CHAPTER 7

FINAL CONCLUSIONS

7.1 CONCLUSIONS

The characterisation of the most novel metallofullerenes up to 2004 has been theoretically and systematically discussed in various chapters of this study. Fullerenes that do not contain metals can be successfully characterized with semiempirical methods, but metallofullerenes require DFT-based methods. These methods provide an interesting framework for performing first-principle calculations of large systems more cheaply than post-HF methods. In the near future, the rapid increase in computer development and the implementation of new algorithms as well as new functionals will provide more powerful tools to scientists for studying the electronic structure of the new metallofullerenes. The way forward has already been initiated.

The vigorous start to fullerene chemistry may seem to have stopped at the end of the 1990s since several authors had already established its chemical principles. Manolopoulos et al. systematized the isomerism in the free fullerenes, and Taylor and Hirsch determined the procedure for

predicting chemical reactivity. Only the appearance of new compounds with unexpected properties and reactivity has given rise to a certain resurgence of fullerene chemistry. Two of these novel compounds are fullerenes that encapsulate a metal unit of four atoms and fullerenes that some carbons are substituted by metals. Both are metallofullerenes. From the structural point of view, metallofullerenes can be divided into three main groups, all of which have been discussed in this study: endohedral, heterohedral and exohedral metallofullerenes. The main families of compounds studied are $Sc_{3-n}M_nN@C_k$ (n = 0-3, M = Y, La; k = 68, 78, 80) (endohedral), C_xM_n (x = 56, 57, 58, 59; M = Pt, Ir, Os; n = 1, 2) (heterohedral) and (η^2-C_k){$M(PH_3)_2$}$_n$ (k = 60, 70, 84; M = Pt, Pd, Ni; n = 1, 2, 4, 6) (exohedral). The present study is a step forward in our knowledge of each of these families of compounds, and in particular, in our understanding of the metal-carbon bond, isomerism and reactivity. The DFT method proved to be an excellent computational tool for providing good geometries, for solving the intricacies of the different metal-carbon bonds, for producing experimental data (ionization potentials and electron affinities) and also for making predictions about isomerism stability and reactivity. The principal conclusions drawn about the species studied here are:

The experimental advances in each field have not been homogeneous. In consequence, the information available for each family of compounds is completely different. Whereas exohedral metallofullerenes were the first metallofullerenes to be studied in depth and their macroscopic quantities had allowed their characterisation by X-ray crystallography and other spectroscopic techniques, heterohedral metallofullerenes are still in their infancy because they have only been detected in tiny quantities by mass spectrometric studies. In the case of TNT endohedral metallofullerenes, huge advances have been made in recent years and they can now be synthesised in bulk quantities. Some of TNT endohedral metallofullerenes have been fully characterised by X-ray, IR and UV-vis techniques.

Many years studying metallofullerenes from a theoretical point of view. At first, fullerene chemistry was written about from the perspective of organic and physical chemistry and also materials science. It was not until

the middle 1990s that inorganic/organometallic chemistry began to take part. The most important characteristic of fullerenes is their ability to react as poorly conjugated and electron-deficient alkenes. Hence, fullerenes can be readily reacted with electron-rich metal species such as nucleophiles, bases, radicals or reducing agents. The perfect combination of fullerenes and metallic units has produced an endless variety of different stoichiometries for metallofullerenes. The first to be detected was the $La@C_{60}$ endohedral metallofullerene and the first to be studied was the exohedral metallofullerene $C_{60}(t\text{-}BuC_5H_5N)_2OsO_4$.

Different types of structures, different types of metal-carbon bonds. The metal units in each family of compounds are located differently in relation to the fullerene carbon framework: inside the cage, within the carbon framework and outside the cage. Each metal position is characterized by a different number of carbon neighbours and is also at different M–C bond lengths. These differences mean that the metal–carbon bond in each family of metallofullerenes has different models. The encapsulation of a trimetallic nitride template unit (TNT, $Sc_{3-n}M_nN$; n = 0-3; M = Y, La) inside the carbon cage to produce TNT endohedral metallofullerenes is explained by an ionic pair (cage-metal) model in which the TNT unit formally transfers six electrons to the cage. Classical endohedral metallofullerenes can also be explained mostly by an ionic model but when other bonding models appear when the guest is bigger or the host have not a big enough hollow (*e.g.* C_{28}). On the other hand, in heterohedral metallofullerenes, metals establish a covalent metal-carbon bond without causing oxidation to the metal. Finally, the $(MPH_3)_2$ metal units situated exohedrally to the fullerene are only coordinated in a η^2 mode to the C–C bond. However, stronger metal-carbon bonds are found in other exohedral metallofullerenes when a different metal unit is involved. For example: $\{Re(CO)_5\}_2$ and $O_2OsO_2(4\text{-}Bu^tC_5H_4N)_2$. This means that exohedral metallofullerenes can be classified as π- and σ-bonded metal-fullerene complexes. The former (studied here) are π-bonded exohedral metallofullerenes whereas the latter are σ-bonded exohedral metallofullerenes. The different strength of each metal-carbon bond can be exemplified by the magnitude and sign of the binding energies of the formation reaction of the endohedral, heterohedral and exohedral metallofullerenes: –11.60 eV for the encapsulation reaction

