

Chain formation during hydrogen loss and reconstruction in non-planar polyaromatic hydrocarbons

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Abstract

We explore the importance of curvature in carbonaceous species transformation and stability, using laser-induced vaporisation to evaporate and ionise a source of curved polyaromatic hydrocarbons: carbon nanobelts. Collision impacts between species cause mass loss and the resultant ions are catalogued via mass-spectrometry. To interpret the mass spectra, we perform a series of “in-silico” simulated systematic hydrogen-loss studies using density functional theory (DFT) modelling, sequentially removing hydrogen atoms using thermodynamic stability as a selection for subsequent dehydrogenation. In an initial sequence of H₂ removal, the rings are maintained through stable carbyne chain and pentagon-chain formation, giving rise to circular strained dehydrobenzoannulene species. The chains subsequently break, releasing CH and C₂. While theoretical closed-cage routes are identified, they are not observed experimentally. The results can serve as a useful guide to high-energy impact conditions observed in some astrochemical environments.

Keywords: Nanobelts, PAH, polyaromatics, cyclic polymers, hydrogen loss, fullerenes, carbon chains.

Molecular carbon formation, transportation and transformation is one of the great scientific challenges in astrochemistry. Complex carbon molecules have been proposed as primary carbon sources in astrochemical environments such as the interstellar medium (ISM)¹, nebulae clouds^{2,3} and supernovae remnants^{4,5}. Carbon is expected to exist in a variety of forms including amorphous carbon and hydrocarbon dust¹ as well as in molecular structures. Of these, three key families are carbon chains⁶, fullerenes^{1-3,7}, and polycyclic aromatic hydrocarbons (PAHs)^{3,4}. UV-irradiation, hydrogen impacts and thermal cooling near supernovae present mechanisms for transformation between different species types. Growth and transformation models have predicted short chain presence during fullerene formation^{8,9} while electron irradiation studies have demonstrated spontaneous transformation of planar aromatics into fullerenes¹⁰, but precise carbonaceous transformation processes and pathways remain a subject of debate.

Curvature should play a critical role in carbonaceous species transformation and stability. As an example, localized curvature has been shown to aid hydrogen trapping in interstellar graphenic dust grain models, catalysing subsequent pairwise release giving H₂ formation¹¹. Curvature destabilises aromaticity and localises reactive sites. It adds a driving mechanism for functionalisation and structural reorganisation in order to relieve curvature-induced strain, either by localising the curvature, or eliminating it through transformation from sp²- to sp³- bonded carbon. It is therefore interesting to examine the transformation behaviour under irradiation of curved aromatic hydrocarbons. Here we have chosen to use carbon nanobelts¹² (CNBs, [(CH)₂-C₆H₂]_{2n}), part of a family of cyclic aromatic species that began with cycloparaphenylenes first synthesised in 2006¹³. Nanobelts are of interest since they only contain hexagons and provide a continuous aromatic structure with uniform curvature. This is dependent purely on the ring circumference selected during synthesis. As such nanobelts can be considered as archetypal curved polycyclic aromatic hydrocarbons.

In this study we use laser-induced vaporisation to evaporate and ionise a source of carbon nanobelts. Collision impacts between species cause mass loss and the resultant ions are catalogued via mass-spectrometry. In order to understand the processes involved we perform a series of “in-silico” simulated systematic hydrogen-loss studies using density functional theory (DFT) modelling. We sequentially remove hydrogen atoms using thermodynamic stability as a selection for subsequent dehydrogenation, allowing us to map and compare sequential hydrogen loss routes. The calculations show good agreement with experiment indicating initial pairwise hydrogen loss and local carbyne chain formation within the nanoring, before the chain ends are released leading to subsequent C₂ and CH loss.

