

環状・籠状ナノ炭素分子の形成・相互作用・解離

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Summary of the following doctoral thesis

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**Formation, interaction and destruction of
ring- and cage-molecular nanocarbons**

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Chapter 1. Introduction

The concept of “nano” is introduced. In the “nano world”, “classical mechanics” does not work any more, but instead, it is necessary to step into “quantum mechanics”.

The behaviour of molecules can be explained by solving the Schrödinger equation. However, in most cases, it is too complicated to solve the problems by hand. Therefore, we use computers specialised for calculations employing some approximate methods (Quantum calculations – **Chapter 2**).

The quantum mechanics can also be applied to quantum computers. A single “qubit” in the quantum computers can represent 0 and 1 simultaneously by superposition without any energy loss [1]; quantum computers can perform multiple calculations at the same time and save a huge amount of time cost. As one of the candidates for qubits, I theoretically investigated in **Chapter 5** the formation of stable radical azafullerene $C_{59}N$; an organic magnetic molecule in which the magnetic dipolar interaction enables qubit coupling. It also overcomes a problem on the synthesis yield of the current fullerene candidate $N@C_{60}$ [2].

Besides the computing technologies, carbon nanomaterials have been paid a wide attention to; e.g., metallofullerenes for stable, nontoxic contrast media, nanorobots for drug delivery systems, and clusters of carbon nanotubes as buckypaper for cell cultivation. If we look up to space over the sky (**Chapter 3**), there are fullerenes particularly around hydrogen-rich stars (**Chapter 6**) as well as carbon chains (**Chapter 7**). We now recognise the importance of nanocarbons in both science and technology/engineering.

The present thesis focuses on the modelling of nanocarbons for a better understanding of astrochemistry, noting that we still cannot obtain any samples such as interstellar substances directly from space, but only indirect data are collectable. Many of the transformation processes are rapid or rare and therefore it is difficult or impossible to characterise those samples experimentally. Modelling is a unique tool to cope with such problems.

Chapter 2. Quantum calculations

In this chapter, differences between classical and quantum mechanics are introduced, followed by a description of various approximations used in quantum chemical calculations, notably those are used in the following sections and chapters.

2.1. Towards DFT calculations

In the classical mechanics, we solve problems by the Newtonian equation. When we tackle nano-scale problems such as molecular behaviour, we instead solve the Schrödinger equation. In the field of quantum mechanics, the state of a particle is expressed by a wave function ψ , and we cannot derive the exact position and momentum simultaneously. Since it is not possible to solve

the Schrödinger equation by hand, we employ several approximation methods with computers. As the first approximation, we apply the Born-Oppenheimer approximation and introduce the density functional theory (DFT). This approximation reduces a number of system variables. Next, the Hohenberg-Kohn theorem is introduced and the Kohn-Sham method is used for the DFT calculations.

In this thesis, the *ab initio* modelling program (AIMPRO) [3–5] is utilised to perform the DFT calculations. Gaussian type orbitals (GTOs) are implemented to express the shape of atomic orbitals [6]. For the pseudopotential, the Hartwisien-Goedecker-Hutter (HGH) potentials [7] which is specialised for Gaussian type basis sets are utilised to approximate the core region of wave functions. In the AIMPRO, several k -points are selected for sampling based on the Monkhorst-Pack method [8]. Particularly a large cell in the real space is used in this thesis and therefore a single k -point at the Gamma point is used.

The calculations are iteratively carried out (self-consistent field (SCF) method) using the AIMPRO code, and the solutions of the Schrödinger equation are finally obtained.

After solving the Kohn-Sham equations, the optimal structures and physicochemical properties of the system can be investigated. The structure optimisation is carried out via the following steps; (a) move the atoms with a certain distance based on the Hellmann-Feynman theorem [9], (b) solve the Kohn-Sham equation to obtain E_{tot} , and (c) find the structure which gives the minimal E_{tot} after the energy conversion.

2.2. Other computational calculation methods

In this thesis, empirical and semi-empirical calculations are used for the structural optimisations. The accuracy of the (semi-)empirical methods is not so high as that of the DFT, therefore its main usage in this thesis is to make a first guess of stable structures among a huge number of candidates, followed by the DFT calculations to compare and validate the results.

Empirical calculations have been established for a fast simulation of large molecules which cannot be handled by the DFT due to the calculation cost. The time-dependent behaviour of the system is calculated by an algorithm based on the molecular dynamics (MD). In this thesis, the calculation package; large-scale atomic/molecular massively parallel simulator (LAMMPS) [10] is utilised with the following 3 types of potentials: adaptive intermolecular reactive empirical bond order (AIREBO) potential [11], reactive empirical bond order (REBO) potential [12], and AIREBO-Morse (AIREBO-M) potential [13].

Semi-empirical calculations have been developed to carry out the Hartree-Fock calculations, by several approximations and reference data obtained by experiments and/or *ab initio* simulations. In this thesis, the molecular orbital package (MOPAC) [14] is utilised with the following 3 methods: PM7 [15–17], PM6+D3 [15,18], and RM1 [19]. Among the semi-empirical methods, semi-empirical extended tight binding method (xTB) [20] is also utilised. It has been already

reported that the xTB simulation showed an excellent structure-energy agreement with the DFT results with the Pearson's correlation coefficient $r=0.998$ [21], for a massive number of C_{60} fullerene isomers.

