

## Towards a Fully Conjugated, Double-Stranded Cycle: A Mass Spectrometric and Theoretical Study

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**Abstract:** The two compounds, **1** and **5**, are investigated by means of collision-induced dissociation experiments by using ion cyclotron resonance mass spectrometry and other mass spectrometric techniques as to their ability to act as precursors for the fully unsaturated double-stranded target compound **2**. These experiments are complemented by flask-type pyrolyses of **5**, the products of which are analyzed by

mass spectrometry. For **1**, no conditions were found under which the expected molecular ion of **2** at  $m/z$  932 appeared, however, for its derivative **5** this was possible. This interesting finding is not in contradiction with the

chemical structure of the long sought for compound **2** but calculations suggest that this compound may have isomerized into one where the conjugation is interrupted by hydrogen shift from the solubilizing alkyl chains into the cycle's perimeter. The key driving force for such an isomerization would be the considerable relief of strain energy.

**Keywords:** aromaticity · collision experiments · gas-phase reactions · molecular belts · pyrolysis

### Introduction

In a recent review article on molecular loops and belts, Y. Tobe pointed out that “[*n*]cyclacenes have been one of the

most fascinating yet unrealized target molecules for synthetic chemists”.<sup>[1]</sup> This statement describes to the point a rather unfortunate situation in which several groups worldwide have undertaken enormous efforts to find access to compounds with the general structure **A** or their closely related congeners **B** (Figure 1).<sup>[2]</sup> So far only potential precursors have been prepared, which all are characterized by an interrupted  $\pi$ -conjugation. Chemical conversions of any of these “precursors” to the respective through-conjugated targets failed altogether, whereas the same conversions worked well when applied to non-cyclic model compounds.<sup>[3]</sup> A recent, rather astonishing observation along these lines is the finding that treatment of **1** (Figure 1) with concentrated sulphuric acid at 150 °C left this material completely unchanged, whereas model **3** underwent clean dehydration to **4** under much milder conditions (Scheme 1).<sup>[4]</sup> The reluctance of cyclic precursors to undergo aromatization led to the perception that such transformations are associated with a considerable energy price, namely the build-up of strain, which “protects” the aromatic targets from forming.<sup>[5]</sup>

In another recent experiment it was reported that precursor **1** in the presence of methylsulfonic acid at 150 °C suffers conversion into an insoluble black material, the structural analysis of which did not yet lead to an unambiguous result but, at the same time, is not in contradiction to the assumption of an intermediately formed, possibly more conjugated transient species which subsequently suffers cross-linking.<sup>[4]</sup>

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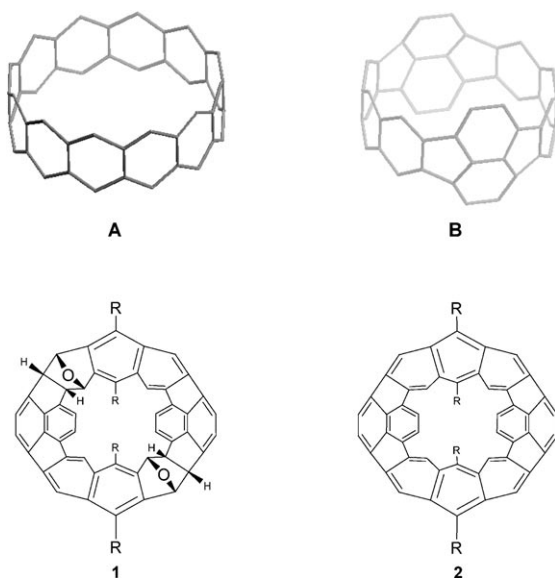
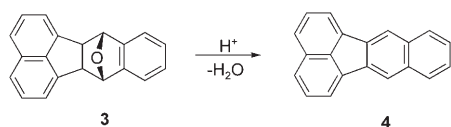


Figure 1. Side view of an (unknown) cyclacene (**A**) and the belt-region of a buckyball (**B**) (Double-bonds and side chains omitted for clarity) as well as the chemical structures of a potential precursor, **1**, for the belt of fullerene  $C_{84}$  ( $D_2$ ), **2**. R = hexyl.



Scheme 1. Dehydration of the non-cyclic model compound **3** to its fully conjugated congener **4**.

Given these findings spanning between “no reaction at all” and possibly “overreaction” into a brickstone-like, black network, it was considered advisable to test other variants of how to generate and analyze target compound **2**. The mass spectrometer has proven a useful tool in the identification of otherwise inaccessible compounds and spectacular cases were reported. Many examples of unique structures that were synthesized and analysed in the gas phase using special mass spectrometric techniques are known, for example, the pioneering finding of fullerenes by Smalley and co-workers.<sup>[6]</sup>

We report here mass spectrometric experiments which shine more light onto possible ways leading to the fully aromatic target structure **2** and related compounds. The interpretation of some mass spectrometric results is supported by quantum-mechanical calculations.<sup>[7]</sup>

## Results and Discussion

**Compound 1, a potential precursor for 2?** Flask-type experiments aiming at generating the fully aromatic derivative **2** of the belt-shaped macrocycle **1** through acid-catalyzed de-