Method

Experimental gas phase studies of C₄₈H₂₄ were performed with a laser cluster source (~5 mJ laser fluence, 532 nm from a pulsed Nd:YAG laser system) coupled to an ultrahigh resolution FT-ICR mass spectrometer. The C₄₈H₂₄ sample is surface coated onto a quartz rod and then laser-desorbed into a pulse of He¹⁴. The resultant gas-phase species expand supersonically into a vacuum chamber where a skimmer creates a narrow beam. The cluster source is coupled directly to a Fourier Transform Ion Cyclotron Mass Spectrometer (FT-ICR-MS)¹⁴ whose very high resolution enables unequivocal identification of the stoichiometry of each and every ionic species produced as the resulting spectra are completely resolved. The resulting nanobelts are isolated in the gas phase by use of the Sustained Off-Resonance Irradiation (SORI) technique¹⁵ and then probed by collision-induced dissociation (CID)¹⁶ to provide circumstantial structural information. We detect only the positive ion distribution created by the totality of all possible sequences of neutral-neutral, neutral-charged and charged-charged processes that result in positively charged species that emanate from the nozzle orifice. The experimental setup allows us to extract the resultant molecular fragments either before or after intermolecular collisions have been allowed to occur.

All calculations were carried out based on the density functional theory (DFT) calculations under the local density approximation (LDA) using the AIMPRO code^{17–19}. Pseudo potentials given by Hartwigsen, Goedecker, and Hutter (HGH)²⁰ were used. Wavefunctions are handled using a basis set of Gaussian type orbitals^{21,22}, in which 38 (12) independent functions and used for carbon (hydrogen) atoms. Charge density is handled using plane waves with a cut-off of 300Ha. Spin polarisation was used in systems with an odd number of electrons ($\mu_B=1$) and averaged for systems with an even number of electrons. Since only positively charged species are measured experimentally, all calculations performed here are in the +1 charge state. Such charging is handled by introducing a uniform homogenous compensating background charge to the cell. Electron temperature is handled using a Fermi function with temperature of 0.04eV to aid convergence. All molecules are modelled in large hexagonal cells with over 20Å until the next molecule to ensure no interaction and to minimize the density of the homogenous background charge. Vibrational modes are determined from numerical energy double derivatives (0.2au atom shifts). Structures were geometrically optimised until system energy was converged to better than 10^{-7} Ha, and positions to within 10^{-7} atomic units. Enthalpies (in eV) are quoted for hydrogen removal via

$$\Delta H = E(C_{48}H_n) - E(C_{48}H_{n-1}) - \frac{1}{2}E(H_2)$$

Where $E(n)$ is the total energy of species n in isolation. For the +1 charge state it is assumed that H_2 always remains neutral, i.e. the positive charge is carried by the nanoring in each case. Note that this approach uses H_2 as a reference state and does not necessarily imply hydrogen extraction as H_2 .

Results

The insert of **Figure 1** shows the relaxed CNB ($C_{48}H_{24}$) structure. The ring has C_3 symmetry, with significant variation in C-C bond-length around the ring. In the +1 charge state the exterior C-C bonds have strong local double bond character (1.35 Å) while the interior bonds become increasing aromatic (1.38-1.43 Å); the neutral charge state is similar with slightly dilated interior bonds (up to 1.45 Å). There are two hydrogen types by symmetry alternating around the ring in pairs: “exterior” hydrogen atom pairs are on neighbouring sites of the same hexagon, and “interior” hydrogen atom pairs on opposing sites of a given hexagon (1.09 Å bond length).

Fragmentation of the $C_{48}H_{24}$ nanobelt after collision-induced dissociation is shown in detail in Figure 1 (higher resolution details in Supplementary **Figure S1**), showing clearly that the primary loss species come from removal of nH_2 , $n = 1...3$. Similar intensity peaks correspond to removal of $3H_2+n_1CH+n_2C_2$, with $(n_1+n_2) \leq 2$, and increasingly weak signals for $2H_2+CH$ and H_2+CH loss. We are confident of the peak assignment since carbon isotopes can be readily distinguished due to the resolution of the spectrometer (**Figure S1**). Molecular dissociation occurs following intermolecular collisions, since the two mass spectrometry figures in **Figure S2** show that exit species collected before collision do not show the presence of dissociated species in any notable amount.