Chapter 3. Astrochemistry of hydrocarbons

In this chapter, the materials and the conditions for the formation, interaction and destruction of the materials, which will be dealt with in this thesis, are explained.

3.1. Interstellar substances

The interstellar medium (ISM) is composed of approximately 90% of hydrogen, and 9% of helium [22]. 99% of interstellar materials are in gas phase, and the rest are dust grains like the nebula, which could be a base of surface reactions [23]. However, most of its exact components are still unclear. What is formed in the interstellar substances is the subject of great interest in the community of astrochemistry.

According to the periodic table of astronomer, approximately 74% of the whole universe consists of hydrogen, 24% helium and the rest 2% other heavy atoms [24]. Hydrogen plays an important role particularly for the formation of polycyclic aromatic hydrocarbons (PAHs), in which the carbon edge favours the hydrogen termination to remove unstable dangling bonds.

Carbon is one of rare elements in space. However, carbon rich regions are sometimes found in interstellar and circumstellar media. From the thick envelope of a carbon-rich star, various molecules such as carbon chains and hydrocarbons have been detected so far [25–28]. Since carbon is a source of life on the earth, investigation of space carbon may reveal the source of life and discovery of extraterrestrial life. Chemical reactions are also of interest. Space carbon experiences a cycle of the formation and deformation of different types of structures by strong energy irradiation in space. Eventually, it results in energetically stable structures such as fullerenes.

3.2. Diffuse interstellar bands and carbon nanostructures

Diffuse interstellar bands (DIBs) bring us some information of molecules present in the interstellar substances. Two of the carriers have been assigned as C_{60}^+ [29] and CN-naphthalene [30] so far. Interestingly, most of the DIB signals have been estimated as hydrocarbon molecules by spectroscopic observation [31], however, most of the DIB signals have not yet been identified.

PAHs are composed of a various number of aromatic rings with edges terminated by hydrogen. The PAHs constitute a large part of the DIB [31], and play an important role as a carrier of carbon in the carbon cycle in space [32]. For the investigation of the DIBs, planar PAHs or open-curved PAHs such as corannulene [33] have been intensively studied so far, while closed-curved PAHs except for fullerenes, such as ring-shaped molecules have not yet been reported. The ring shapes

are also interesting from a chemical point of view since they are expected to encapsulate alien molecule(s) inside. In this thesis, so-called carbon nanobelt ([12]isocyclophenacene, $C_{48}H_{24}$) [34] and carbon nanoring ([10]cycloparahenylene, $C_{60}H_{40}$) are studied.

Fullerenes are well known as physically stable and chemically reactive cage-shaped carbon nanomaterials and they have also been detected in the interstellar bands [35,36]. Theoretical or experimental studies on fullerenes from C_{20} [37], C_{2n} where n is a natural number, grown by a C_2 unit have been reported (except for C_{24}). Since fullerenes smaller than C_{60} and giant fullerenes are less stable and therefore it is hard to synthesise them experimentally, they have mainly been studied theoretically. Interestingly in space, fullerenes are efficiently formed in hydrogen-containing circumstances in which hydrogenated amorphous carbons (HACs) are abundant [38,39].

3.3. Fullerene growth and the isolated pentagon rule

There are two well-known fullerenes formation models; top-down dissociation [40] and bottom-up growths [41]. In this thesis, the bottom-up growth is focused on, and in this case carbon clusters are grown into fullerene cages, keeping pentagons separated by hexagons following the isolated pentagon rule (IPR) [42] as far as possible, except for several endohedral fullerenes [43].

In addition, the isolated pentagon rule (IPR) is another important factor for the fullerenes geometry. Since fullerene cages are formed by a mixture of 12 pentagons and several hexagons, curvature is introduced in the structure. The localisation of pentagons results in a high degree of curvature which causes strong strain, and as a result, the fullerene structure becomes less stable [42]. Therefore in order to delocalise the strain, pentagons must be surrounded by hexagons, not to be adjacent to each other [42]. The smallest fullerene that satisfies the IPR is C_{60} ; this is why C_{60} is the most stable fullerene.

Fullerenes are stable but chemically active. Active sites on the cages depend on the symmetry and size of the cages. In order to investigate the active sites for the chemical modification, several local parameters are considered to evaluate the local properties of fullerenes in this thesis; geometric and electronic parameters.

As the geometric parameters, the following 3 approaches are made based on the bond angle in order to evaluate the curvatures; pyramidalisation angle in atom A (PyrA) [44], hybridisation value [45–47], and bond lengths sum. For the electronic parameters, the following 2 approaches are made focusing on electrons distributed on the surface of the fullerene cage;: Mulliken charge, and frontier orbital values.

3.4. Heterofullerenes

Interesting molecules analogous to the conventional fullerenes; Heterofullerenes, have been reported. In the structure of heterofullerenes, at least 1 carbon atom is replaced with another atom, such as N [48,49] called azafullerene. $C_{59}N$ possesses a radical due to the replacement of

C atom with N which causes 1 dangling bond and therefore it is detectable by electron spin resonance (EPR) analysis. This very active molecule rapidly forms a dimer $(C_{59}N)_2$ and loses the radical.

