Abstract
Some examples of atropoisomeric pseudorotaxanes in which the isomerism arises by the different conformations adopted by the wheel are reported here. Upon threading hexahexyloxycalix[6]arene 1 with ammonium axles 2+ or 3+ bearing biphenyl or trifluoro-methylbenzyl moieties, respectively, two atropoisomeric pseudorotaxanes were formed in which the calix[6]-wheel 1 adopts the 1,2,3-alternate and cone conformations. The interconversion between them cannot be obtained by simple rotation around the ArCH2Ar bonds of the calixarene wheel, which is blocked by the presence of the axle inside its cavity. Therefore, it can only be obtained through a mechanism of de-threading/re-threading of the axle. In all the examined cases, the 1,2,3-alternate and cone atropoisomers are, respectively, the kinetic and the thermodynamic ones.

Introduction
Mechanomolecules [1-4], such as rotaxanes and catenanes show interesting properties as nanodevices for catalysis [5-8], recognition, and sensing [9-13]. Beyond these ascertained potentialities, interpenetrated architectures show fascinating structures that still stimulate the imagination of scientists.

An amazing aspect of rotaxanes and catenanes is their ability to adopt novel forms of isomerism. More in detail, (pseudo)rotaxane or catenane architectures can show novel stereoisomeric forms as a result of the "social" [14] relationship between their components.

Recently, Goldup’s group assembled a mechanically planar chiral rotaxane [15,16] (I and I*, Figure 1) consisting of achiral components. The combination of a macrocycle with rotational asymmetry and a directional thread with non-equivalent ends is the cause of chirality in this example (Figure 1). Interestingly, our group showed that a chiral pseudorotaxane can be generated upon threading a tertiary ammonium axle in a directional (non-flat) calixarene-wheel (II and II*, Figure 1) [17]. In this case the chirality is created by the directionality of the calixarene wheel in a cone conformation, which differentiates the two alkyl chains around the prochiral ammonium center.
In 2010, for the first time, an example of sequence isomerism was reported by Leigh’s group [18], caused by two different flat wheels that can be located differently along a directional thread III and IV (Figure 2). As an evolution of this concept, we envisaged a sequence stereoisomerism if two directional non-flat wheels, such as calixarenes or cyclodextrins, are threaded along an axle to give a pseudo[3]rotaxane architecture V–VII (Figure 2), where three sequential stereoisomers can arise. We showed that this stereoisomerism can be effectively controlled when two calix[6]arene wheels are threaded along a bis(benzylalkylammonium) axle [19], where the stereoselective formation of the pseudo[3]rotaxane with endo-alkyl orientation VIII was observed [19].

Calixarene macrocycles [22] have found numerous applications in several areas of supramolecular chemistry, such as (bio)molecular recognition [23] and catalysis [24]. The widespread use of the calixarene derivatives is due to their convenient synthesis and to their chemical and conformational versatility [25]. In fact, calixarene macrocycles present a conformational isomerism that in the case of calix[6]arenes gives rise to eight discrete conformations (Figure 3) [26]: cone, partial-cone, 1,2-alternate, 1,3-alternate, 1,4-alternate, 1,2,3-alternate, 1,2,4-alternate, and 1,3,5-alternate. This conformational versatility has long attracted much attention, and therefore empirical rules have been reported in order to assign the calixarene conformations [27,28]. The "1H NMR Δδ" rule reported by Gutsche [29], is focused on the difference of chemical shifts between each pair of calixarene ArCH2Ar methylene protons. These can show diasterotopicity resulting in AX or AB systems. Specifically, a 1H NMR methylene proton Δδ value of at least 0.7 shows that the two respective proximal aromatic rings are oriented syn, as in the cone conformation. In contrast, a Δδ value of 0.3 or less is attributable to an anti-orientation between the phenol rings, as in alternate conformations. The de Mendoza’s "13C NMR single rule" [30,31], is focused on the 13C NMR chemical shift of the ArCH2Ar methylene C, which is 30–33 ppm with the syn-orientation of the proximal phenol rings and typically 36–39 ppm with anti-positioned phenol rings as in alternate conformations.