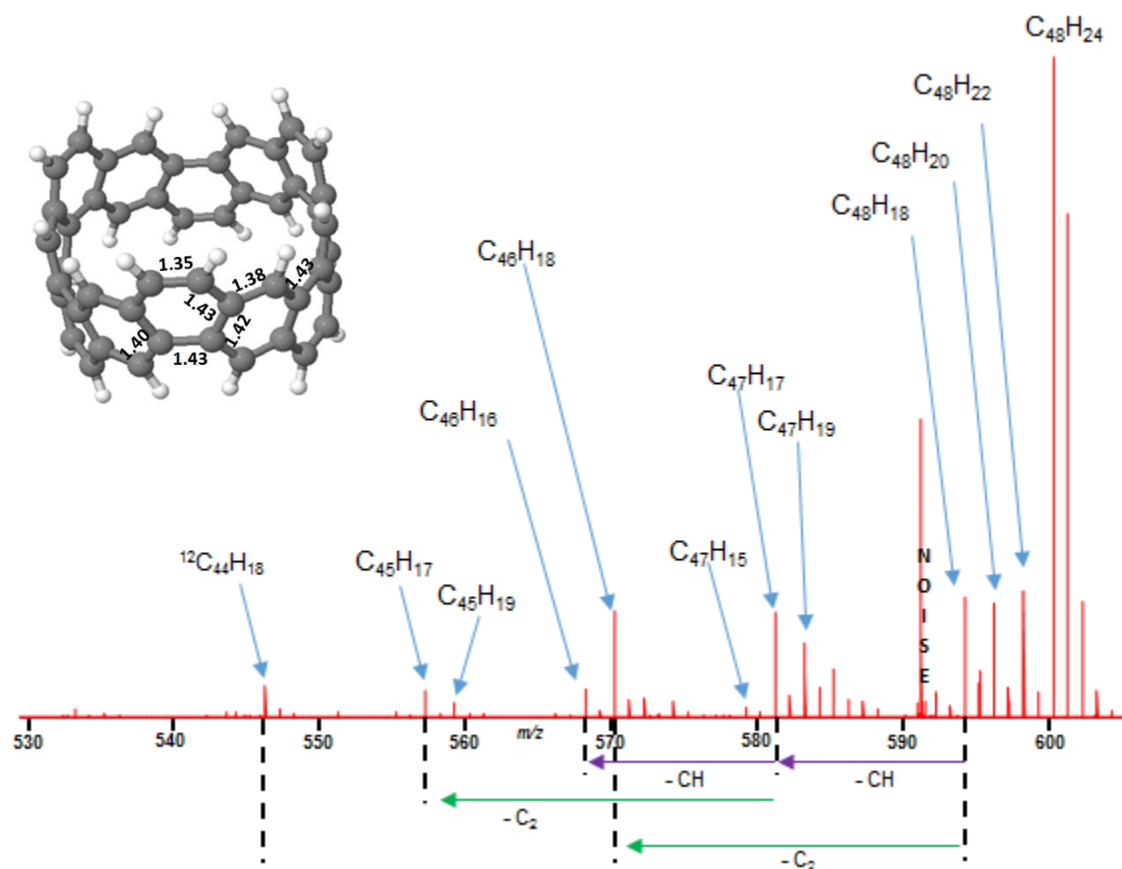


Figure 1: FT-ICR mass spectrum of $C_{48}H_{24}$ nanobelts showing dissociation through loss of varying quantities of H_2 , $(CH)+H_2$ and $(C_2)+H_2$. X-axis indicates m/z ratio for positive ion species. Inset shows the DFT-optimised nanoring structure in +1 charge state, calculated bond lengths marked in Angstroms.

We now turn to simulations to examine potential dehydrogenation routes. **Figure 2** shows three possible single dehydrogenation sites: exterior and “interior” hydrogenated sites (i.e. sites furthest and closest to the ring equator respectively), and a third alternative where the structure in **Figure 2b** undergoes a 90° C-C bond rotation (Stone-Wales rotation) about the bond centre, for the non-circumferential bond of the dehydrogenated carbon atom. The result is that two hexagons are replaced with a pentagon-heptagon pair, with the dehydrogenated carbon sitting in the heptagon. Single hydrogen atom removal is highly endothermic (+3.49eV for the interior site, +3.67eV exterior and +4.21eV for the bond rotated structure) due to the creation of a dangling carbon bond.