hydration reactions at elevated temperatures did not lead to success as yet. This failure initiated thoughts whether it would be possible to enforce the elimination of **1**'s two formal water molecules (water: oxygen bridge plus adjacent two hydrogen atoms) under mass spectrometric conditions. In the initial publication on compound **1**, its electron impact (EI) mass spectrum was reported to show the molecular ion peak at  $m/z$  968 and also a peak at  $m/z$  484, which had the highest intensity. This latter peak appeared at half the mass of the parent ion which may indicate that fragmentation under EI conditions passes through a retro-Diels–Alder (RDA) channel. The present work started therefore in applying different mass spectrometric conditions to **1** to see whether other fragmentation paths could be activated. Therefore, MALDI spectra were run both in the presence and absence of acidic matrix materials [2,3-dihydroxybenzoic acid (DHB)]. In either case very similar spectra were obtained as the above EI spectrum, revealing the presence of both ions. In order to make sure that it was in fact RDA which generated the peak at  $m/z$  484 and not a sequence of fragmentations which may comprise dehydration, collision induced dissociation (CID) experiments were performed with cationized **1** that was generated in an electrospray ionization (ESI) source connected to an ion cyclotron resonance (ICR) mass spectrometer. For this purpose compound **1** was converted into a charged species by injecting it into the ESI source in methanol ( $\sim 10^{-5}$  g mL<sup>-1</sup>) in the presence of AgNO<sub>3</sub> (addition of 5  $\mu$ L of a 0.001 g mL<sup>-1</sup> stock aqueous solution to 1 mL of sample in methanol). The resulting [**1**+<sup>109</sup>Ag]<sup>+</sup> ions were isolated as single entities in the gas phase and then activated by collisions with argon atoms. This treatment afforded exclusively the product ion of  $m/z$  484 (Figure 2) which strongly supports the proposed RDA fragmentation channel (Scheme 2). Thus, not only the pyrolysis of **1** during the MALDI experiment but also the gas phase experiments show that the availability of higher energy does not enable the formation of **2** from **1** and that, therefore, compound **1** does not seem to be an appropriate precursor for **2**.

**Tetraacetate 5, a precursor for “2”:** These findings made it necessary to use potential precursors for **2** which could not undergo RDA. This prerequisite was fulfilled with com-

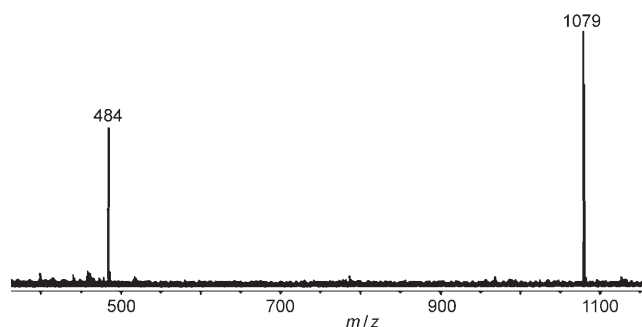
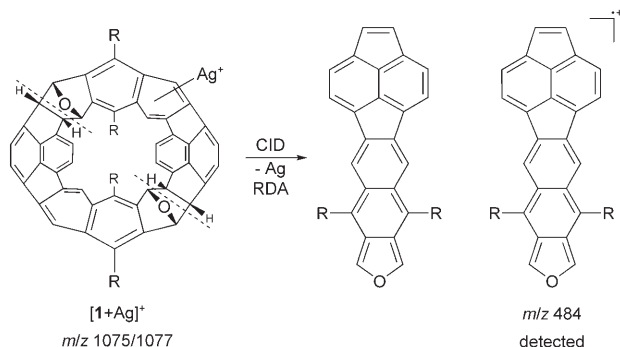


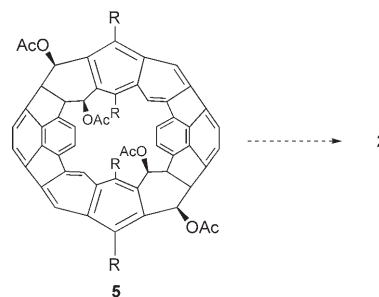
Figure 2. Isolated [**1**+<sup>109</sup>Ag]<sup>+</sup> ion and its decomposition product at  $m/z$  484 after collision with argon atoms.



Scheme 2. Proposed decomposition of  $[1+^{109}\text{Ag}]^+$  according to a retro-Diels–Alder (RDA) pathway in CID experiments using argon.

compound **5**<sup>[4]</sup> which, as a tetraacetate, had the additional benefit of potentially being able to undergo acetic acid eliminations, which are well-established organic chemistry tools for synthesizing olefins under pyrolytic conditions.<sup>[8]</sup> In the concrete case, four such eliminations would lead directly to target **2** (Scheme 3).

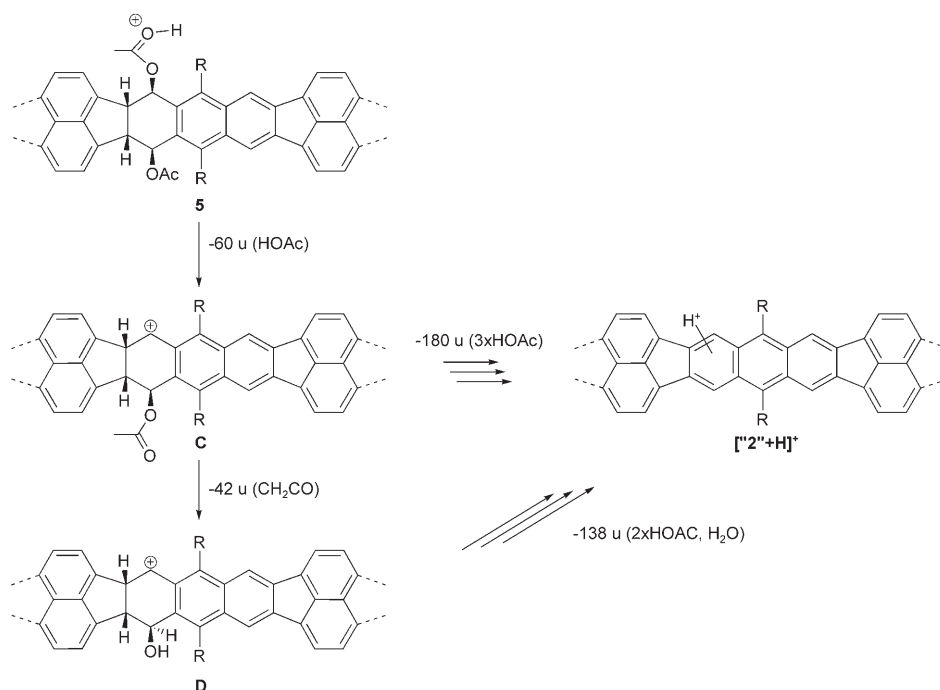
Compound **5** was analyzed by MALDI mass spectrometry (without matrix) and showed the expected molecular ion of  $m/z$  1172. Upon electrospray ionization,<sup>[9]</sup> the  $[M+H]^+$  ion could not be observed but instead its decomposition product, the  $[M+H-\text{AcOH}]^+$  ion of  $m/z$  1113 was detected. This ion, which in Scheme 4 and Figure 3a is referred as **C**, was subjected to collisions with argon atoms under CID conditions and the resulting fragmentation studied. There seem to be two competing channels for the fragmentation of the acetic acid moieties which involve either the direct fragmentation of the entire moiety ( $-60$  Da) or a two-step event in which first ketene ( $-42$  Da) is cleaved off which is then followed by loss of a water molecule ( $-18$  Da).<sup>[10]</sup> Thus, according to the first variant, the formation of **H** from **C** (Figure 3a) passes through the ions **E** and **F** by three sequential losses of acetic acid, finally giving rise to ion **H** at  $m/z$  933 which corresponds to the mass expected for protonated **2** ( $[2+H]^+$ ). In the second variant, the fragmentation of **C** starts with the well-known<sup>[10]</sup> elimination of ketene ( $-42$  Da) affording ion **D** of  $m/z$  1071. This ion then further dissociates by the loss of water to give **E**. Ketene fragmentation is also observed for **F**