$Sc_3N + C_{80} \rightarrow Sc_3N@C_{80}$; 7.35 eV for the substitution reaction $Pt + C_{60} \rightarrow C_{58}Pt + C_2$; and –0.96 eV for the coordination reaction $Pt(PH_3)_2 + C_{60} \rightarrow (\eta^2\text{-}C_{60})Pt(PH_3)_2$.

Chemometric tools applied to isomerism studies. Classical methodology (which pre-determines all the isomers that are to be calculated) is used to study the isomerism in endohedral and exohedral metallofullerenes. It has been successful because the number of isomers is very limited. Nevertheless, the regioisomers of heterohedral metallofullerenes can be much more numerous: for example, the stoichiometry $C_{57}Pt_2$ has 43 distinct regioisomers. Thus, other techniques which can manage considerable amounts of data must be used if we want to understand regioisomerism in heterohedral metallofullerenes. Also, we are interested in the factors that govern the stability of isomers. As regard to this, chemometric tools have been very useful for drawing conclusions from the considerable quantities of data provided by the factors which affect the stability of regioisomers. These tools have been used not only for analysing data but also for predicting the stability of other heterofullerenes.

TNT encapsulation stabilizes fullerene isomers that are not available as free fullerenes. TNT endohedral metallofullerenes are formed by the encapsulation of a metallic nitride template inside the following cages: D_3-C_{68}:**6140**, $D_{3h'}$-C_{78}:**5**, D_{5h}-C_{80}:**6** and I_h-C_{80}:**7**. The $D_{3h'}$-C_{78}:**5** and I_h-C_{80}:**7** cages have never been detected experimentally because these cages are not the most stable IPR isomers for C_{78} and C_{80} stoichiometries. Even the C_{68} fullerene is not an IPR fullerene, which means that atom for atom it is less stable than the IPR fullerenes. So, endohedral metallofullerenes can make non-classical fullerene isomers available for study. Furthermore, on the basis of the electronic structure we predicted that no other IPR fullerenes between C_{60} and C_{84} will be capable of encapsulating a TNT unit, apart from the fullerene isomers that are already known. TNT encapsulations keep open for the non-IPR fullerenes. This is because only free fullerene isomers with a high LUMO+3-LUMO+4 gap can encapsulate and stabilize metal units that formally transfer six electrons to the cage. The only free fullerene isomers that obey this rule are the abovementioned cages.

Stability of the carbon skeleton is the principal factor that determines the regioisomer stability of the heterofullerenes. DFT calculations carried out on numerous regioisomers of $C_{57}Pt_2$ and $C_{56}Pt_2$ clearly show that the metal atoms occupy neighbouring positions in the most stable structures. Metal substitution deforms the carbon framework and partially destroys the fullerene aromaticity. This is the *key* factor in determining the stability of these disubstituted clusters. Indeed, it is much easier to make a big hole that permits the incorporation of two Pt atoms in the carbon cage than two smaller holes in two opposite sites of the fullerene. The structures with two neighbouring Pt atoms retain the most C–C bonds, which is another important factor in determining the stability of the cluster. In addition, clusters with short Pt–Pt contacts may contain weak metal-metal interactions, which also favor the stability of the cluster but are not a fundamental stability element. In our opinion, these results go beyond the particular cases of the $C_{57}Pt_2$ and $C_{56}Pt_2$ regioisomers and we believe that the present conclusions can be extended to any transition metal derivative. Calculations performed on the ionic species of the Pt-derivatives and on some Ti homologues confirm the hypothesis that disubstituted C_{60} fullerenes contain the heteroatoms in adjacent sites. The behaviour of larger fullerenes such as C_{70}, should be similar although in this case the curvature of the fullerene could also be important.