3.5. Cyclodehydrogenation

Dehydrogenation is a possible reaction occurring in high energy regions in space. Cyclodehydrogenation is also one of the interesting intramolecular reactions which transform molecular structures from even 2D to 3D. For example, a planar PAH $C_{60}H_{30}$, which is the development of C_{60} , is transformed into C_{60} losing the hydrogen atoms by nitrogen laser [50].

Chapter 4. Experimental background

In this chapter, the principles of experiments carried out in this thesis are explained. Experiments of **electron spin resonance** are carried out supported by colleagues at Institut "Jožef Stefan" in Slovenia.

When a particle with spin angular momentum like an electron (spin quantum number: $s=1/2$) is placed in a magnetic field, the energy state is split into two with an energy difference of ΔE . For example, in the case of an electron, it is split into two states; magnetic spin quantum number: $m_s = +1/2$ (α , up spin) and $m_s = -1/2$ (β , down spin). α spin is antiparallel while β spin is parallel to the external magnetic field, and it results in unstable α and stable β states, i.e., the Zeeman effect. Their energy difference is in proportion to the strength of the external magnetic field. When applied external magnetic flux density is equivalent to ΔE , electron spin jumps from β to α , and there will be strong absorption.

In the same way, spin orientation of a nucleus with nuclear spin quantum number $I \neq 0$ such as $^{13}C(I=1/2)$ and $^{14}N(I=1)$ splits in $m_I = I, I-1, \dots, -I$ in a magnetic field. In the case of nuclei, α spin becomes more stable than β in the magnetic field. When we irradiate energy equivalent to the specific resonance condition, nuclear spin jumps from α to β , and there will also be strong absorption. This absorption spectrum is complexed by magnetic interactions between neighbouring spins of electrons and nuclei.

In the EPR analysis, hyperfine structures originated from coupling of the electron spin and nuclear magnetic moment give the most important information about radicals in a sample. If we assume that an electron ($s=1/2$) and nucleus ($I=1/2$) are in an external magnetic field, the electron spin is split into two states $m_s=+1/2$ and $m_s=-1/2$, and the nuclear spin would also be $m_I=+1/2$ and $m_I=-1/2$. Then, the local magnetic field would be affected by the nuclear spin and therefore, absorption peaks appear as two spikes with a width of a . The intensity of the two peaks become half of the original peak from the electron.

Chapter 5. Structural change during the synthesis of powder radical azafullerene monomer

Azafullerene $C_{59}N$ radical has an unpaired electron on a carbon atom next to the nitrogen atom and therefore it is an organic magnetic molecule. $C_{59}N$ is expected to be an alternative to another organic magnet $N@C_{60}$ thanks to its size proximity and electron-spin dephasing time [51].

One problem on the practical application of $C_{59}N$ is that $C_{59}N$ is immediately polymerised into a dimer and becomes a stable non-magnetic molecule. In order to prevent the monomer from dimerisation, a complexation method with [10]CPP in a liquid phase has been established by Stergiou *et al.* so far [51].

In this chapter, I theoretically investigated the structural change during the synthesis of [10]CPP- $C_{59}N$ complex (hereinafter [10]CPP $\supset C_{59}N$) in a solid (powder) phase which enables practical application of [10]CPP $\supset C_{59}N$ particles as qubit arrays [52].

A solid state sample of [10]CPP $\supset (C_{59}N)_2 \subset$ [10]CPP was prepared by Dr A. Stergiou at the National Hellenic Research Foundation in Greece. By the X-band EPR analysis, which was carried out by the group of Prof. Denis Arčon at the Jožef Stefan Institute in Slovenia, several unique signals were observed. The transformation of the EPR signal during heating up to 290°C indicated that the thermolysis of the dimer proceeds via two steps. DFT calculations indicated that the stable pristine dimer starts rotating the cage with intermittent bond breaks at 100-150°C and form trimers and tetramers with neighbouring molecules. Expected EPR signals of the mixture of trimers and tetramers based on the unpaired electron distribution matched the experimental signals. Further heating up caused complete bond breaks between the $C_{59}N$ cages and finally they formed radical monomers, the signal of which has already been known [51].

The obtained $C_{59}N^\bullet$ showed the signal with an extremely long lifetime at room temperature. The signal intensity was still high even 158 days after the experiment. Surprisingly, the EPR signal was still detected even 30 months after the experiment unlike $C_{59}N^\bullet$ without [10]CPP.

Chapter 6. Hydrogenation of non-IPR smaller fullerenes

In this study [54], I focus on the bottom-up growth of small fullerenes from C_{20} to C_{52} , which are non-IPR species, in the presence of hydrogen. In order to avoid the time cost using the DFT, this study aims to test and validate various simulation methods; i.e., (a) sequential hydrogenation to pursue the most stable structure, (b) introduction of geometric and electronic parameters to select the next hydrogenation site, and (b) employment of some empirical, semi-empirical, and tight-binding methods to increase the speed of calculations keeping consistency with the DFT.

Structural optimisation of pure carbon cages C_x ($x=20, 24, 26, \dots 52$) by the DFT-LDA calculations indicated that the instability of the cage structures is generally in proportion to the number of

atoms surrounded by triple fused pentagons. Since there are a too large number of isomers for the following hydrogenation steps, 4 representative structures are focused on; C_{28} (1- T_d and 2- D_2 , referring to the indices of Yoshida's library[54]-symmetry symbol) and C_{40} (38- D_2 and 40- T_d).