Scheme 3. Starting compound **5** for mass spectrometry and flask-type experiments aiming at cleaving off the four acetic acid moieties on the way to the fully aromatic belt **2**.

which results in the formation of **G**. Subsequently **G** suffers loss of water to give **H**.

Thus, upon acid-catalyzed fragmentation of the tetraacetate precursor **5**, a species is generated in the gas phase whose molar mass corresponds to the one expected for the protonated form of **2**. The simplest (and perhaps most appealing) assumption would be that this species is in fact  $[2+H]^+$ . It is important to note, however, that eventual rearrangements of either the carbon skeleton of **2**<sup>[11]</sup> or its protons<sup>[12]</sup> would not be detected by this mass spectrometry experiment and can therefore not be excluded. This is why the number of this product is put into quote (“**2**”) throughout the paper. A theoretical treatment of some rearrangements is given below.



Scheme 4. Possible fragmentation paths of compound **5** under acidic conditions. Note that the intermediates **C** and **D** in this representation still contain two acetate units in their non-shown parts. Also note that there is no information about the regiochemical course of the fragmentation. It may well be that the first two acetates are not cleaved off at the same six-membered ring as this scheme suggests. R = hexyl.

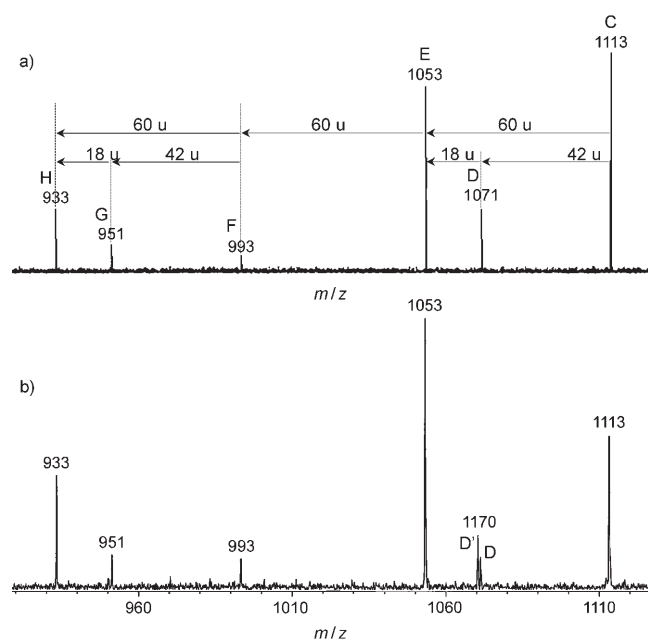
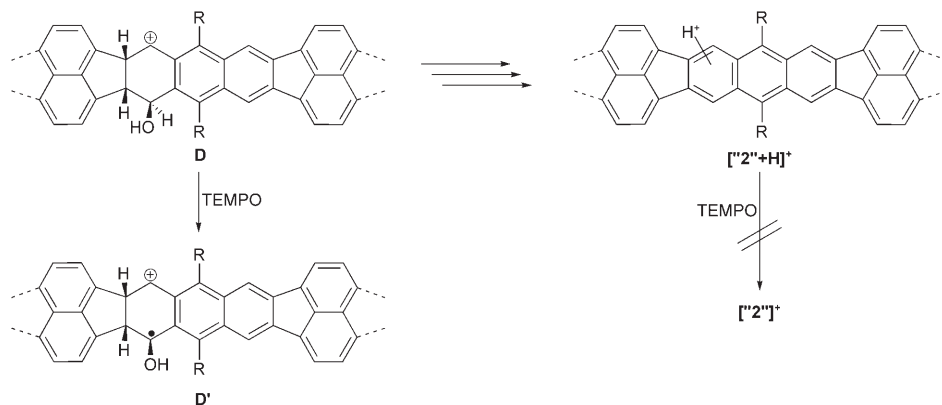


Figure 3. CID mass spectra of the  $[5+H-AcOH]^+$  ion (C) in the absence (a) and presence of TEMPO (b). The spectrum in a) shows the two different decomposition paths. The ion  $D'$  in b) is generated from  $D$  by collision with TEMPO which is concluded from the fact that only when TEMPO is present, a signal at  $m/z$  1070 is observed. For further explanation see Scheme 4 and text.

In order to generate the non-protonated molecular ion of “2” in the gas phase, the  $[M+H]^+$  ion of  $m/z$  933 (H) has to lose a hydrogen atom. Hence the CID experiment was repeated in the presence of the persistent radical tetramethylpiperidine oxide (TEMPO) which is known to abstract labile hydrogen atoms (Scheme 5).<sup>[13]</sup> The CID spectrum of the  $[M+H-AcOH]^+$  ion of “2” in the presence of TEMPO (Figure 3b), however, indicated the abstraction to take place only from ion  $D$ , giving rise to radical cation  $D'$ , and not from  $H$ . Unfortunately, the ion  $[“2”+H]^+$  itself stayed unchanged. At this point it was concluded that by this technique it was not easily possible to get a direct proof for the existence of the molecular ion of “2”.