As exemplified above, the calix[6]arene macrocycle has been widely used as wheel for the assembly of pseudorotaxane architectures [32,33], where it usually adopts a cone conformation. The examples reported by us [33-38] (Figure 4b) and by Arduini [32,39] (Figure 4a) showed that the directionality of the calixarene wheel in the cone conformation plays a pivotal role in the formation of stereoisomeric directional pseudo[2]rotaxanes, rotaxanes, and catenanes. Also in this case [38], we were able to obtain a stereoselective threading of the cone calix[6]arene-wheel with alkylbenzylammonium axles (Figure 4b), in which the endo-alkyl pseudo[2]rotaxane stereoisomer was the favoured one [38].

The threading of calix[6]arene macrocycles in conformations different than the cone one has been rarely observed [17]. Interestingly, the assembling of interpenetrated structures in which
Figure 3: The possible 8 discrete conformations of a calix[6]arene macrocycle [26].

The wheel adopts different conformational isomers, could pave the way to mechanomolecules which exhibit novel isomeric forms.

Prompted by these considerations, some examples of pseudorotaxane isomers in which the isomerism arises by the different conformations adopted by the calixarene wheel are reported here.

Results and Discussion

With this goal in mind, we conducted an initial screening in order to select the ammonium axles and the calix[6]arene-wheel most suitable for our purposes. At the end of our screening, we focused our attention on hexahexyloxycalix[6]arene 1 as the wheel and bis(4-biphenylmethyl)ammonium (2+) and bis(4-trifluoromethylbenzyl)ammonium (3+, TFPB− salts) as the threads. The synthetic pathway to 2+·TFPB− and 3+·TFPB− salts is outlined in Scheme 1, while calix[6]arene 1 was obtained following a known procedure [40].

The 1H NMR spectrum of hexahexyloxycalix[6]arene 1 in CDCl3 at 298 K shows broad ArCH2Ar signals indicative of a conformational mobility of the macrocycle in which the inversion between the calix[6]arene conformations (Figure 5), occurs by means of rotation around the ArCH2Ar bonds.

By lowering the temperature, the ArCH2Ar signal decoalesced to form a single AX system (3.34/4.49 ppm) and one broad singlet (3.77 ppm). This pattern is only compatible with the presence of a 1,2,3-alternate conformation of calix[6]arene 1 (Figure 5). This was confirmed by a 2D HSQC spectrum of 1 at 233 K which evidenced the presence of ArCH2Ar correlations between the AX system at 3.34/4.49 ppm with a carbon resonance at 29.4 ppm, related to syn-oriented Ar rings [29]. Diagnostic of the presence of the 1,2,3-alternate conformation of 1 is the presence of the broad singlet at 3.71 ppm which correlates in the HSQC spectrum with a carbon resonance at 34.1 ppm [30], related to anti-oriented Ar rings. A close inspection of the 1D and 2D NMR spectrum of 1 in CDCl3 at 233 K...
clearly evidenced the presence of a less abundant conformer of 1. The nature of this minor conformer can be inferred by the work of Reinhoudt and co-workers which showed [41] that the conformations preferentially adopted by calix[6]arene hexaethers are the cone and 1,2,3-alternate ones. In accordance, 2D COSY and HSQC spectra of 1 at 233 K clarified that this minor conformer was the cone one through the presence of an AX system at 3.35/4.42 ppm (COSY), which correlates with a
Scheme 1: Synthesis of threads $2^*$ and $3^*$. Reagents and conditions: a) hexamethyldisilazane, LiClO$_4$, 30 min, 60 °C; b) CH$_3$OH, NaBH$_4$, 2 h, 25 °C; c) TFPBNa, dry MeOH, 25 °C, 18 h.