6.1. Sequential hydrogenation

In order to save the calculation costs, first, a sequential hydrogenation method was tested. In this method, the first hydrogen atom binds to a site on a cage and each structure was optimised by the DFT-LDA. The second hydrogen atom was added to a site in the same way without moving the first hydrogen atom and the most stable structure was obtained. By repeating this sequence, the structures with up to the fifth hydrogen addition were obtained. This approach dramatically saved a number of structures to calculate, and also worked properly for halogenated fullerenes, such as chlorinated fullerenes [55].

As a result of the sequential hydrogenation, for T_d - C_{28} , hydrogen atoms bound to the 4 triple fused pentagons on the tetrahedral corners. The fifth hydrogen attached to the fused pentagon site with lower binding energy was observed. These hydrogenated structures originally from T_d - C_{28} were more stable than those from D_2 - C_{28} . On the other hand, in the case of C_{40} , the T_d isomer was less stable than the D_2 isomer. For T_d - C_{40} , the obtained structure with 4 hydrogen atoms was not hydrogenated tetrahedrally, different from the C_{28} case. In both cases hydrogenation occurred at fused pentagon sites and at the fifth hydrogenation the T_d structure became more stable than the D_2 structure. This change in the order of stability suggests that we cannot make a guess for the stable hydrogenated fullerenes from the stability of pure carbon isomers.

6.2. Hydrogenation based on geometric and electronic parameters

As another approach, prediction methods using geometric parameters; the pyramidalisation angle (PyrA), hybridisation value, 3 bond lengths sum and 2 bond lengths sum, were tested. In these methods, one reactive site was selected for hydrogenation by the largest value of the geometric parameter before carrying out the hydrogenation. The hydrogenated structure was optimised by the DFT-LDA calculations. This operation was repeated up to the fifth hydrogenation. This method saved tremendously the calculation costs, for example, it reduced 130 calculations into 5 in the case of $C_{28}H_5$.

It was found that pyrA and hybridisation gave the same hydrogenated structures. These two parameters successfully predicted the lowest energy structures of T_d - $C_{40}H$ and T_d - $C_{40}H_2$. However, except for these two structures, none of the tested parameters gave the lowest energy structures.

In the same way, local electronic parameters of fullerene cages were considered; local Mulliken charges and frontier orbital (FO) values, considering that charged sites may also be hydrogenated to stabilise the whole structure.

The results showed that generally the frontier orbital values predict lower energy structures than the Mulliken values, and most of the derived structures were more stable than the ones given

by the geometric parameters. However, none of them predicted the sequence of structures with the lowest energy. Although the electronic parameters did not give the reliable hydrogenation routes, interestingly, the lowest frontier orbital value calculated by 0.1 electron addition provided negative ΔE for D_2 - $C_{28}H_3$ and for D_2 - $C_{28}H_5$. It indicates that the parameter derived more stable structures than the sequential hydrogenation. This is an important result that invalidates the first hypothesis, i.e., the sequential hydrogenation is not applicable to small fullerenes. It also implies that added hydrogen atoms can rearrange their positions on the cage surface when another hydrogen atom is added to stabilise the whole molecule.

6.3. Empirical and semi-empirical calculations

As the next approach, every possible hydrogenated structure was tested by quick (semi-) empirical calculations and the results were compared to those obtained by the DFT sequential calculations. The empirical calculations carried out by LAMMPS [10] utilised the empirical potentials of AIREBO, REBO, and AIREBO-M. For semi-empirical calculations, MOPAC [14] was utilised with PM7, PM6+D3, and RM1 methods. In addition, the semi-empirical extended tight binding method (GFN2-xTB) was also employed.

It was found that in the case of $C_{28}H_5$, $C_{40}H$, and $C_{40}H_5$, the empirical methods showed a very low Pearson's correlation coefficient ($r < 0.4$); in other words, the results obtained by the empirical potentials have essentially no consistency with those obtained by the DFT-LDA.

In contrast, the GFN-xTB method gave an excellent agreement with the DFT-LDA with the correlation $r = 0.98$. For simpler fullerenes (a smaller cage, and the same cage with less hydrogenation), the agreement was even better showing $r = 0.993$ - 0.998 . Furthermore, the most stable structures obtained by the xTB coincided with those obtained by the DFT. Therefore, DFT-LDA can be safely switched to GFN2-xTB, which gains over 600 times less computational time.

6.4. Testing all of the possible combinations of the hydrogenation sites using xTB

All of the possible combinations of the hydrogenation sites were tested by GFN-xTB up to the fourth hydrogen atom addition. This method gives the total energy of all possible hydrogenated structures C_nH_m ($n = 28$ and 40 , $m = 1, \dots, 4$), which is different from that obtained by the sequential hydrogenation. Although the number of structures tested is huge, the isomer with the lowest energy can be definitely obtained by this method.