Scheme 5. CID experiments aiming at the generation of the molecular ion of “2”. R = hexyl.

In a closely related CID experiment the starting compound **5** was treated with  $AgNO_3$  prior to electrospray ionization. In contrast to the above experiment, where the  $[M+H]^+$  ion ( $[5+H]^+$ ) was not stable enough to be subjected to CID, the corresponding  $[M+Ag]^+$  ion ( $[5+Ag]^+$ ) could in fact be isolated and provided the opportunity to monitor the entire fragmentation process (Figure 4). Here however the ketene variant is less prominent.

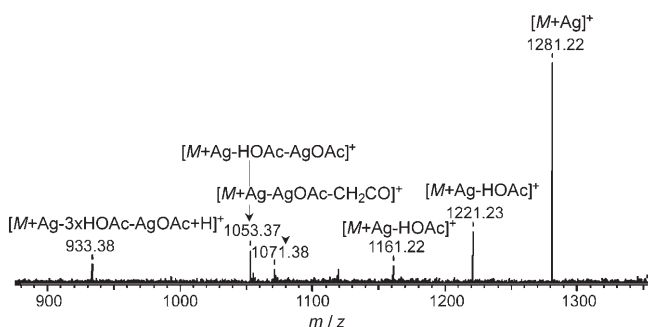


Figure 4. CID mass spectrum of the  $[5+Ag]^+$  ion showing the entire fragmentation process from  $[M+Ag]^+$  all the way to  $[M+Ag-3HOAc-AgOAc]^+$  which corresponds to ion **H** of Figure 3. The ketene variant does not seem to be very relevant here.

**Pyrolysis of compound 5 to generate “2”:** Stimulated by the promising finding that four acetates can be cleaved off the starting compound **5**, its pyrolysis was also tried in preliminary flask-type experiments and the products analysed by mass spectrometry. 10–40 mg of the fine, yellow powder of **5** were placed in a small flask together with a large excess of freshly sublimed, parent anthracene to discourage eventual oligomerization. After evacuation, the flask was immersed into a pre-heated metal bath (330 °C), whereupon the anthracene melted within approximately 1 min and a homogeneous mixture formed.<sup>[14]</sup> After 3 min the flask was removed from the bath and allowed to cool. The entire mixture had changed its color to deep-red and was applied as obtained to a recycling, high-pressure GPC. During the first cycle several fractions were isolated, whose comprehensive analysis is rather complex and will be reported later.<sup>[15]</sup> In one such experiment a fraction with a medium retention time was isolated and analyzed by MALDI-TOF mass spectrometry (Figure 5).

The spectrum of this fraction indicates a mixture of compounds, only some of which could be identified. An abundant ion was observed around  $m/z$  933, while the mass of the expected target **2** is 932 Da. It is also apparent that the group of peaks around  $m/z$  933 is

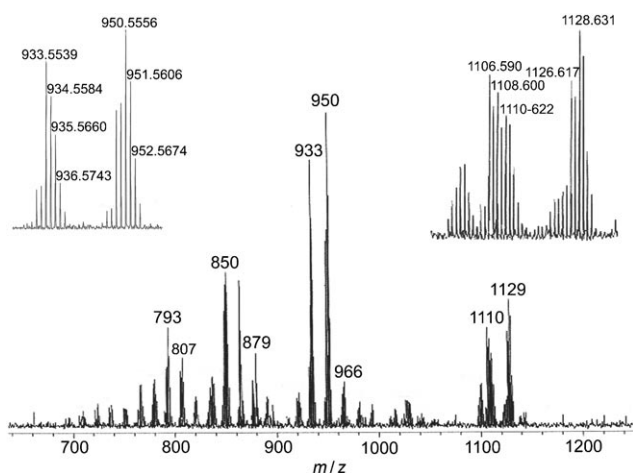


Figure 5. MALDI-TOF mass spectrum of an intermediate fraction of the flask-type pyrolysis of compound **5** in the presence of a large excess of anthracene (no matrix).

rather complex and therefore reasonable to assume that ionized, protonated and reduced species coexist. The reduced species would result from dihydrogen additions which are not typical for aromatic compounds (see below). Also present is a group of peaks at  $m/z$  950, the relative intensities of which vary from one experiment to the next and appear as a mixture of ions differing from one another by 1 Da. This signal group has tentatively been assigned to the [ $\text{“2”} + \text{H}_2\text{O}$ ] $^+$  ion and may either be the product of a covalent water addition to  $\text{“2”}$ <sup>[16]</sup> or one of the pyrolysis products that is reluctant to eliminate a water molecule. The former assignment may be considered unusual but is backed by the results of a calculation according to which such an addition is enthalpically feasible (see below). Finally, the ions at  $m/z$  1110 and 1128 indicate addition of anthracene to  $\text{“2”}$  and to  $\text{“(2+H}_2\text{O)”}$ , respectively. The latter assignment may have future mechanistic implications<sup>[17]</sup> and was therefore confirmed by independent high resolution MALDI mass spectrometry which afforded  $m/z$  1110.622 (calcd: 1110.6104) and  $m/z$  1128.631 (calcd: 1128.6209), respectively. A structural proposal for the anthracene adducts cannot be made at present. It should be noted that the fraction did not contain any free anthracene and that therefore the anthracene adducts could not have been formed in the mass spectrometer.

