notable deviations from planarity (Table 2, Figs. 1-3). **1**-CHCl<sub>3</sub>, in which a benzyl substituent from another calixarene is complexed in the cavity shows a geometry essentially identical to **1**-toluene. **1**-toluene seems the most suitable conformer to facilitate octahedral metal coordination. O-O and N-N distances of 3.6 and 4.2 Å, respectively, approach those for *cis*-positioned phenoxy (2.6 Å) and *trans*-positioned phenoxyethers (4.2 Å) in (O,O'-dimethylcalixarene)TiCl<sub>2</sub>.<sup>13</sup>





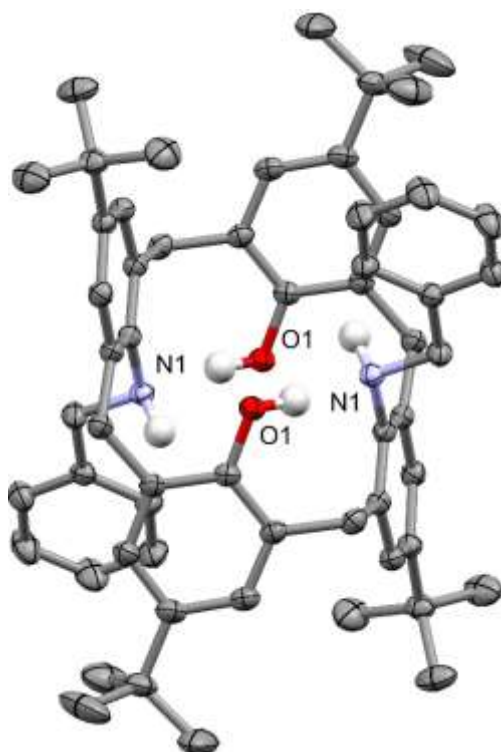
**Figure 3.** Space-filling diagram of the cavity without the complexed guest for **1**·MeCN and **1**·toluene. The anisotropy of toluene (right) leads to an elliptical distortion of the cavity (flattening of the phenols, pinching of the anilines), which in turn effects the geometry of the  $\text{N}_2\text{O}_2$  fragment.

**NMR studies.** NMR studies have been useful to characterize the conformations of calixarenes in solution. In Mendoza's rule, the chemical displacement of the methylene group bridging the phenol rings in  $^{13}\text{C}$  NMR spectra is typically used to assign cone (all-*syn*,  $\delta(\underline{\text{C}}\text{H}_2)=31$  ppm), 1,3-alternate (all-*anti*,  $\delta(\underline{\text{C}}\text{H}_2)=37$  ppm), or 1,2-alternate conformations (*syn-anti*,  $\delta(\underline{\text{C}}\text{H}_2)=31$  & 37 ppm or intermediate).<sup>15</sup> In the  $^1\text{H}$  spectra, the relative displacement between the two methylene protons, i. e. between the axial and the equatorial proton, was used to characterize the deformation of the cavity in solution: values of  $\Delta\delta = 0.9\pm 0.2$  ppm are typically considered indicative of rather symmetrical cavities, while values around  $\Delta\delta = 0.5\pm 0.1$  ppm indicate more distorted, "pinched" or "flattened" conformations.<sup>14</sup> Diamino-calixarene **1** was studied in solution to verify whether the same NMR characteristics persist when two oxygen atoms are replaced by amine groups.

$^1\text{H}$  NMR spectra of **1** show apparent  $C_{2v}$  symmetry (Table 1) due to fast tautomerism between NH and OH protons, which consequently appear as one signal with an intensity of 4. The methylene groups bridging the aromatic rings appear as two doublets, in agreement with the cone conformation observed in the solid state and the absence of fast calixarene inversion. Lack of inversion was likewise observed for the benzylated parent calixarene, carrying 1,3-benzyl ether groups<sup>16</sup> and is in general expected for substituents larger than ethyl.<sup>14</sup> The chemical displacement of the methylene groups between two aryl rings was  $\delta=34\text{-}35$  ppm in various solvents (Table 3, Fig. S2), instead of the expected value of 31 ppm for *syn* aryl rings.<sup>15</sup> Compound **2**, the 1,2-