It was found that for $C_{28}H_4$, the tetrahedrally hydrogenated T_d structure is the most stable structure among a huge number of isomers. This structure coincided with that characterised by experiment [56] and also with the one given by the sequential addition carried out by DFT-LDA, GFN2-xTB, PM7, PM6+D3 and RM1. In contrast, D_2 - $C_{28}H_4$ molecules were less stable. The most stable molecule had 2 pairs of hydrogen atoms on the opposite sides, thanks to which the local strain was released and the aromaticity was increased. For C_{40} species, the tetrahedrally

hydrogenated T_d -C₄₀H₄ structure was the most stable among the T_d -C₄₀H₄ isomers. However, interestingly, D_2 -C₄₀H₄, which was transformed into tube-like structure, was more stable and this structure corresponded to the one given by the sequential addition carried out by DFT-LDA. These results suggest that the sequential hydrogenation may be applicable to the numerical investigation of larger hydrogenated fullerenes, such as C₄₀H_m. It would be a great benefit in terms of the computational cost reduction.

Chapter 7. Dehydrogenation of carbon nanobelts

As one of the candidate molecules in the DIBs, in this chapter I investigated a curved structure; carbon nanobelt (CNB). It is also interesting to study CNBs from a carbon chemical point of view since the energy absorption in space may be explained by dehydrogenation, particularly cyclodehydrogenation, and single-walled carbon nanotubes of a uniform diameter may be grown via polymerisation of CNBs. Introducing curvature into carbonaceous structures decreases aromaticity and localises reactive sites. Structural reorganisation occurs, transforming the carbon bonds of sp²- to sp³-, which is similar to hydrogenation of small fullerene, to delocalise the strain originated from the curvature. Thus, the investigation of transformation of curved aromatic hydrocarbons by dehydrogenation is also of great interest and importance.

In this study, [(CH)₂-C₆H₂]_{2n} ([12]CNB) [34] was chosen as a curved polyaromatic hydrocarbon to investigate the structural change during hydrogen removal. In order to imitate the extreme conditions in the ISM, dehydrogenation routes were simulated by sequential hydrogen removal. The results obtained by the calculations were compared to those of the collision-induced dissociation (CID) experiments of CNBs, where the fragment molecules were analysed by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), carried out by Dr Paul Dunk at Florida State University.

7.1. Mass spectrometry and DFT calculations

FT-ICR MS experiments were carried out for pure CNB samples with and without molecular fragmentation by the CID, and several specific fragment ions were detected as “magic numbers”. In order to explain the mechanism of the dissociation, DFT calculations were carried out at a charge state of +1 which demonstrates the MS and CID systems.

First, one hydrogen atom was removed from the optimised pristine CNB molecule. Considering the molecular symmetry, there are only 2 structures; i.e., hydrogen removal from an (a) exterior; armchair, or (b) interior; zigzag carbon edge, for 1H-loss CNB molecules (C₄₈H₂₃). Another structure (c) can be constructed from (b) by Stone-Wales bond rotation. For the next hydrogenation, another hydrogen atom was removed from each of optimised C₄₈H₂₃ structures and the 2H-loss structures; C₄₈H₂₂, were optimised. The most stable isomer was selected for the next hydrogen removal. For (c), the bond rotation was performed and the energy was compared

with that without the bond rotation. This operation was repeated to obtain nH-loss structures up to n=8.

It was found that the dissociation proceeds by pairwise hydrogen loss, and from the 4H-loss, the routes (a) and (b) join (c), and two parallel carbyne chains with pentagon ends are formed, which gives the lowest energies among the three routes. After 6H-loss, the intensity of the experimentally detected signals of dehydrogenated CNB were very low. It can be attributed to the carbyne chains, i.e, too long *sp* chains localise the curvature on the rest of six-membered rings and the aromaticity is decreased, resulting in the difficulty in the extension of the chains. Instead, CH-loss from the six-membered rings and 2C-loss from the chains are preferred for further dissociation. These results well matched the experimental MS spectra.

7.2. FT-IR signals calculated by DFT

For the most stable structure of each isomer (pristine, 2H-, 4H-, and 6H-loss) in the optimal route (c), IR spectra were simulated by the DFT calculations focusing on the vibration modes attributed to pentagons. Comparing the absorption peaks of several planetary nebulae in the Magellanic cloud with the obtained spectra of dehydrogenated CNBs, these unique structures of “pentagons in a ring” cannot be a candidate for interstellar PAHs. However, CNB species become a good example of curved PAHs, which is a new concept in astrochemistry.

Chapter 8. Conclusions

This thesis explored three fields; (1) the radical formation of azafullerenes encapsulated in carbon nanoring, (2) the formation and growth behaviour of small fullerenes notably in the presence of hydrogen, and (3) the dehydrogenation routes for curved hydrocarbons, and the following results were obtained.

- (1) The radical formation mechanism of powdered $C_{59}N^*[10]CPP$ was revealed. The radicals are protected by [10]CPP ring, thanks to which the lifetime of radicals with the sharp triplet was more than 158 days. The signal was detected even 30 months after the experiment unlike bare $C_{59}N^*$ which rapidly dimerises. Powdered $C_{59}N^*[10]CPP$ radicals are expected to be a building block of quantum circuits of qubits thanks to the stability and higher yield compared to other qubit candidates such as $N@C_{60}$.
- (2) For the growth of small fullerenes in the presence of hydrogen, a variety of methodologies were investigated to systematically predict the most stable structures of hydrogenated small fullerenes (C_{28} and C_{40}). Full-combination sites testing was also performed by xTB. It was found that the sequential hydrogenation is applicable to the investigation of larger non-IPR fullerenes such as C_{40} , whereas full-testing using GFN2-xTB is reliable for smaller fullerenes such as C_{28} . These results will directly contribute to a mapping of the hydrogen-catalysed non-IPR fullerene growth.