In an independent pyrolysis the last fraction of the recycling GPC separation was analyzed in somewhat more detail which led to a deeper insight into the composition of the rather complex patterns in which relevant ions appear in the mass spectrum depicted in Figure 5. Figure 6 contains the low and high mass range parts of a MALDI-TOF spectrum of this fraction together with calculated isotope distributions of relevant intermediates. From the bottom lines of Figure 6 it seems that this fraction<sup>[18]</sup> consists of three components, which give rise to the molecular ion minus two, three and four acetic acid molecules. The signals show an increasing complexity in this order. For an assignment they were compared with calculated isotopic distributions taking reduc-

tions by two hydrogen atoms into account. The experimental signal at  $m/z$  1052 ([ $\text{5-2HOAc}$ ] $^+$ ) is almost identical with the calculated one (Figure 6, right column, line two from top) which indicates that negligible reduction has taken place if any. The experimental signal group above  $m/z$  990 consists of two isotopic patterns, the one that starts at  $m/z$  992 is corresponding to the [ $\text{5-3HOAc}$ ] $^+$  ion and the one starting at  $m/z$  994 to [ $\text{5-3HOAc} + 2\text{H}$ ] $^+$ . The latter is thus a reduction product. The most important signal group, finally, appears at above  $m/z$  930 and consists of three superimposed isotopic patterns as the comparison with the three calculated spectra on top of it show. First, the pattern of the [ $\text{5-4HOAc}$ ] $^+$  ion at  $m/z$  932 can be identified. This is superimposed by two series of reduction products, namely [ $\text{5-4HOAc} + 2\text{H}$ ] $^+$  starting at  $m/z$  934 and [ $\text{5-4HOAc} + 4\text{H}$ ] $^+$  starting at  $m/z$  936. The fact that the isotopic series starting at  $m/z$  932 can actually be detected shows that in contrast to the measurements discussed above the present experiments provide an opportunity to get hold of the true molecular ion of  $\text{“2”}$ . Compound  $\text{“2”}$  obviously has a tendency to add two hydrogen atoms in each of the two consecutive reduction steps and not more. It should be noted that this hydrogen addition does not take place in the mass spectrometer. Repeated measurements under different conditions leave the proportion between hydrogenated and non hydrogenated compounds unaltered.

This observation supports  $\text{“2”}$  to have two anthracene units, the reduction of each of which at the 9,10-positions would be energetically favourable in light of the proven desire of **2** to reduce its strain (see next section).

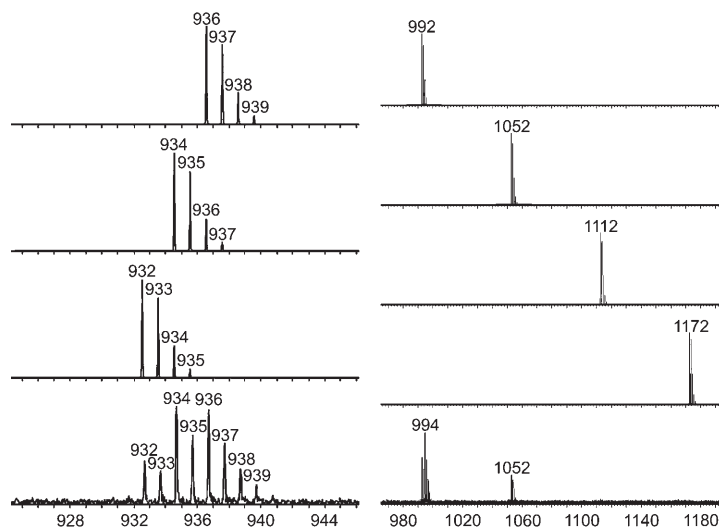
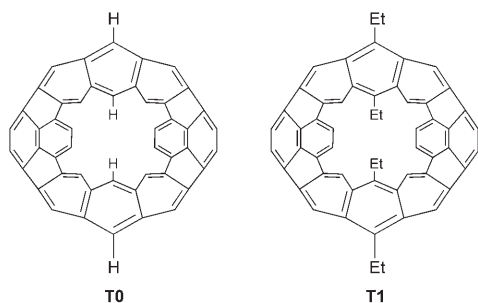


Figure 6. The low molar mass (left, bottom line) and high molar mass parts (right, bottom line) of a pyrolysis product's MALDI mass spectrum of compound **5** [first fraction ( $\text{“2”}$ )]. These parts of the spectrum are compared with calculated isotope patterns of the parent molecular ion [ $\text{“2”}$ ] $^+$  (left, lower center line) and the ion of its first and second reduction products [ $\text{“2”} + 2\text{H}$ ] $^+$  (left, higher center line) and [ $\text{“2”} + 4\text{H}$ ] $^+$  (left, top line), respectively, as well as the molecular ions of **5** (right, lower center line) and its fragmentation products [ $\text{5-HOAc}$ ] $^+$  (right, lower center line), [ $\text{5-2HOAc}$ ] $^+$  (right, higher center line), and [ $\text{5-3HOAc}$ ] $^+$  (right, top line), respectively.

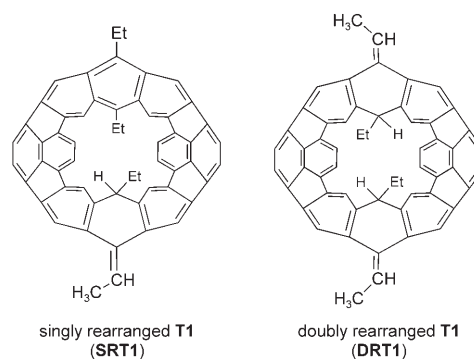


## Structure and reactivity aspects: A theoretical study

**Models:** The molecules under study are large, thus not suited for high level computational studies. Appropriate models had to be chosen therefore. It was shown that a model which contains only the structural motif that represents one of the two repeating units does not properly represent the belt system **2**.<sup>[19]</sup> Thus, the only acceptable simplification was to use the unsubstituted belt (referred to as **T0**, whereby T stands for theory) and the tetraethyl-belt (**T1**) as models for the tetrahexyl-belt **2**.