Carbon resonance at 29.1 ppm (HSQC), related to syn-oriented Ar rings (cone conformation). The coalescence temperature of the methylene protons was ascertained at 328 K in CDCl$_3$; below this temperature the conformations of $1$ were frozen, while at temperatures above 328 K the conformational interconversion is fast with respect to the NMR time scale (400 MHz). From the coalescence data we calculated a barrier of 14.6 kcal/mol for this process. In summary, the VT $^1$H NMR studies indicate that the 1,2,3-alternate is the most stable conformation for hexahexyloxycaix[6]arene $1$ in solution. This conclusion is in perfect accord with the results previously reported by Reinoudt [41], which evidenced an increased stabilization of the 1,2,3-alternate conformation of calix[6]arenes when the alkyl substituents at the lower rim are increased in size [41].

As expected [40], no evidence of interaction between $2^*$ and $1$ was detected by NMR, when $2^*$ was added as its chloride salt to a CDCl$_3$ solution of $1$. However, when $2^+$ was added as its TFPB$^-$ salt to a CDCl$_3$ solution of $1$, then dramatic changes were observed in the $^1$H NMR spectrum of $1$ (Figure 6).

In detail, immediately after the mixing of $1$ and $2^+$ we observed the sharpening of all signals and the appearance of an AX system at 5.50/6.70 ppm attributable to aromatic H-atoms of the axle $2^+$ shielded inside the calixarene cavity. These changes were indicative of the formation of a pseudorotaxane $2^+\cdot 1$. With this result in hand, we turned our attention to the conformation adopted by the calix[6]arene-wheel $1$ in pseudorotaxane $2^+\cdot 1$. A 2D COSY spectrum of 1:1 mixture of
I and 2⁺, immediately after mixing in CDCl₃, revealed the presence of a single AX system at 3.53/4.73, which correlates with a carbon resonance at 28.9 ppm, respectively, due to the ArCH₂Ar methylene groups between syn-oriented Ar rings. A close inspection of the 2D HSQC spectrum revealed the presence of a cross-peak at 3.93/36.5 ppm attributable to an ArCH₂Ar methylene bridge between anti-oriented Ar rings. These data clearly indicate that calixarene-wheel 1 adopts the 1,2,3-alternate conformation in pseudorotaxane 2⁺⁺₁₁,₂,₃-alt (Figure 5 and Figure 6).

A further inspection of the 1D and 2D (COSY-45 and HSQC) spectra of the 1:1 mixture of I and 2⁺ in CDCl₃ immediately after mixing, revealed the presence of a less abundant pseudo[2]rotaxane species in which probably the calixarene wheel 1 adopts a cone conformation 2⁺⁺₁cone (Figure 5). Initially, the ratio between the two isomeric pseudorotaxane 2⁺⁺₁cone/2⁺⁺₁₁,₂,₃-alt is 1/20, as calculated by integration of the corresponding ¹H NMR signals. Interestingly, after 10 h at 298 K (Figure 6), the intensity of the ¹H NMR signals of pseudorotaxane 2⁺⁺₁₁,₂,₃-alt was decreased while that of
Figure 6: $^1$H NMR spectra (600 MHz, CDCl$_3$, 298 K) of, from bottom to top: hexahexyloxycalix[6]arene 1; a 1:1 mixture (0.003 M) of 1 and $2^+\text{TFPB}^-$ immediately after mixing; after 10 h; after 18 h.

$2^+c\text{cone}$ 1 was increased. After 18 h at 298 K, the disappearance of $2^+c1^{1,2,3-alt}$ was complete and only $2^+c\text{cone}$ pseudorotaxane could be detected by 1D and 2D NMR studies (Figure 6). In fact, a 2D COSY spectrum of the 1:1 mixture of 1 and $2^+$ in CDCl$_3$, after 18 h at 298 K, showed the presence of an ArCH$_2$Ar AX system at 3.47/4.62 ppm which correlates in the HSQC spectrum with a carbon resonance at 28.4 ppm related to syn-oriented Ar rings. An AX system was present in the COSY spectrum at 4.78/5.68 ppm attributable to aromatic protons of the axle $2^+$ shielded inside the calixarene cavity. This
shielded AX system correlates in the HSQC spectrum with aromatic carbon resonances at 129.8 and 126.8 ppm, respectively.