- (3) For the dehydrogenation of carbon nanobelts (CNB), “Magic numbers” appeared in the mass spectra were successfully explained by the sequential dehydrogenation simulation carried out by the DFT. FT-IR absorption of the most stable structures was also investigated. It is believed that CNB species become a good example of curved PAHs, which is a new concept in astrochemistry.

Bibliography

1. Benioff, P. Quantum Mechanical Models of Turing Machines That Dissipate No Energy. *Phys. Rev. Lett.* **1982**, *48*, 1581–1585, doi:10.1103/PhysRevLett.48.1581.
2. Harneit, W.; Huebener, K.; Naydenov, B.; Schaefer, S.; Scheloske, M. N@C60 Quantum Bit Engineering. *physica status solidi (b)* **2007**, *244*, 3879–3884, doi:https://doi.org/10.1002/pssb.200776193.
3. Rayson, M.J.; Briddon, P.R. Highly Efficient Method for Kohn-Sham Density Functional Calculations of 500-10000 Atom Systems. *Physical Review B - Condensed Matter and Materials Physics* **2009**, doi:10.1103/PhysRevB.80.205104.
4. Rayson, M.J. Rapid Filtration Algorithm to Construct a Minimal Basis on the Fly from a Primitive Gaussian Basis. *Computer Physics Communications* **2010**, doi:10.1016/j.cpc.2010.02.012.
5. Briddon, P.R.; Rayson, M.J. Accurate Kohn–Sham DFT with the Speed of Tight Binding: Current Techniques and Future Directions in Materials Modelling. *physica status solidi (b)* **2011**, *248*, 1309–1318, doi:https://doi.org/10.1002/pssb.201046147.
6. Magalhães, A.L. Gaussian-Type Orbitals versus Slater-Type Orbitals: A Comparison. *J. Chem. Educ.* **2014**, *91*, 2124–2127, doi:10.1021/ed500437a.
7. Hartwigsen, C.; Goedecker, S.; Hutter, J. Relativistic Separable Dual-Space Gaussian Pseudopotentials from H to Rn. *Phys. Rev. B* **1998**, *58*, 3641–3662, doi:10.1103/PhysRevB.58.3641.
8. Monkhorst, H.J.; Pack, J.D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* **1976**, *13*, 5188–5192, doi:10.1103/PhysRevB.13.5188.
9. Feynman, R.P. Forces in Molecules. *Phys. Rev.* **1939**, *56*, 340–343, doi:10.1103/PhysRev.56.340.
10. Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *Journal of Computational Physics* **1995**, *117*, 1–19, doi:10.1006/jcph.1995.1039.
11. Stuart, S.J.; Tutein, A.B.; Harrison, J.A. A Reactive Potential for Hydrocarbons with Intermolecular Interactions. *J. Chem. Phys.* **2000**, *112*, 6472–6486, doi:10.1063/1.481208.
12. Brenner, D.W.; Shenderova, O.A.; Harrison, J.A.; Stuart, S.J.; Ni, B.; Sinnott, S.B. A Second-Generation Reactive Empirical Bond Order (REBO) Potential Energy Expression for Hydrocarbons. *J. Phys.: Condens. Matter* **2002**, *14*, 783–802, doi:10.1088/0953-8984/14/4/312.
13. O’Connor, T.C.; Andzelm, J.; Robbins, M.O. AIREBO-M: A Reactive Model for Hydrocarbons at Extreme Pressures. *J. Chem. Phys.* **2015**, *142*, 024903, doi:10.1063/1.4905549.
14. Stewart, J.J.P. *MOPAC2016*; Stewart Computational Chemistry, Colorado Springs: CO, USA;
15. Stewart, J.J.P. Optimization of Parameters for Semiempirical Methods V: Modification of NDDO Approximations and Application to 70 Elements. *J Mol Model* **2007**, *13*, 1173–1213, doi:10.1007/s00894-007-0233-4.