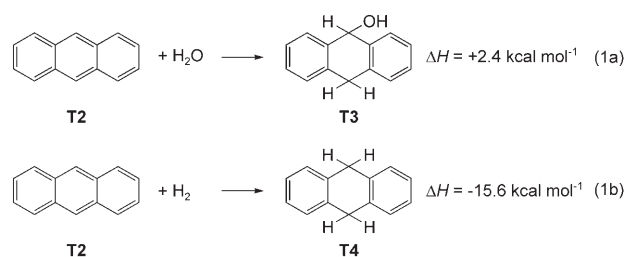


**Structural aspects:** The possibility of carbon skeletal rearrangements exists,<sup>[11]</sup> but such reactions are unlikely to occur. Unless the macrocycle is opened, skeletal rearrangements do not lead to any isomer that should be significantly more stable than **2**. Since the system undergoes rather unique addition reactions such as addition of water and hydrogen which are not typical to aromatic systems it is concluded that the macrocycle does not open. However, regarding hydrogen shift the picture is different. It was shown in experimental and computational studies that the rearrangement of a hydrogen atom from the methyl group of 9-methylanthracene to the 10-position to yield 9-methylene-10-hydroanthracene is endothermic, but annulation of aromatic rings decreases this endothermicity, and the process is about thermoneutral in a pentacene derivative.<sup>[20]</sup> Although it has been shown that the anthracene and naphthalene moieties in **T0** behave much like free anthracene and naphthalene, respectively<sup>[21]</sup> and thus the electronic conjugation is minimal, the possibility of a hydrogen shift was studied for **T1**. In such a process one hydrogen atom moves from the CH<sub>2</sub> ethyl group positioned at C-9 to C-10 (for simplicity the numbering is chosen like in parent anthracene), forming a double bond at C-9 and an sp<sup>3</sup> center at C-10.<sup>[22]</sup> A single such rearrangement (to form **SRT1**) is exothermic by 13.8 kcal mol<sup>-1</sup>. A second rearrangement on the opposite side of the belt system (to form **DRT1**; SR and DR stands for singly rearranged and doubly rearranged, respectively) can lead to two products, where the methylenes are on the same rim or on opposite rims, each as *syn* and *anti* isomers. The distance between the two methylenes and the symmetry of the system suggests that in both cases the *syn* and *anti* isomers are of the same energy. However, the second rearrangement is exothermic by additional 15.1 kcal mol<sup>-1</sup> to



form either the isomer where two methylenes are on the same rim (the one shown) or the one where the methylenes are on opposite rims. The reasons for this exothermicity and its implication on the chemistry of the compound are discussed below. At this point, it looks feasible that the structure of “**2**” may be either **2** or its singly or doubly hydrogen shifted isomers.

The compound—above referred to as “**2**”—undergoes addition of hydrogen and possibly even water easier than many other conjugated compounds. These additions were studied computationally. As mentioned above, **T0** and **T1** were used as models, but the computational level (B3LYP/6-311G\*, see Experimental Section) was not good enough for obtaining reliable absolute enthalpies for these reactions. In order to nevertheless have a good estimation of the thermochemistry involved, the following procedure was applied here. The addition of water and dihydrogen to the 9,10-positions of anthracene (**T2**) to yield 9-hydroxy-9,10-dihydroanthracene (**T3**) and 9,10-dihydroanthracene [**T4**, Eq. (1a) and (1b), respectively] were calculated at the G3 computational level which furnishes extremely accurate heats of formations (within 1 kcal mol<sup>-1</sup> from experimental values). The additions to **T0** and **T1** were compared with the same respective additions to **T2** through isodesmic reactions. This enabled to conclude quite precisely how much an addition to **T0** or **T1** is more or less exothermic from the respective addition to **T2**. Application of the energies obtained from equation 1 allows a good estimation of the absolute thermochemistry of the additions to **T0** and **T1**. The numbers reported are  $\Delta H^\circ$  in kcal mol<sup>-1</sup>.

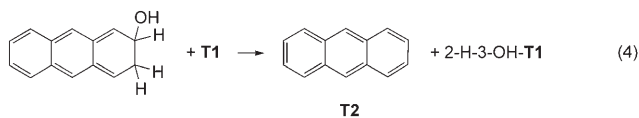
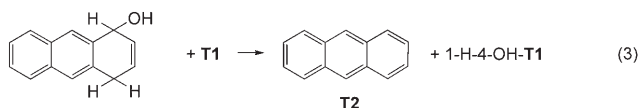
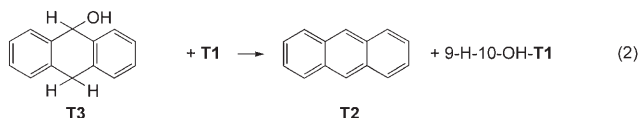


Equations (2–5) compare the water addition to anthracene and **T1** (and **T0**) at the same respective positions. The results (Table 1) indicate that the addition of water to **T0**

Table 1. ZPE-corrected  $\Delta E$  and  $\Delta H$  values for Equations (2-8).

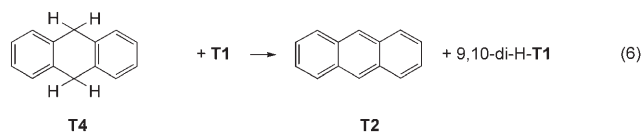
Equation	ZPE-corrected $\Delta E$	$\Delta H$
(2)	-22.0	-22.4
(3)	-20.7	-20.7
(4)	-23.8	-23.9
(5)	-1.3	-1.5
(6)	-23.0	-23.2
(7)	-2.3	-2.2
(8)	-2.5	-2.6

and **T1** is more exothermic by 20.7-23.9 kcal mol<sup>-1</sup> than to anthracene. Note that the difference between **T0** and **T1** is minimal [Eq. (5)] which suggests that for thermochemistry purposes **T0** is a good model. A comparison between the stability of the different isomers of the water addition to **T1** (see Supporting Information for the energies) suggests that the addition to the 9,10-positions is the most exothermic, and to the 1,4 and 2,3-positions it is less exothermic by 12.0 and 37.2 kcal mol<sup>-1</sup>, respectively. Thus, since the addition of water to the 9,10-positions of a **T1** is more exothermic by 22.4 kcal mol<sup>-1</sup> than the addition of water to the 9,10-positions of anthracene [Eq. (2)], and the absolute heat of water addition to the 9,10-positions of anthracene is 2.4 kcal mol<sup>-1</sup> [Eq. (1a)], it can be concluded that the addition of water to **T1** is exothermic by 20.0 kcal mol<sup>-1</sup>. Therefore, this reaction, which is not very common for aromatic compounds, should be a feasible one for **2**.



Because of the above-described results, the addition of dihydrogen to **T1** was studied only for the 9,10-positions. Equation (6) suggests that the hydrogenation of **T1** is more exothermic than that of anthracene by 23.2 kcal mol<sup>-1</sup>. Adding to this result the energy for hydrogenation of anthracene [-15.6 kcal mol<sup>-1</sup>, Eq. (1b)], it is concluded that the addition of hydrogen to **T1** is rather exothermic by 38.8 kcal mol<sup>-1</sup>. The bond separation Equations (7) and (8)

compare the addition of a second water and hydrogen molecule to the other 9,10-positions of **T1** with 10-hydroxy-9,10-dihydro-**T1** and dihydro-**T1**, respectively, and **T1**.