Prediction of the exohedral reactivity taking into account the full characterization of the different C–C bond types. In order to predict the exohedral reactivity of a fullerene cage such as endohedral metallofullerenes and free fullerenes, we first performed a full characterization of all C–C bond types. The fullerenes characterized were: I_h-C_{60}:**1**, D_3-C_{68}:**6140**, D_{5h}-C_{70}:**1**, $D_{3h'}$-C_{78}:**5**, I_h-C_{80}:**7**, D_2-C_{84}:**22** and D_{2d}-C_{84}:**23**. Each C–C bond type is characterized by its topology, length, pyramidalization angle and Mayer bond order. This systematization enabled us to identify which sites were most reactive to a nucleophilic addition to free fullerenes or a [4 + 2] cycloaddition to TNT endohedral metallofullerenes. They are the most pyramidalized C–C bonds that also have a high Mayer bond order. However, these features are often not found simultaneously and so the most reactive site is usually a compromise between a highly pyramidalized C–C bond with a lower pyramidalization angle, and a C–C bond with a high

Mayer bond order but a lower pyramidalization angle. The most reactive site always goes to the pyracylene 6:6 C–C bond types.

Metal doping as a tool for modifying physical properties. In general, fullerenes have relatively large electron affinities and ionization potentials, because of the presence of low-lying unoccupied and occupied orbitals, respectively. The endohedral and heterohedral functionalization can modify these physical properties because these transformations change the electronic structure of fullerenes. It is interesting to see that heterohedral and endohedral metal doping reduce the ionization potentials, making the fullerenes better electron-donor compounds. Endohedral TNT doping reduces the EA of the fullerene whereas heterohedral metal doping increases and thus improves the electron acceptor character of free fullerenes.

7.2 PERSPECTIVES

Without doubt, the main theoretical challenges in the field of metallofullerenes are provided by heterohedrals and endohedrals. To date, only simple stoichiometries have been studied: those with a single carbon atom or C_2 unit replaced by a metal atom. But other structures, which are created by the loss of C_2 units in the former, have still to be studied. There are two main experimental methods for producing heterohedral metallofullerenes: (1) Branz's method, which involves gas phase clusters: $C_{60}M_n$ and (2) Balch's method, which involves polymeric, covalently bound chains: …$C_{60}ML_n{\cdot}C_{60}ML_n$…. Depending on the production method different stoichiometries may be preferred. So Branz's method tends to produce carbon cages with an odd number of carbons whereas Balch's method produces higher yields of carbon cages with an even number of carbons. So the mechanism for forming heterohedral metallofullerenes remains unsolved. On the other hand, theoreticians are waiting for experimental evidence of metal doping in other fullerenes such as C_{70}, C_{78}, C_{80} or C_{84} which exist as free fullerenes. These fullerenes will make it possible to study the effect of substituting C–C bonds with different pyramidalization angles in the problem of the regioisomerism. Furthermore, the fact that the variability in the topology and bond strength of higher fullerenes is greater than that of the two previously studied C–C bonds of

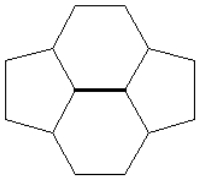
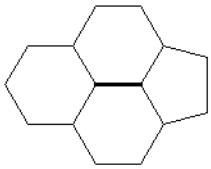
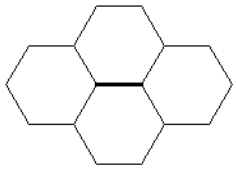
the C_{60} will give us the final clues about the factors which govern the regioisomerism.

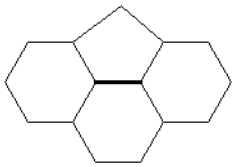
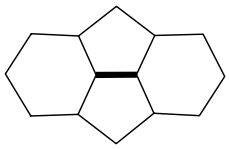
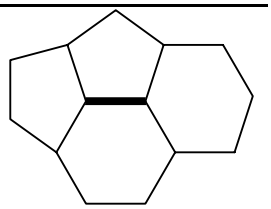
Apparently no more TNT endohedral metallofullerenes will be synthesized from IPR isomers between C_{60} and C_{84}. Researchers should focus on discovering new non-IPR cages which can encapsulate these TNT units. This is interesting because TNT encapsulation can make fullerene cages available that would otherwise remain unstable. To date only endohedral metallofullerenes can do this. Theoreticians should also pay greater attention to exohedral reactivity. Some progress in this area has already been made for $Sc_3N@C_{80}$. But, the exohedral reactivity of $Sc_3N@C_{68}$ and $Sc_3N@C_{78}$ complexes is almost completely unknown. Although progress in this research area is very fast, there are still many open questions concerning the electronic structure of the classical endohedral metallofullerenes such as $M_2@C_{80}$ (M = La, Ti). In the case of exohedral metallofullerenes, it seems necessary to focus on how the computational effort can be reduced before moving on to new and bigger fullerene complexes with metal units added exohedrally.