The $^1$H NMR spectrum of the mixture of 1 and $2^+$ in CDCl$_3$ remained unchanged after 48 h at 298 K, thus showing that the system had reached the equilibrium condition. At this point, an apparent association constant of $6.2 \pm 0.3 \times 10^3$ M$^{-1}$ was calculated by quantitative $^1$H NMR analysis (tetrachloroethane as internal standard) [37] for the formation of $2^+ \text{c}1^\text{cone}$ pseudorotaxane. In conclusion, after the initial formation of the kinetically favored pseudorotaxane $2^+ \text{c}1^\text{1,2,3-alt}$ (Figure 5), the thermodynamic pseudorotaxane $2^+ \text{c}1^\text{cone}$ prevails (Figure 5 and Figure 6). As demonstrated above, the 1,2,3-alternate conformation of 1 is the most populated in solution, consequently, the threading of this conformation, besides being faster, it is also favored by its abundance in solution.

The greater thermodynamic stability of the $2^+ \text{c}1^\text{cone}$ atropoisomer over the $2^+ \text{c}1^\text{1,2,3-alt}$ one, was confirmed by DFT calculations at the B3LYP/6-31G(d,p) level of theory using Grimme’s dispersion corrections (IOp(3/124=3)) [42]. The DFT-optimized structure of the $2^+ \text{c}1^\text{cone}$ atropoisomeric pseudorotaxane (Figure 7, left) results stabilized by two H-bond interactions between the ammonium group and the oxygen atoms of the calixarene wheel 1, (average N···O distance = 3.10 Å; average N–H···O angle = 157°). In addition, C–H···π interactions were detected among the methylene groups of the axle $2^+$ inside the calix cavity, and the aromatic rings of 1 (average C–H···π centroid distance = 3.17 Å [42]; average C–H···π centroid angle = 160° [43]).

In addition, the biphenyl portion of $2^+$ hosted inside the calix cavity was involved in π···π interactions with the aromatic walls (Figures S11–S13, Supporting Information File 1) and C–H···π interactions with the tert-butyl groups of the calixarene wheel (Figure S13, Supporting Information File 1). Differently, in the DFT-optimized structure of $2^+ \text{c}1^\text{1,2,3-alt}$ atropoisomer (Figure 7, right), the stabilization of the $2^+ \text{c}1^\text{1,2,3-alt}$ atropoisomer was brought, principally by two H-bonding interactions between the ammonium group of $2^+$ and the oxygen atoms of anti-oriented phenol rings of 1 with an average N···O distance of 3.05 Å and a narrower N–H···O angle of 167.1°. Single-point calculations at the B3LYP/6-31G(d,p) level of theory using Grimme’s dispersion corrections (IOp(3/124=3)), indicated that the $2^+ \text{c}1^\text{cone}$ atropoisomer was more stable than the $2^+ \text{c}1^\text{1,2,3-alt}$ one by 2.4 kcal mol$^{-1}$. At this point, it is worthy to consider the interconversion between the two isomeric pseudorotaxane $2^+ \text{c}1^\text{1,2,3-alt}$ and $2^+ \text{c}1^\text{cone}$. It could take place through two possible mechanisms (Figure 5): a) de-threading of axle $2^+$ from

**Figure 7:** DFT-optimized structures of the: (left) $2^+ \text{c}1^\text{cone}$ and (right) $2^+ \text{c}1^\text{1,2,3-alt}$ pseudorotaxane atropoisomers calculated at B3LYP/6-31G(d,p) level of theory and using Grimme’s dispersion corrections (IOp(3/124 = 3)).
$2^+\cdot 1^{1,2,3\text{-alt}}$ and a subsequent re-threading with $1$ in a cone conformation; b) a direct conformational interconversion between the $1,2,3$-alternate and cone conformations of the calixarene wheel $1$ in both $2^+\cdot 1$ pseudorotaxanes. Previously reported data [34] clearly showed that the mechanism “b” in Figure 5 can be ruled out because the presence of an axle inside the cavity of $1$ impedes the "through-the-annulus" passage of both rims of $1$. From this consideration, we concluded that the two pseudorotaxanes $2^+\cdot 1^{1,2,3\text{-alt}}$ and $2^+\cdot 1^{\text{cone}}$ can be considered as two atropoisomeric forms. In fact, the interconversion between them cannot be obtained by simple rotation around chemical bonds of the calixarene wheel, which is blocked by the presence of the axle inside its cavity.