alternate rotamer of **1** in which the benzylamino groups are in an *anti*-conformation, was obtained as a minor impurity from the mother liquor of recrystallisations of **1** (Fig. 4). Heating of **2** to 70 °C for several days did not show any evidence for the formation of **1**, in agreement with the absence of *anti-syn* isomerization of the benzylaniline moieties. Isomer **2** is thus likely obtained from a 1,2-alternate conformer of the calixarene bistriflate precursor used in synthesis or, alternatively, by a “through the cavity attack” of benzylamine during synthesis. The NMR spectrum of **2** is expected to show four doublets in the <sup>1</sup>H NMR spectrum and 2 signals in the <sup>13</sup>C NMR spectrum for the methylene groups between the aryl rings, which are either in a *syn* or in an *anti* configuration. Instead, we observed two doublets in the <sup>1</sup>H NMR and one single, slightly broadened peak for the methylene group in the <sup>13</sup>C NMR spectrum, indicative of fast phenol inversion, even if aniline inversion is slow. The averaged methylene peak for **2** appears at 37.1 ppm in CDCl<sub>3</sub>. Given that the *syn*-CH<sub>2</sub> in **1** has a chemical shift of 34.8 ppm, we can estimate the position of the *anti*-CH<sub>2</sub> signal at 39.4 ppm. Mendoza’s rule thus still applies in general, with a significant upfield shift of the *anti*-CH<sub>2</sub> signal, but the presence of the amino substituents displaces the chemical shifts downfield from 31 and 37 ppm to 35 and 39 ppm.



**Figure 4.** X-ray structure of **2**, the 1,2-alternate conformation of ONON<sup>Bn</sup>H<sub>2</sub>. A second molecule in the asymmetric unit of identical geometry, the minor fractions of disordered *tert*-butyl groups, and hydrogen atoms on carbon were omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

**Table 3.** NMR displacements of the bridging methylene groups of **1** in various solvents

Solvent	$\delta$ ( $^1\text{H}$ )	$\Delta\delta$ ( $^1\text{H}$ )	$\delta$ ( $^{13}\text{C}$ )
$\text{CDCl}_3$	3.34, 4.00	0.66	34.8
benzene- $d_6$	3.41, 4.19	0.78	35.1
$\text{CD}_3\text{CN}$	3.37, 3.92	0.55	34.0
methanol- $d_4$	3.35, 3.98	0.63	n.d.

The chemical shift difference  $\Delta\delta$  between the axial and the equatorial protons in the  $^1\text{H}$  NMR spectrum should offer information about the shape of the calixarene cavity, with symmetric calixarenes having  $\Delta\delta$  values around 0.9 ppm and distorted calixarenes smaller values around 0.5 ppm. The observed chemical shifts of **1** in various solvents (Table 3), however, do not correlate with the observation made in the solid state. All  $\Delta\delta$  values were in the range of 0.6-0.8, with MeCN and methanol having smaller values (indicating higher distortion) than benzene. Given the small range of  $\Delta\delta$  values and the contradictions between predicted solution structures and observed solid-state structures, the chemical shift difference between axial and equatorial protons seems not to be a useful structural characteristic in bisamino-derivatized calix[4]arenes, eventually due to the increased hydrogen bonding in the lower rim.

## Conclusions

As in dialkylated calixarenes, ONON-calixarenes distort their cavity to accommodate guest molecules. Mendoza's rule is still useful to predict *syn* or *anti* arrangements of the phenyl rings, albeit with adaptations of the expected chemical shifts. The splitting of equatorial and axial methylene protons, on the other hand, seems not to be related to the shape of the cavity. X-ray crystallographic studies show that upon inclusion of a solvent molecule in the cavity, the calixarene ligand deforms in two distinctive ways: Solvents with a roughly cylindrical shape, such as acetonitrile, ethanol or hexane, result in a roughly symmetric flattening of the calixarene cavity, which is slightly more pronounced for the phenol moieties. More anisotropic, flat solvents, such as THF or toluene, lead to asymmetric cavities with a resulting non-planar  $\text{N}_2\text{O}_2$  fragment in the lower rim. Prearranging the conformation of the ligand is a known concept to facilitate metal coordination. Solvents such as acetonitrile, ethanol or hexane might thus be most suitable for the preparation of square-planar complexes, while THF or toluene are more suitable to obtain tetrahedral or octahedral complexes. On the other hand, incorporating a mismatched solvent in the cavity of a ONON metal complex might force a distortion of its optimal coordination geometry, with potential increases reactivity. A study of this solvent influence is currently in progress.

## Experimental Section

**General considerations.** Calixarene **1** was prepared according to literature,<sup>8</sup> but hexane was used for extraction instead of chloroform, since this allowed separation from the minor byproduct **2**. <sup>1</sup>H and <sup>13</sup>C NMR spectra were acquired on Bruker Avance 300 and 400 spectrometers. Chemical shifts were referenced to the residual signals of the deuterated solvents (CDCl<sub>3</sub>: <sup>1</sup>H:  $\delta$  7.26 ppm, <sup>13</sup>C:  $\delta$  77.16; C<sub>6</sub>D<sub>6</sub>: <sup>1</sup>H:  $\delta$  7.16 ppm, <sup>13</sup>C:  $\delta$  128.38 ppm).