appendix

A.1 GENERAL DESCRIPTION

All different C–C bonds types in IPR fullerenes (***A***-***D*** types) and two additional types found in the non-IPR D_3-C_{68} (***E*** and ***F*** types). The bold line determines the considered C–C bond. The 6:6 ring junction in the ***A*** type is abutted by two pentagons (pyracylene C–C bond type), by a hexagon and a pentagon in the ***B*** type and by two hexagons in the ***C*** type (pyrene C–C bond type). The ***D*** type is called corannulene C–C bond type and represents a 6:5 ring junction abutted by two hexagons. The ***E*** type called pentalene C–C bond type is a 5:5 ring junction abutted by two hexagons and the ***F*** type is a 6:5 ring junction abutted by a pentagon and a hexagon. The two last types (the ***E*** and ***F*** types) are very destabilizing and only found in non-IPR fullerenes.

6:6		
Pyracylene type	--	Pyrene type
		
A	***B***	***C***

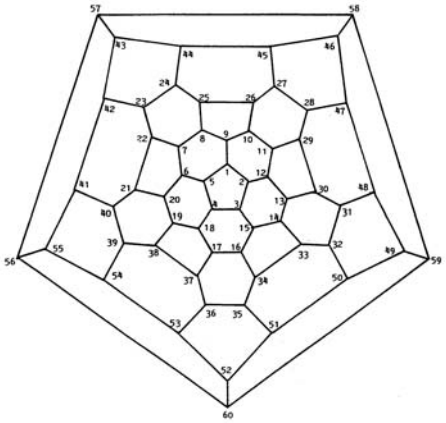
6:5	5:5	6:5
Corannulene type	Pentalene type	--
		
D	***E***	***F***

A.2 I_h-C_{60}:**1**

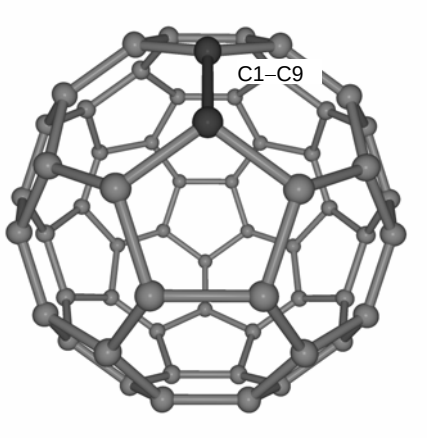
Description of the 90 C–C bonds of the I_h-C_{60}:**1** IPR fullerene divided into 2 non-equivalent sets

C–C bond [1]	*Ring junction*	*Type* [2]	*Bond lengths (Å)*	θ_p (°) [3]	*MBO* [4]
1,9/66	6:6	pyracylene, ***A***	1.397	11.67	1.342
1,2/65	6:5	corannulene, ***D***	1.452	11.67	1.136

Schlegel diagram showing the numbering system for I_h-C_{60}:**1** (a) and the structure with the C1–C9 bond marked (b)