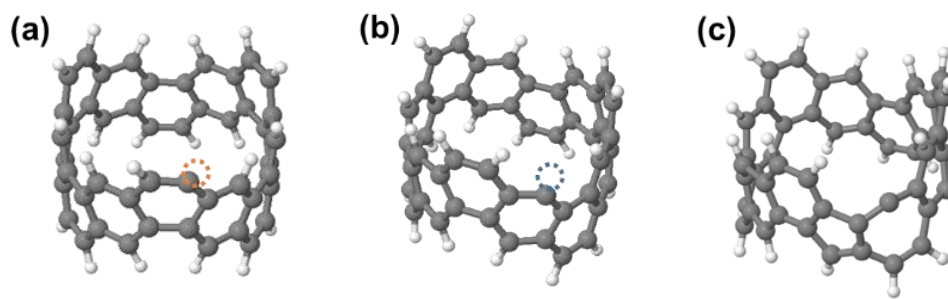


Figure 2. Molecular structures of $C_{48}H_{23}$, i.e., 1H-loss structures from an (a) exterior site and (b) interior site. Orange and blue dotted circles indicates dehydrogenated sites. (c) a pentagon-heptagon structure formed by Stone-Wales bond rotation of structure (b). Grey and white spheres indicate carbon and hydrogen atoms respectively.

We next remove a second hydrogen atom from all possible symmetrically distinct sites of these three structures, testing this way nearly 30 2H-loss structures. Second hydrogen removal is always much easier than the first due to the electronic closed shell produced from pairwise dehydrogenation (the energetic cost for the second dehydrogenation step is typically less than half that of the first). This is consistent with a picture of pairwise dehydrogenation as seen experimentally in Figure 1.

Three structures show significantly lower energy than all others (**Figure 3**). For the external dehydrogenation (**Figure 2a**), the most stable $C_{48}H_{22}$ loses a neighbouring pair of external hydrogen atoms (Figure 3a). The C-C bond between the dehydrogenated carbon neighbours stabilises the dangling bonds by rehybridising from a double (1.35 Å, **Figure 1**) to a geometrically distorted triple bond (1.23 Å, **Figure 3a**). This can be regarded as the shortest carbyne chain.

For interior dehydrogenation (**Figure 2b**), the most stable structure has the two closest internal hydrogen atoms removed. In this case the resultant dangling bonds point towards each other and are removed by forming a new single bond and creating a square (**Figure 3b**). The three interior C-C bonds of the square remain at 1.41-1.42 Å, while the fourth bond, newly formed after dehydrogenation, is 1.52 Å, showing its single bond character. This rebonding creates a curved surface resembling locally the curved surface of a fullerene cage.

For the bond-rotated structure (**Figure 2c**), the lowest energy dehydrogenation process is the mirror of the first, i.e. removal of the nearest internal hydrogen followed by another bond rotation (SW) on the other side of the heptagon. The result is a conversion from three hexagons in the initial nanoring structure, to pentagon-heptagon-hexagon for the first dehydrogenation step, to pentagon-octagon-pentagon for the second. The two dehydrogenated carbon atoms form the exposed side of the octagon, rehybridising to a carbyne chain with bonds of 1.24 and 1.34 Å (**Figure 3c**).

Thus we have three candidate structural routes for dehydrogenation resulting in either carbyne chains (**Figure 3a**), cage closing towards fullerene structures (**Figure 3b**) or carbyne chain formation linked with end pentagons (Figure 3c). For 2H-loss, this latter SW-carbyne route (c) is the least stable and the fullerene route (b) the most stable, although the energetic difference is very small (+0.03 eV/H atom).