Previously [34] we reported a similar case in which the monostoppered alkylbenzylammonium axle $6^+$ gives rise to two atropoisomeric pseudorotaxanes $6^+\cdot 1^{\text{cone}}$ and $6^+\cdot 1^{1,2,3\text{-alt}}$ (Figure 8). Also in this instance, the pseudorotaxanes $6^+\cdot 1^{1,2,3\text{-alt}}$ and $6^+\cdot 1^{\text{cone}}$ were observed as the kinetic and thermodynamic adduct, respectively, with an interconversion time of 12 h at 353 K. A further example regards the threading of the narrower penta-$O$-methyl-$p$-tert-butylcalix[5]arene $7$ with pentylbenzylammonium axle $8^+$ [35]. Two atropoisomeric pseudorotaxanes were formed, namely $8^+\cdot 7^{\text{cone}}$ and $8^+\cdot 7^{\text{pacu}}$ (Figure 9), in which the calix[5]-wheel adopted a cone and a partial-cone conformation, respectively [35]. Also in this case, the atropoisomer with an "inverted" calixarene wheel $8^+\cdot 7^{\text{pacu}}$ is the kinetic product, while the other with a calix-cone conformation $8^+\cdot 7^{\text{cone}}$ is the thermodynamic one [35].

At this point we turned our attention to the threading properties of bis(4-trifluoromethylbenzyl)ammonium axle $3^+$. When $1$ and $3^+\cdot$ TFPB$^-$ were mixed in CDCl$_3$ two atropoisomeric pseudo[2]rotaxane, $3^+\cdot 1^{\text{cone}}$ and $3^+\cdot 1^{1,2,3\text{-alt}}$ (Figure 10), were formed in a 1/10 ratio, as revealed by 1D and 2D NMR studies. Also in this case, after equilibration at 298 K for 24 h, this preference was reversed in favour of the $3^+\cdot 1^{\text{cone}}$ atropoisomer, with a $3^+\cdot 1^{\text{cone}}/3^+\cdot 1^{1,2,3\text{-alt}}$ ratio of 8/1. From the equilibrium mixture, an apparent association constant of $9.3 \pm 0.4 \times 10^2$ M$^{-1}$ was calculated by quantitative $^1$H NMR analysis (tetrachloroethane as internal standard) for the formation of $3^+\cdot 1^{\text{cone}}$ pseudorotaxane. In a similar way, an apparent association constant of $120 \pm 15$ M$^{-1}$ was found for $3^+\cdot 1^{1,2,3\text{-alt}}$ pseudorotaxane.

As evidenced for axle $2^+$, also in this case, after the initial formation of the kinetic pseudorotaxane $3^+\cdot 1^{1,2,3\text{-alt}}$ (Figure 10), the thermodynamic atropoisomer $3^+\cdot 1^{\text{cone}}$ prevails. However, differently from the $2^+$ case where the kinetic product was no longer detectable in the final equilibrium mixture, here a size-

\[2120\]
Figure 9: The two pseudorotaxane atropoisomers obtained by threading penta-O-methyl-p-tert-butylcalix[5]arene 7 with pentybenzylammonium axle 8*.
Figure 10: $^1$H NMR spectra (600 MHz, CDCl$_3$, 298 K) of, from bottom to top: hexahexyloxycalix[6]arene 1; a 1:1 mixture (0.003 M) of 1 and $3^*$ TFPB$^-$ immediately after mixing; after 2 h; after 18 h, mechanism for the formation of the two atropoisomeric pseudo[2]rotaxanes $3^*_{\text{1 cone}}$ and $3^*_{\text{1,2,3-alt}}$. 
pressure, to give secondary amine derivative. Amine was used without further purification in the next step. Secondary amine derivative (1.16 mmol) was dissolved in MeOH (20 mL) at room temperature and an aqueous solution of HCl (37% w/w, 0.20 mL) was added dropwise. The mixture was kept under stirring for 30 min, until the formation of a white precipitate. The solid was collected by filtration, washed with MeOH (10 mL) and CH₂CN (10 mL) and dried under vacuum to give the ammonium chloride derivative. The chloride salt (0.68 mmol) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (0.60 g, 0.68 mmol) were dissolved in dry MeOH (15 mL). The solution was stirred for 18 h in the dark, then the solvent was removed and deionized water was added, obtaining a light brown precipitate, that was filtered off and dried under vacuum to give threads 2⁺ or 3⁺.