The results (Table 1) suggest that the addition of a second molecule is even more exothermic than the first one, so that the addition of two water molecules to **T1** is exothermic by 42.2 kcal mol<sup>-1</sup> and the addition of two dihydrogen molecules to **T1** is exothermic by as much as 80.2 kcal mol<sup>-1</sup>.

These data are in qualitative agreement with the mass spectrometric observation which proved an unusual reduction of “2” by two times two hydrogen atoms. A mass that fits a single water addition to **2** was observed as well, but a mass that fit [2+2H<sub>2</sub>O] was not observed, although the calculations indicate that a second water addition is more exothermic than the first. This may be due to the difficulty of isolating compounds from the complexed product mixture, but may also indicate that the structure of “2” is not **2** but rather a hexyl analogue of **SRT1** or **DRT1**.

Why is the addition to **T0** and **T1** exothermic by an almost constant amount (21–24 kcal mol<sup>-1</sup>) from the respective addition to anthracene regardless at which (respective two) positions the hydrogens or OH and H (H<sub>2</sub>O) are attached to the anthracene moieties of **T0** or **T1**? Is this finding related to the fact that the 1,5-H-shifts (to yield **SRT1** and **DRT1** from **T1**) are exothermic whereas they are endothermic in 9-methylanthracene? Figure 7 shows side views of **T1**, 9,10-dihydro-**T1**, and 9,9',10,10'-tetrahydro-**T1**. The symmetric structure of **T1** forces it to be completely round. Consequently all the carbon atoms are considerably non-

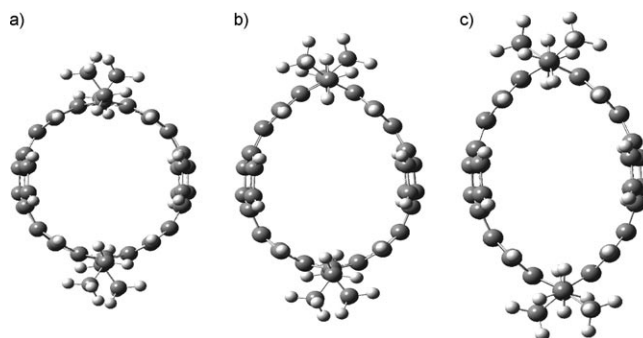


Figure 7. Side view of a) **T1**, b) 9,10-dihydro-**T1** and c) 9,9',10,10'-tetrahydro-**T1**.

planar. The addition of H<sub>2</sub> (or H<sub>2</sub>O) results in a drop-shaped system, allowing for the release of strain energy by planarizing some of the sp<sup>2</sup> carbon atoms. The addition of the second H<sub>2</sub> results in an ellipsoidal shape where all sp<sup>2</sup> carbon atoms are almost planar. Addition of H<sub>2</sub> (or water) at any of the positions results in a similar drop-shaped molecule, thus releasing almost the same amount of strain regardless to which position the hydrogen or water were added and regardless the absolute exothermicity or endothermicity of the addition reactions. The high amount of strain which is released upon addition (which is the difference between the belt and anthracene, namely, ca. 23 kcal mol<sup>-1</sup> for the first addition and additional ca. 25 kcal mol<sup>-1</sup> for the second addition) allows reactions that are intrinsically endothermic to nevertheless occur here on the bent structures.

Figure 8 shows the side view of **SRT1** and **DRT1**. A comparison to the hydrogenated **T1** (Figure 7) suggests that the rearrangements cause change of structures similar to the hydrogenation. Obviously, strain is released in the 1,5-rearrangements.

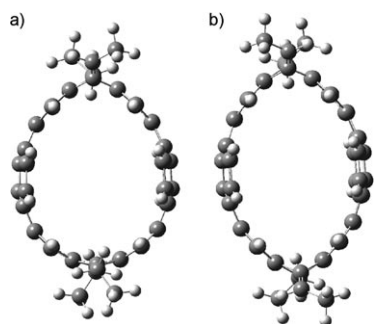
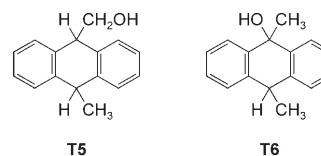


Figure 8. Side view of a) **SRT1** and b) **DRT1**.

Let us examine the addition of water and dihydrogen to anthracene and **T1**. A single addition of water and H<sub>2</sub> to **T1** is more exothermic than the respective additions to anthracene by 22.4 and 23.2 kcal mol<sup>-1</sup>, respectively. Addition of the second water and dihydrogen is more exothermic by 24.6 and 25.8 kcal mol<sup>-1</sup> than to anthracene. Since both reactions are very different [Eq. (1)] it is concluded that these (almost equal) numbers represent the release of strain upon additions to **T1**. From looking at the shapes of the single and double rearranged products of **T1** (Figure 8) it is concluded that strain is released by these rearrangements. If it is assumed that the amount of strain that is released upon rearrangement is equal to that released on additions, then electronically the single rearrangement is endothermic by 8.6–9.4 kcal mol<sup>-1</sup>, and the second rearrangement is endothermic by 9.5–10.7 kcal mol<sup>-1</sup>. These numbers are very similar to those obtained for the rearrangements in 9-methyl anthracene to 9-methylene-10-hydroanthracene (11.0 kcal mol<sup>-1</sup> at B3LYP/6-311+G(d,p) theoretical level).<sup>[20]</sup> These results support the NICS-scan results which suggest that the conjugation between the anthracenic and naphthalenic moi-

eties in **2** is minimal and suggest the possibility of “**2**” being actually the single and/or double rearranged product.