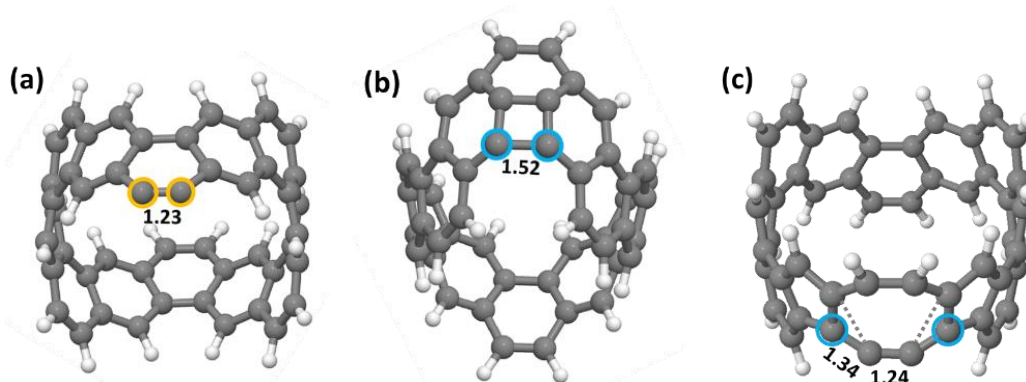


Figure 3. The most stable $C_{48}H_{22}$ structures (2H-loss) obtained by further hydrogen atom removal from the $C_{48}H_{23}$ structures in Figure 2. Values under bonds indicate the C-C bond lengths (Å). Orange and blue circles represent carbon atoms which have lost an external and internal hydrogen atom, respectively.

Dotted lines indicate the original C-C bonds, which were rotated and reformed with the adjacent atoms (Stone-Wales bond rotations).

We now continue sequentially removing hydrogen atoms from each structure, in each case selecting the most stable structure for subsequent hydrogen removal. The full sequences are given in **Figure S3**, a summary with key steps in Figure 4.