16. Stewart, J.J.P. Optimization of Parameters for Semiempirical Methods VI: More Modifications to the NDDO Approximations and Re-Optimization of Parameters. *J Mol Model* **2013**, *19*, 1–32, doi:10.1007/s00894-012-1667-x.
17. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *Journal of Computational Chemistry* **2006**, *27*, 1787–1799, doi:10.1002/jcc.20495.
18. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104, doi:10.1063/1.3382344.
19. Rocha, G.B.; Freire, R.O.; Simas, A.M.; Stewart, J.J.P. RM1: A Reparameterization of AM1 for H, C, N, O, P, S, F, Cl, Br, and I. *Journal of Computational Chemistry* **2006**, *27*, 1101–1111, doi:10.1002/jcc.20425.
20. Bannwarth, C.; Caldeweyher, E.; Ehlert, S.; Hansen, A.; Pracht, P.; Seibert, J.; Spicher, S.; Grimme, S. Extended Tight-Binding Quantum Chemistry Methods. *WIREs Computational Molecular Science* **2021**, *11*, e1493, doi:10.1002/wcms.1493.
21. Sure, R.; Hansen, A.; Schwerdtfeger, P.; Grimme, S. Comprehensive Theoretical Study of All 1812 C60 Isomers. *Phys. Chem. Chem. Phys.* **2017**, *19*, 14296–14305, doi:10.1039/C7CP00735C.
22. Ferrière, K.M. The Interstellar Environment of Our Galaxy. *Rev. Mod. Phys.* **2001**, *73*, 1031–1066, doi:10.1103/RevModPhys.73.1031.
23. Ehrenfreund, P.; Charnley, S.B. Organic Molecules in the Interstellar Medium, Comets, and Meteorites: A Voyage from Dark Clouds to the Early Earth. *Annual Review of Astronomy and Astrophysics* **2000**, *38*, 427–483, doi:10.1146/annurev.astro.38.1.427.
24. Croswell, K. *Alchemy of the Heavens: Searching for Meaning in the Milky Way*; Bantam Doubleday Dell Publishing Group, Inc., New York: New York, 1995;
25. Cernicharo, J.; Cabezas, C.; Pardo, J.R.; Agúndez, M.; Bermúdez, C.; Velilla-Prieto, L.; Tercero, F.; López-Pérez, J.A.; Gallego, J.D.; Fonfría, J.P.; et al. Discovery of Two New Magnesium-Bearing Species in IRC+10216: MgC₃N and MgC₄H. *A&A* **2019**, *630*, L2, doi:10.1051/0004-6361/201936372.
26. Anderson, J.K.; Ziurys, L.M. Detection of CCN (x 2πr) in IRC+10216: Constraining Carbon-Chain Chemistry. *The Astrophysical Journal Letters* **2014**, *795*, L1, doi:10.1088/2041-8205/795/1/L1.
27. Agúndez, M.; Cernicharo, J.; Guélin, M. New Molecules in IRC +10216: Confirmation of C5S and Tentative Identification of MgCCH, NCCP, and SiH3CN. *Astronomy and Astrophysics* **2014**, *570*, A45, doi:10.1051/0004-6361/201424542.
28. Agúndez, M.; Cernicharo, J.; Guélin, M.; Kahane, C.; Roueff, E.; Kłos, J.; Aoiz, F.J.; Lique, F.; Marcelino, N.; Goicoechea, J.R.; et al. Astronomical Identification of CN⁻, the Smallest Observed Molecular Anion. *Astronomy and Astrophysics* **2010**, *517*, L2, doi:10.1051/0004-6361/201015186.
29. Campbell, E.K.; Holz, M.; Gerlich, D.; Maier, J.P. Laboratory Confirmation of C60(+) as the Carrier of Two Diffuse Interstellar Bands. *Nature* **2015**, *523*, 322–323, doi:10.1038/nature14566.
30. McGuire, B.A.; Loomis, R.A.; Burkhardt, A.M.; Lee, K.L.K.; Shingledecker, C.N.; Charnley, S.B.; Cooke, I.R.; Cordiner, M.A.; Herbst, E.; Kalenskii, S.; et al. Detection of Two Interstellar Polycyclic Aromatic Hydrocarbons via Spectral Matched Filtering. *Science* **2021**, *371*, 1265–1269, doi:10.1126/science.abb7535.