Addition of two water and H<sub>2</sub> molecules to the double rearranged **T1** leads to the same products as the respective double additions to the non-rearranged **T1**. The hydrogenation is thus exothermic by 50.0 kcal mol<sup>-1</sup> but the addition of two water molecules is exothermic by only 13.3 kcal mol<sup>-1</sup>, out of which about 7–8 kcal mol<sup>-1</sup> are released for the first water addition and 5–6 kcal mol<sup>-1</sup> are released upon the second (assuming that the amount of strain released for addition of water and rearrangement are similar). There is also another factor that has to be considered. The mechanism of hydration involves the formation of a carbenium ion. It may be that protonation of **SRT1** and/or **DRT1** occurs at the belt carbon and not at the alkylidene one leading to a more stable carbenium ion than the protonation of the alkylidene carbon in the rearranged **T1**. In this case the product of the hydration will have the hydroxyl group on the alkyl carbon. Calculations (at B3LYP/6-311G\*) show that **T5** is less stable than **T6** by 3.6 kcal mol<sup>-1</sup>. In summary, addition of water to



**SRT1** is slightly exothermic and addition of two water molecules to **DRT1** is either slightly exothermic or slightly endothermic. Throughout the discussion only *exo* additions were considered. The reason is that *endo* additions are unlikely for kinetic and thermodynamic reasons. a) For an *endo* attack the reactant has to approach from the inside of the macrocycle, thus kinetically less feasible. b) Due to the curvature of the macrocycle the p<sub>π</sub> orbitals have higher coefficients outside the macrocycle, thus are more prone to an *exo* attack. c) the product of the *endo* addition should be less stable than the one of the *exo* addition due to steric repulsion between the alkyl groups across the 9,10-positions.

As mentioned above, the absence of a mass that corresponds to [2+2H<sub>2</sub>O] is not conclusive evidence that the compound doesn't exist in the complex product mixture. However, the experimental evidence obtained so far together with the computational results favor the structure of the hexyl analogues of **DRT1** as the structure of “**2**”, although the possibility of “**2**” being the hexyl analogue of **SRT1** or **2** cannot be ruled out at this stage.

## Conclusion

This paper describes experimental work supported by DFT and G3 computations getting the closest to one of the major targets on the “wishlist” of chemistry, namely a fully conjugated, double-stranded cycle like target **2**. First it is de-



scribed that compound **1** is not a precursor for this bucky-belt-type compound. Neither could an indication for a mass spectrometrically induced dehydration be found, nor RDA of **1** be prevented. However, the tetraacetate **5** allowed carrying out exciting steps towards the generation of “**2**”. Its pyrolysis at 330 °C upon chromatographic separation gave a deeply red fraction with a molecular ion at  $m/z$  932 which is exactly the expected mass for **2**. In addition, high resolution MALDI MS matches the molecular composition of **2**. Calculations suggest, however, that this mass may not be due to target compound **2** but rather rearranged isomers which underwent one or two 1,5-hydrogen shifts with formation of one or two exocyclic double bonds, respectively (analogues to **SRT1** and **DRT1**). The key argument here is that each of the rearrangement steps results in a considerable loss of strain energy through which the system is stabilized. Surprisingly the mass spectra of the pyrolysis product not only show the isotopic pattern at  $m/z$  932 but also two superimposing patterns starting at  $m/z$  934 and 936 which may indicate an unprecedented high propensity of the compound with  $m/z$  932 (whatever its structure may be) to undergo two (and not more) consecutive hydrogenation steps. Target **2** contains two opposing, strained anthracene units, whose hydrogenations at the 9,10-positions—based on the calculations—result in a relief of strain energy on the same order of magnitude than that expected for the (potential) rearrangement of target **2** into the isomers which suffered single and double 1,5-hydrogen shifts, respectively. The simplest but not necessarily correct assumption is that precursor **5** upon pyrolysis forms in fact the desired target **2** as a transient species which, however, then suffers either fast rearrangements to the corresponding rearranged products (same structures than **SRT1** and **DRT1** except for hexyl chains instead of ethyl) and/or similarly fast hydrogenations. The calculations indicate that also the single and double rearranged products may show hydrogenation(s). In any case, the fraction under consideration contains a mixture and further work including complicated separations is required. This will be reported subsequently. At present it cannot be decided with certainty whether the compound that gives rise to  $m/z$  932 is actually **2** or one of its rearranged isomers.

## Experimental Section

Compounds **5** and **6** were prepared as previously reported.<sup>[4,18]</sup>

**Column chromatography:** 10–40 mg of the fine, yellow powder of **5** were placed in a small flask together with a large excess of freshly sublimed anthracene. After evacuation, the flask was immersed into a pre-heated metal bath (330 °C), whereupon the anthracene melted within approximately 1 min and a homogenous mixture formed. The colour of the reaction mixture changed quickly from yellow to orange to deep-red. After 3 min (using a stop-watch) the flask was removed from the bath and allowed to cool. The reaction mixture was dissolved in chloroform and fractionated using a preparative recycling GPC (Japan Analytical Industry Co. Ltd., LC 9101) equipped with a pump (Hitachi L-7110, flow rate 3.5 mL min<sup>-1</sup>), a degasser (GASTORR-702), a RI detector (Jai RI-7), a UV detector (Jai UV-3702,  $\lambda=254$  nm) and two columns (Jaigel 2H and

2.5H, 20×600 mm for each) using chloroform as eluent at room temperature.

**Mass spectrometry:** Samples were dissolved in dichloromethane and after short drying at RT analyzed by MALDI MS at the positive mode. Mass analyses were performed with the aid of a micro MX MALDI-TOF instrument (Waters, Manchester) using 337 nm radiation from a nitrogen laser. The mass spectrometer was operated in the reflectron mode, at 12 kV accelerating voltage. Matrix suppression was not used and mass spectra were averaged over ~10 individual laser shots. The laser intensity was adjusted just over the threshold for ion production.

**Computational details:** Gaussian 03<sup>[7]</sup> code was used. All the molecules under study underwent full geometry optimizations at the B3LYP/6-311G(d) hybrid density functional theoretical level and analytical frequencies calculations to ensure real minima (i.e.,  $N_{\text{imag}}=0$ ) and to obtain zero point energies necessary for the thermodynamic calculations. The number reported are  $\Delta H^\circ$ , in kcal mol<sup>-1</sup> unless otherwise noted.

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