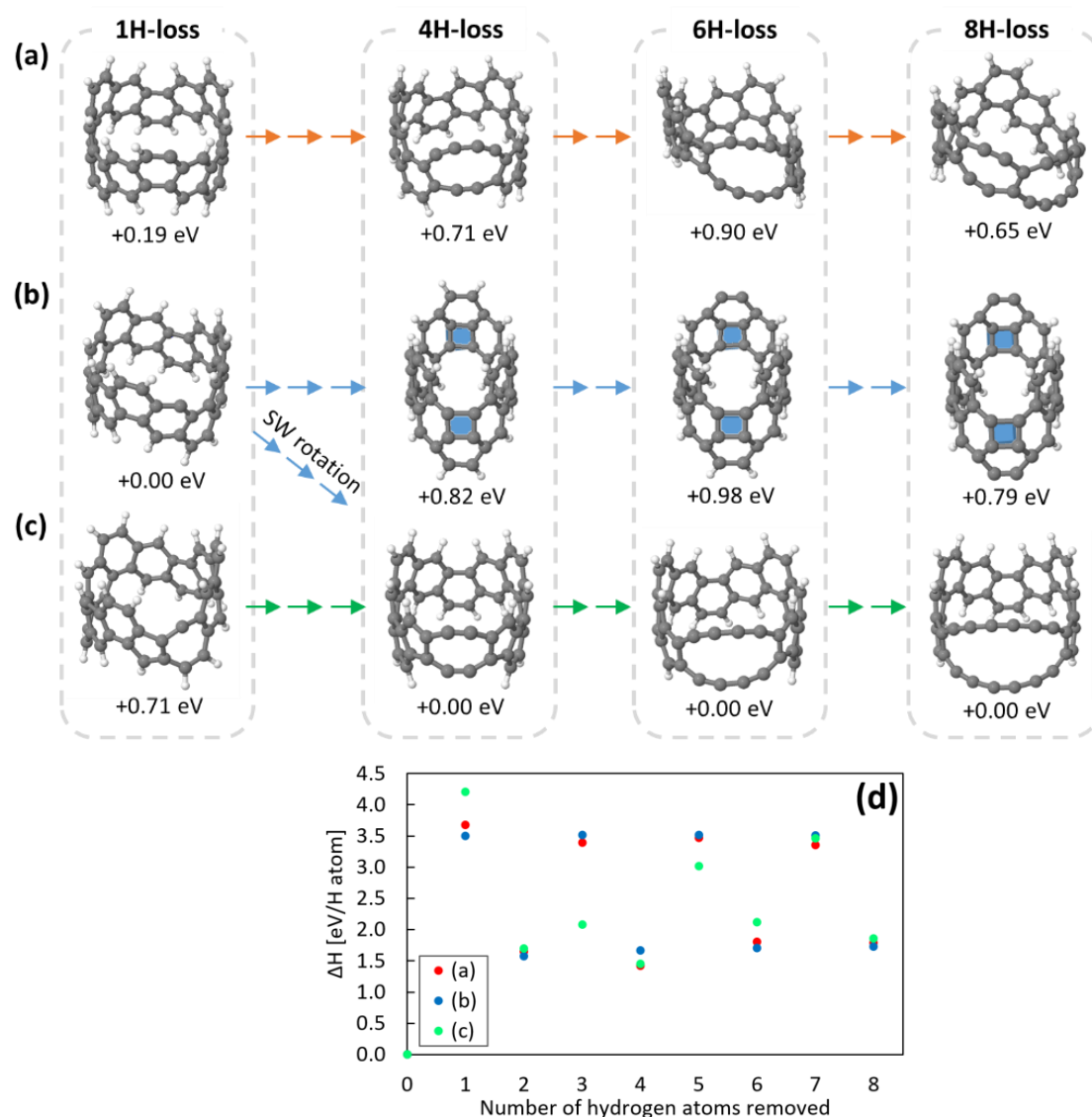


Figure 4. Carbon nanobelt maps (a-c) show key steps in the sequence of structures formed after sequential dehydrogenation. Route (a) begins with removal of exterior hydrogen atoms, route (b) with interior hydrogen atoms, and route (c) interior hydrogen atoms coupled to C-C bond rotations, as described in the text. The 1H-loss structures for (a-c) are shown in more detail in Figure 2. Grey and white spheres represent carbon and hydrogen atom, respectively. Each single arrow represents the removal of one hydrogen atom. Carbon squares are shaded in blue. The enthalpy value under each molecular model indicates the relative stability between the three isomers grouped vertically by grey dashed lines, i.e. between structures with the same number of hydrogen atoms (+0.00eV is the most stable structure each time). Importantly, the 4H-loss structure formed along the route (c) can also be formed from the 1H- and

2H-loss structures formed along (b) by the bond rotation. (d) shows the calculated enthalpy for removal of a single hydrogen atom from the previous structure for the three routes (a-c). A complete map showing every step is included in Supplementary Materials Figure S3.

For the “fullerene” closure route (Figure 2b), the next step involves formation of a second square on the opposing side of the ring (Figure 4b). This localizes curvature at the two “ends” with squares, allowing the rest of the ring to flatten and increase aromaticity. However thereafter there is no symmetrically obvious location for a third subsequent H_2 removal via this route, and instead we see a diversity of possible structures. Notably external hydrogen removal (as via the orange route) is energetically almost identical to the formation of further squares along the sides of the ring. Since this route is energetically much less stable than the alternatives, we do not pursue it further.

For the “carbyne” route starting with removal of two exterior hydrogen atoms (Figure 2a), for 4H it becomes more stable to break a cross-linking C-C bond, allowing the structure to rehybridise and open out into two carbyne chains (Figure 5a). While this process also results in strain relaxation in the ring with an increase in overall ring circumference, the two chains formed are not of equal length (containing two and four carbon atoms respectively), which creates strong compression and tension, destabilizing the structures. Thus, this route is also energetically relatively unfavourable. Bond length distribution shows a clear polyyne (single-triple) bonding in the shorter chain, with more cumulene-type bonding in the centre of the longer chain.