**Derivative 2⁺**

Light brown solid, 0.73 g, 0.60 mmol, 88% yield (respect chloride salt); mp 135–138 °C; ESI(+) MS (m/z): 350.2 (M⁺);

**¹H NMR** (400 MHz, CDCl₃, 298 K) δ 3.74 (s, 4H), 7.30–7.32 (overlapped, 20H); 13C NMR (100 MHz, CDCl₃, 298 K) δ 51.7, 118.4, 118.4, 118.5, 121.7, 124.4, 127.1, 128.0, 128.8, 129.0, 130.0, 130.2, 130.3(2), 130.5(2), 130.6, 131.2, 131.5, 135.8, 141.3, 143.9, 161.2, 162.6, 163.1, 163.6; anal. calcd for C₂₄H₂₆BF₂₃N₂: C, 57.40; H, 2.99; found: C, 57.39; H, 3.01.

**Derivative 3⁺**

Light brown solid, 0.57 g, 0.48 mmol, 70% yield (respect chloride salt); mp 125–128 °C; ESI(+) MS (m/z): 334.1 (M⁺);

**¹H NMR** (300 MHz, CDCl₃, 298 K) δ 3.73 (s, 4H), 7.30–7.32 (overlapped, 20H); 13C NMR (75 MHz, CDCl₃, 298 K) δ 52.6, 118.3, 118.5, 118.6, 122.0, 125.4, 127.3, 128.3, 128.9, 129.1, 130.0, 130.4, 130.5(2), 130.6, 131.2, 131.6, 135.8, 141.4, 144.0, 162.2, 162.7, 163.2, 163.5; anal. calcd for C₄₈H₃₆BF₂₄N₂: C, 48.14; H, 2.19; found: C, 48.13; H, 2.17.

**General procedure for the preparation of pseudorotaxane derivatives**

The calixarene derivative 1 (3.0 mM) and ammonium salt 2⁺ or 3⁺ (3.0 mM) were dissolved in CDCl₃ (0.5 mL). Each solution was sonicated for 15 min at room temperature and then was transferred into a NMR tube for 1D and 2D NMR spectra acquisition.

**Determination of apparent Kₐ value for pseudorotaxanes**

The sample was prepared by dissolving calixarene 1 (3.0 × 10⁻³ M) and the ammonium TFPB salt 2⁺ or 3⁺ (3.0 × 10⁻³ M) in CDCl₃ (0.5 mL) containing 1.0 µL of TCHE (d = 1.596 g/mL) as an internal standard. The complex concentration [complex] was evaluated by integration of the ¹H NMR signal of TCHE versus the signals of the pseudorotaxane. The following equation was used to obtain the moles of the complex:

\[ \frac{G_a}{G_b} = \frac{F_a}{F_b} \times \frac{N_b}{N_a} \times \frac{M_a}{M_b}, \]

where \( G_a \) = grams of TCHE, \( G_b \) = grams of pseudorotaxane, \( F_a \) and \( F_b \) = areas of the signal of the TCHE and shielded aromatic protons of axle inside the calixarene cavity, \( N_a \) and \( N_b \) = numbers of nuclei that cause the signals (\( N_a \) for TCHE; \( N_b \) for pseudorotaxane) and \( M_a \) and \( M_b \) = molecular masses of TCHE (a) and pseudorotaxane (b).

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**Supporting Information**

**Supporting Information File 1**

VT NMR studies of hexyloxycalix[6]arene 1, 2D COSY and HSQC spectra of atropoisomeric pseudorotaxanes, details of DFT calculations and atomic coordinates.

[https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-14-186-S1.pdf]

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