**X-ray diffraction.** Single crystals were obtained by slow evaporation of **1** in the respective solvent. For **1**·MeCN, crystals were obtained by dissolving **1** in warm acetonitrile and cooling to ambient temperature. Diffraction data were collected on a Bruker Venture METALJET diffractometer (Ga K $\alpha$  radiation) using the APEX2 software package.<sup>17</sup> Data reduction was performed with SAINT,<sup>18</sup> absorption corrections with SADABS.<sup>19</sup> Structures were solved by dual-space methods (SHELXT).<sup>20</sup> All non-hydrogen atoms were refined anisotropic using full-matrix least-squares on  $F^2$  and hydrogen atoms on carbon were refined with fixed isotropic U using a riding model (SHELXL).<sup>21</sup> Hydrogen atoms on nitrogen and oxygen were located on the electron density map and refined using restraints (SADI) on related bonds. (This was not possible for **1**·CHCl<sub>3</sub> and a riding model was used instead.) The complexed solvent in the cavity, cocrystallized solvent (THF and CHCl<sub>3</sub>), and in several cases tert-butyl groups were found disordered and refined with appropriate restraints (SADI, SIMU and RIGU). Further experimental details can be found in the supporting information (CIF).

**anti,syn,anti,syn-Bis(benzylamino)calix[4]arene, 2.** The 1,2-alternate conformer **2** crystallized on evaporation of the mother liquor of recrystallisations of **1** in CHCl<sub>3</sub>/MeCN.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K):  $\delta$  1.12 (s, 18H, *t*Bu), 1.32 (s, 18H, *t*Bu), 3.61 (t,  $J$  = 6 Hz, 2H, NH), 3.73 (d,  $J$  = 15 Hz, 4H, CH<sub>2</sub>), 3.81 (d,  $J$  = 6 Hz, 4H, CH<sub>2</sub> Bn), 3.86 (d,  $J$  = 15 Hz, 4H, CH<sub>2</sub>), 6.62 (d,  $J$  = 8 HZ, 4H, *ortho* Bn),  $\delta$  6.95 (s, 4H, Ar), 7.04-7.13 (6H, *meta&para* Bn), 7.15 (s, 4H, Ar),  $\delta$  10.49 (s, 2H, OH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz, 298 K):  $\delta$  31.5 (*CMe*<sub>3</sub>), 31.6 (*CMe*<sub>3</sub>), 33.9 (*CMe*<sub>3</sub>), 34.4 (*CMe*<sub>3</sub>), 37.1 (CH<sub>2</sub>), 54.7 (CH<sub>2</sub> benzyl), 125.6 (*meta*-NAr), 125.6 (*meta*-OAr), 127.0 (*para*-Ph), 127.2 (*ortho*-Ph), 127.3 (broad peak, *ortho*-OAr), 128.4 (*meta*-Ph), 136.2 (*ortho*-NAr), 137.9 (*ipso*-Ph), 139.6 (*para*-NAr), 142.5 (*para*-OAr), 148.1 (*ipso*-NAr), 151.4 (*ipso*-OAr).

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## Supporting Information

Crystal structure data (tables), ORTEP plots of all structures, details on geometric calculations.  
Crystal structure data (CIF).