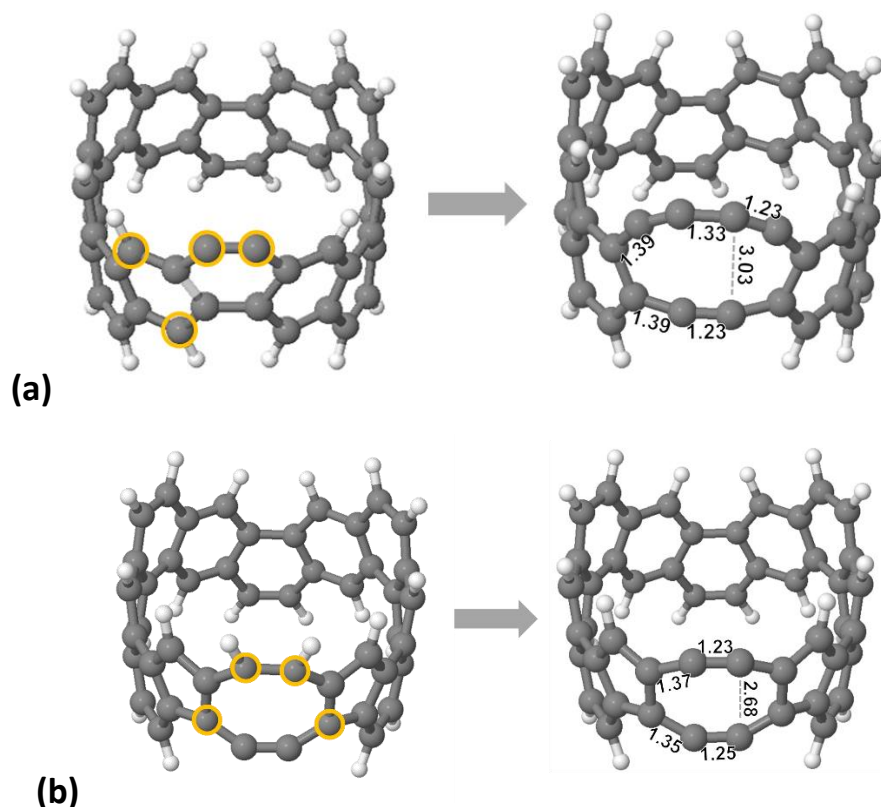


Figure 5: Further 2H loss from $C_{48}H_{22}$ to $C_{48}H_{20}$ (dehydrogenated carbon atoms circled in orange), for (a) the exterior route and (b) the SW-carbyne route. The bond grey-shaded in $C_{48}H_{22}$ breaks, creating two carbyne chains. Bond-lengths (Å) are symmetric about the two chain centres and for clarity are shown only once.

The third, SW-carbyne route (Figure 2c, 3c, 4c) results in significantly more stable structures than the other routes. Although these are also carbyne chains (Figure 4c), in this case the pentagon cross-bonding is maintained, the two carbyne chains are symmetric and contain only one C-C triply bound pair each (Figure 5b). In particular, this stabilizes removal of the third hydrogen atom (Figure 4d), and as a result these structures are 0.7-0.8eV more stable than the alternatives. The equivalent chain lengths avoids inter-chain strain while still allowing an increase in diameter, relieving curvature-induced strain in the rest of the ring. These structures form part of the family of strained dehydrobenzoannulenes²³, organic species with cross-linking triple-bonded chains.

We note furthermore that these routes are not mutually exclusive. As marked on Figure 4a, by rotating a C-C bond it is possible to shift from the “interior” fullerene route onto the SW-carbyne route. Thus although the fullerene structures are energetically favoured for the initial hydrogen removal steps, they can easily divert to the more stable SW-carbyne structures upon further dehydrogenation.

As dehydrogenation continues (Figure 4), this route always results in the most stable structures, extending the two carbyne chains symmetrically. While this process can in principle continue around the ring, after removal of six hydrogen atoms, the carbyne chains are already very long (4 carbon atoms each). From this point on, the system becomes increasingly fragile and susceptible to breakage during intermolecular collisions. When the ends of the chains break away this allows the nanorings to open out and will not be reversible. Thereafter the unbonded ends of the carbyne chains will easily fragment during collision, losing C₂ and CH species as seen experimentally (Figure 1).

We have calculated the vibrational modes associated with the SW-Carbyne chain structures. With 2H removal (**Figurec**) a triple bond stretch mode appears at 2060.4 cm⁻¹. This is slightly lower than the 2150 cm⁻¹ mode associated with triple bonds in ion-implanted graphite²⁴ and is due to the local curvature and the +1 charge state in the current case, which will weaken the carbyne bonding and lead to frequency downshift. Long chain coupling, which can also downshift this mode, does not apply to the short carbyne chains in the current case²⁵. In the 4H-loss case (Error! Reference source not found.**b**), this mode splits into two at 2068.3 and 2033.7 cm⁻¹ due to the symmetry difference between the upper and lower chain respectively (the lower lying more axially), showing weak vibronic coupling between the chains. In the 6H-loss case the chains are longer, the ring-induced curvature is less dominating and the +1 charge more distributed, and as a result the frequencies rise towards the conventional triple bond values, reaching 2080.8-2051.6cm⁻¹. For the simple 2H-loss structure in **Figurea** where no bond rotation has occurred, the triple bond is less linear and its stretch frequency is only 2046 cm⁻¹. These frequencies are all higher than those seen during damage-induced merging of double walled nanotube bundles at 1855 cm⁻¹ ascribed to short linear carbon chains (3 to 7 atoms long) forming as bridging precursors to the merging of the tubes²⁶. This is likely because short chain bonding will be highly sensitive to the nature of the end connections to the host nanocarbon.