31. Snow, T.P. Diffuse Interstellar Bands: Past and Present. *Proceedings of the International Astronomical Union* **2013**, 9, 3–12, doi:10.1017/S1743921313015512.
32. Henning, T.; Grün, E.; Steinacker, J. *Cosmic Dust—Near and Far*; Astronomical Society of the Pacific, 2009; Vol. 414;.
33. Pilleri, P.; Herberth, D.; Giesen, T.F.; Gerin, M.; Joblin, C.; Mulas, G.; Mallocci, G.; Grabow, J.-U.; Brünken, S.; Surin, L.; et al. Search for Corannulene (C₂₀H₁₀) in the Red Rectangle. *Monthly Notices of the Royal Astronomical Society* **2009**, 397, 1053–1060, doi:10.1111/j.1365-2966.2009.15067.x.
34. Povie, G.; Segawa, Y.; Nishihara, T.; Miyauchi, Y.; Itami, K. Synthesis of a Carbon Nanobelt. *Science* **2017**, doi:10.1126/science.aam8158.
35. Cami, J.; Bernard-Salas, J.; Peeters, E.; Malek, S.E. Detection of C₆₀ and C₇₀ in a Young Planetary Nebula. *Science* **2010**, doi:10.1126/science.1192035.
36. Sellgren, K.; Werner, M.W.; Ingalls, J.G.; Smith, J.D.T.; Carleton, T.M.; Joblin, C. C₆₀ in Reflection Nebulae. *Astrophysical Journal Letters* **2010**, doi:10.1088/2041-8205/722/1/L54.
37. Jarrold, M.F. The Smallest Fullerene. *Nature* **2000**, 407, 26–27, doi:10.1038/35024178.
38. García-Hernández, D.A.; Manchado, A.; García-Lario, P.; Stanghellini, L.; Villaver, E.; Shaw, R.A.; Szczerba, R.; Perea-Calderón, J. V. Formation of Fullerenes in H-Containing Planetary Nebulae. *Astrophysical Journal Letters* **2010**, doi:10.1088/2041-8205/724/1/L39.
39. García-Hernández, D.A.; Rao, N.K.; Lambert, D.L. Are C₆₀ Molecules Detectable in Circumstellar Shells of R Coronae Borealis Stars? *Astrophysical Journal* **2011**, doi:10.1088/0004-637X/729/2/126.
40. Self-Assembly of the Fullerenes | Accounts of Chemical Research Available online: <https://pubs.acs.org/doi/10.1021/ar00015a001> (accessed on 21 April 2021).
41. Dunk, P.W.; Kaiser, N.K.; Hendrickson, C.L.; Quinn, J.P.; Ewels, C.P.; Nakanishi, Y.; Sasaki, Y.; Shinohara, H.; Marshall, A.G.; Kroto, H.W. Closed Network Growth of Fullerenes. *Nature Communications* **2012**, 3, 855, doi:10.1038/ncomms1853.
42. Kroto, H.W. The Stability of the Fullerenes C_n, with n = 24, 28, 32, 36, 50, 60 and 70. *Nature* **1987**, 329, 529–531, doi:10.1038/329529a0.
43. Cai, W.; Abella, L.; Zhuang, J.; Zhang, X.; Feng, L.; Wang, Y.; Morales-Martínez, R.; Esper, R.; Boero, M.; Metta-Magaña, A.; et al. Synthesis and Characterization of Non-Isolated-Pentagon-Rule Actinide Endohedral Metallofullerenes U@C₁(17418)-C₇₆, U@C₁(28324)-C₈₀, and Th@C₁(28324)-C₈₀: Low-Symmetry Cage Selection Directed by a Tetravalent Ion. *J. Am. Chem. Soc.* **2018**, 140, 18039–18050, doi:10.1021/jacs.8b10435.
44. Haddon, R.C. Comment on the Relationship of the Pyramidalization Angle at a Conjugated Carbon Atom to the σ Bond Angles. *J. Phys. Chem. A* **2001**, 105, 4164–4165, doi:10.1021/jp010023f.
45. Haddon, R.C. C₆₀: Sphere or Polyhedron? *J. Am. Chem. Soc.* **1997**, 119, 1797–1798, doi:10.1021/ja9637659.
46. Haddon, R.C.; Scott, L.T. π -Orbital conjugation and rehybridization in bridged annulenes and deformed molecules in general: π -orbital axis vector analysis. *Pure and Applied Chemistry* **1986**, 58, 137–142, doi:10.1351/pac198658010137.
47. Haddon, R.C. Hybridization and the Orientation and Alignment of π -Orbitals in Nonplanar Conjugated Organic Molecules: π -Orbital Axis Vector Analysis (POAV2). *J. Am. Chem. Soc.* **1986**, 108, 2837–2842, doi:10.1021/ja00271a009.

48. Averdung, J.; Luftmann, H.; Schlachter, I.; Mattay, J. Aza-Dihydro[60]Fullerene in the Gas Phase. A Mass-Spectrometric and Quantumchemical Study. *Tetrahedron* **1995**, *51*, 6977–6982, doi:10.1016/0040-4020(95)00361-B.
49. Lamparth, I.; Nuber, B.; Schick, G.; Skiebe, A.; Grösser, T.; Hirsch, A. C₅₉N⁺ and C₆₉N⁺: Isoelectronic Heteroanalogues of C₆₀ and C₇₀. *Angewandte Chemie International Edition in English* **1995**, *34*, 2257–2259, doi:10.1002/anie.199522571.
50. Boorum, M.M.; Vasil'ev, Y.V.; Drewello, T.; Scott, L.T. Groundwork for a Rational Synthesis of C₆₀: Cyclodehydrogenation of a C₆₀H₃₀ Polyarene. *Science* **2001**, doi:10.1126/science.1064250.
51. Stergiou, A.; Rio, J.; Griwatz, J.H.; Arčon, D.; Wegner, H.A.; Ewels, C.P.; Tagmatarchis, N. A Long-Lived Azafullerenyl Radical Stabilized by Supramolecular Shielding with a [10]Cycloparaphenylene. *Angewandte Chemie International Edition* **2019**, *58*, 17745–17750, doi.org/10.1002/anie.201909126.
52. Tanuma, Y.; Stergiou, A.; Bobnar, A.B.; Gaboardi, M.; Rio, J.; Volkmann, J.; Wegner, H.A.; Tagmatarchis, N.; Ewels, C.; Arcon, D. Robust coherent spin centers from stable azafullerene radicals entrapped in cycloparaphenylene rings. *Nanoscale* **2021**, doi.org/10.1039/D1NR06393F.
53. Tanuma, Y.; Maekawa, T.; Ewels, C. Methodological Investigation for Hydrogen Addition to Small Cage Carbon Fullerenes. *Crystals* **2021**, *11*, 1334, doi:10.3390/cryst11111334.
54. Yoshida, M. Yoshida's Fullerene Library Available online: <http://www.jcrystal.com/steffenweber/gallery/Fullerenes/Fullerenes.html> (accessed on 18 November 2020).
55. Vlandas, A.; Ewels, C.P.; Lier, G.V. Controlling Fullerene Addition Sequences, Regioselectivity and Magic Numbers via Metal Encapsulation. *Chem. Commun.* **2011**, *47*, 7051–7053, doi:10.1039/C1CC11072A.
56. Veljković, M.; Nešković, O.; Djerić, A.; Veličković, S.; Šipka, V. Hypervalent Molecular Cluster: C₂₈H₄. *Materials Science Forum* **2005**, *494*, 181–186, doi:10.4028/www.scientific.net/MSF.494.181.