## References

1. Santoro, O.; Redshaw, C., Metallocalix[n]arenes in catalysis: A 13-year update. *Coord. Chem. Rev.* **2021**, *448*, 214173.
2. Murphy, P.; Dalgarno, S. J.; Paterson, M. J., Transition Metal Complexes of Calix[4]arene: Theoretical Investigations into Small Guest Binding within the Host Cavity. *J. Phys. Chem. A* **2016**, *120*, 824-839.
3. Harvey, P. D.; Gagnon, J.; Provencher, R.; Xu, B.; Swager, T. M., Tungsten and molybdenum oxo complexes of tetrakis(phenyldiazenyl)calix[4]arene substituted derivatives: EHMO calculations, spectroscopic characterization, and perturbations of the photophysical properties by neutral guest molecules. **1996**, *74*, 2279-2288.
4. Danil de Namor, A. F.; Chahine, S.; Castellano, E. E.; Piro, O. E., Thermodynamics of Host–Guest Interactions in Lower Rim Functionalized Calix[4]arenes and Metal Cations: The Medium Effect. *J. Phys. Chem. B* **2004**, *108*, 11384-11392.
5. Danil de Namor, A. F.; Chahine, S.; Kowalska, D.; Castellano, E. E.; Piro, O. E., Selective Interaction of Lower Rim Calix[4]arene Derivatives and Bivalent Cations in Solution. Crystallographic Evidence of the Versatile Behavior of Acetonitrile in Lead(II) and Cadmium(II) Complexes. *J. Am. Chem. Soc.* **2002**, *124*, 12824-12836.
6. Olmstead, M. M.; Sigel, G.; Hope, H.; Xu, X.; Power, P. P., Metallocalixarenes: syntheses and x-ray crystal structures of titanium(IV), iron(III), and cobalt(II) complexes of p-tert-butylcalix[4]arene. *J. Am. Chem. Soc.* **1985**, *107*, 8087-8091.
7. Tanaka, S.; Serizawa, R.; Morohashi, N.; Hattori, T., Ullmann coupling reaction of 1,3-bistriflate esters of calix[4]arenes: facile syntheses of monoaminocalix[4]arenes and 4,4':6,6'-diepithiobis(phenoxathiine). *Tetrahedron Lett.* **2007**, *48*, 7660-7664.
8. Nakamura, Y.; Tanaka, S.; Serizawa, R.; Morohashi, N.; Hattori, T., Synthesis of Mono- and 1,3-Diaminocalix[4]arenes via Ullmann-Type Amination and Amidation of 1,3-Bistriflate Esters of Calix[4]arenes. *J. Org. Chem.* **2011**, *76*, 2168-2179.
9. Rawat, V.; Press, K.; Goldberg, I.; Vigalok, A., Straightforward synthesis and catalytic applications of rigid N,O-type calixarene ligands. *Org. Biomol. Chem.* **2015**, *13*, 11189-11193.

10. Keck, M.; Hoof, S.; Herwig, C.; Vigalok, A.; Limberg, C., Oxygen-Depleted Calixarenes as Ligands for Molecular Models of Galactose Oxidase. *Chem. - Eur. J.* **2019**, *25*, 13285-13289.
11. Morohashi, N.; Kurusu, Y.; Akasaka, K.; Hattori, T., Extraction of Pd(ii) and Pt(ii) from aqueous hydrochloric acid with 1,3-diaminocalix[4]arene: switching of the extraction selectivity by using different extraction modes. *RSC Adv.* **2020**, *10*, 35473-35479.
12. Rawat, V.; Vigalok, A.; Sinha, A. K.; Sachdeva, G.; Srivastava, C. M.; Rao, G. K.; Kumar, A.; Singh, M.; Rathi, K.; Verma, V. P.; Yadav, B.; Pandey, A. K.; Vats, M., Synthesis of a Zirconium Complex of an N,O-type p-tert-Butylcalix[4]arene and Its Application in Some Multicomponent Reactions. *ACS Omega* **2022**, *7*, 28471-28480.
13. Radius, U., Shaping the Cavity of the Macrocyclic Ligand in Metallocalix[4]arenes: The Role of the Ligand Sphere. *Inorg. Chem.* **2001**, *40*, 6637-6642.
14. Gutsche, C. D., Shaping the Baskets: Conformations of Calixarenes. In *Calixarenes: An Introduction*, The Royal Society of Chemistry, 2008; pp 77-115.
15. Jaime, C.; De Mendoza, J.; Prados, P.; Nieto, P. M.; Sanchez, C., Carbon-13 NMR chemical shifts. A single rule to determine the conformation of calix[4]arenes. *J. Org. Chem.* **1991**, *56*, 3372-3376.
16. Dijkstra, P. J.; Brunink, J. A. J.; Bugge, K. E.; Reinhoudt, D. N.; Harkema, S.; Ungaro, R.; Ugozzoli, F.; Ghidini, E., Kinetically stable complexes of alkali cations with rigidified calix[4]arenes: synthesis, x-ray structures, and complexation of calixcrowns and calixspherands. *J. Am. Chem. Soc.* **1989**, *111*, 7567-7575.
17. *Apex2*, Release 2.1-0; Bruker AXS Inc.: Madison, USA, 2006.
18. *Saint*, Release 7.34A; Bruker AXS Inc.: Madison, USA, 2006.
19. Sheldrick, G. M. *Sadabs*, Bruker AXS Inc.: Madison, USA, 1996 & 2004.
20. Sheldrick, G., Shelxt - Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, *71*, 3-8.
21. Sheldrick, G. M., A Short History of Shelx. *Acta Crystallogr.* **2008**, *A64*, 112-122.