There are no strongly localized characteristic modes on the pentagons at the chain ends, their modes instead strongly coupled to the rest of the structure. Two peaks at 1283/1302 cm⁻¹ show relatively strong pentagon character, but as these lie very close to conventional damage peaks in carbon materials such as the D-peak in graphite they cannot serve as indicators for the presence of local hydrogenated pentagons.

Discussion and Conclusions

Despite the extensive available literature of damage-induced structural change in nanocarbons, it is very difficult to examine the breakdown process stepwise. This is because samples are typically non-uniform and data is either statistical across a range of related but different configurations, or based on observation of a single event (e.g. via HRTEM). In the current case, we are able to examine with statistical rigour the

breakdown of identical, uniform nanoring samples, allowing us to identify the individual matter loss and transformation steps. Collision-induced mass loss of laser-ablated gas-phase $C_{24}H_{24}$ nanorings occurs through the loss of nH_2 , $n=1-3$, followed by subsequent loss of nC_2 and/or nCH , $n=0-2$. Theoretical modelling of dehydrogenation routes, selecting favoured structures based on their relative enthalpic stability, provides a complete picture that is fully consistent with the experimental collision-induced dissociation mass spectrometry data.

Initial pairwise hydrogen removal of up to six hydrogen atoms occurs through the formation of two parallel carbyne chains. In order to obtain parallel symmetric carbynes it is necessary to rotate carbon-carbon bonds at their ends, creating local pentagons that connect the chain pair to the rest of the nanoring. The carbyne chains stabilize the dangling bonds produced through dehydrogenation by rehybridising to triple bonds, with the added energetic advantage that the ring diameter can increase, relieving the internal curvature induced strain of the ring.

As dehydrogenation progresses and the chains become longer, intermolecular collisions break open the rings at the carbyne ends, and subsequent mass loss occurs through removal of C_2 and CH from the chain ends. Alternative mass-loss routes, notably through introduction of further local curvature and closure towards fullerene-type structures, are energetically unfavourable beyond the first dehydrogenation step.

There are many literature examples of damage giving rise to both carbyne²⁷, and fullerene-like structures. Electron irradiation of small carbon flakes on graphene produces vacancies and results in closure to fullerenes¹⁰, and metal templating also appears to catalyse fullerene formation during both growth and irradiation^{8,14}. Carbyne formation is seen during irradiation damage of double-walled nanotube bundles²⁶ and graphite²⁴, and spontaneous short-lived chains are predicted to form during fullerene growth from small amorphous carbon clusters⁹. A common argument for carbyne production during irradiation is constrained thinning, where carbon is removed at a junction between nanoobjects, resulting in an increasingly thin connecting region which stabilizes as a carbyne chain before eventually breaking^{28,29}. The current study is a limiting example of this; rather than thinning the connection between two carbon nanoobjects, there is instead thinning of the connection between two ends of the same curved nanoobject. Curvature in the aromatic network induced by the ring structure is thus a critical factor, applying tension to the damaged zone and thereby favouring carbyne formation. Additionally the two hydrogenated nanoring edges in close proximity provide an easy route to rehybridisation into dual carbyne chains once dehydrogenated. Wider rings with more hexagons along their axis may become harder to rehybridise, although we note that field emission experiments from carbon nanotube tips suggested indirect evidence of carbon chain formation^{30,31}.

Finally we note that these structures with parallel attached carbyne chains form part of the family of strained dehydrobenzoannulenes²³. These molecules, of interest for their optoelectronic behaviour, are extremely difficult to synthesise through bottom-up organic chemistry routes, and the current 'top-down' route of collision-induced dehydrogenation may be of interest as an alternative route to their production.

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