(a) Schlegel diagram of I_h-C_{60}:**1**



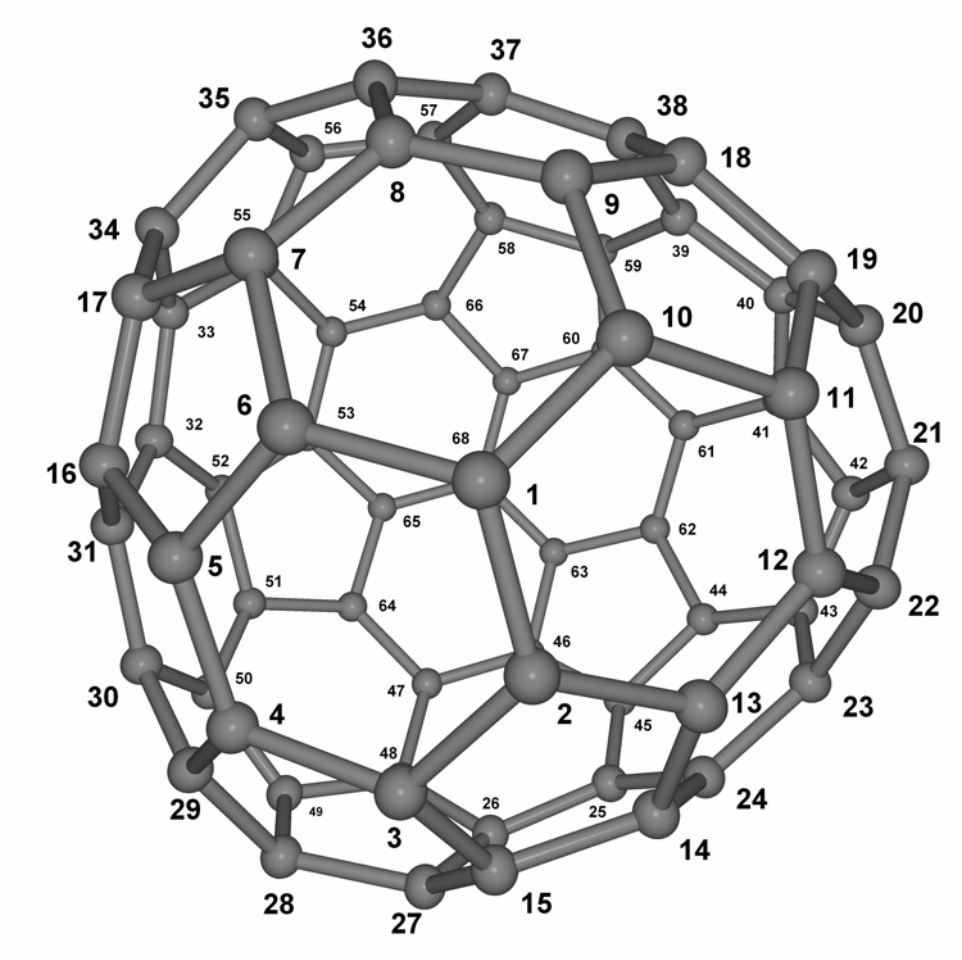
(b) Structure of I_h-C_{60}:**1**

A.3 D_3-C_{68}:**6140**

Description of 102 C–C bonds of the D_3-C_{68}:**6140** non-IPR isomer divided into 18 non-equivalent sets

C–C bond	*Ring junction*	*Type* [2]	*Bond lengths (Å)*	θ_p (º) [3]	*MBO* [4]
15,27	6:6	*pyracylene,* ***A***	1.396	11.52	1.266
23,24	6:6	***B***	1.418	9.93	1.257
14,24	6:6	***B***	1.429	9.71	1.252
12,13	6:6	***B***	1.413	9.72	1.247
11,12	6:6	***B***	1.433	10.48	1.235
21,22	6:5	***F***	1.421	13.77	1.224
1,2	6:6	***B***	1.431	9.58	1.215
2,3	6:5	corannulene, ***D***	1.433	10.90	1.210
22,23	6:5	corannulene, ***D***	1.450	11.31	1.199
13,14	6:5	corannulene, ***D***	1.443	10.54	1.194
20,21	6:5	***F***	1.424	14.49	1.185
3,15	6:5	corannulene, ***D***	1.447	11.27	1.165
2,13	6:5	corannulene, ***D***	1.449	10.14	1.159
21,42	5:5	***E***	1.436	16.20	1.156
12,22	6:6	***B***	1.446	10.27	1.151
26,27	6:5	corannulene, ***D***	1.458	11.78	1.136
14,15	6:5	corannulene, ***D***	1.438	10.80	1.133
24,25	6:6	pyrene, ***C***	1.488	8.58	1.118

Structure of the D_3-C_{68}:**6140** non-IPR isomer showing the numbering system

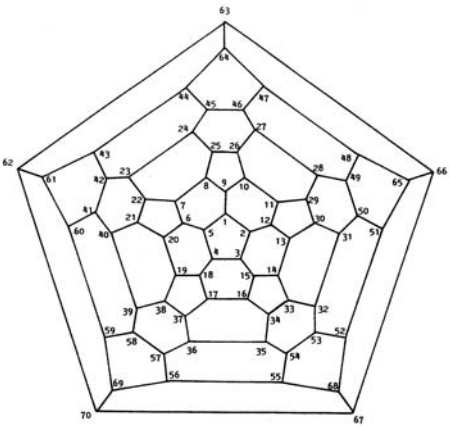


A.4 D_{5h}-C_{70}:**1**

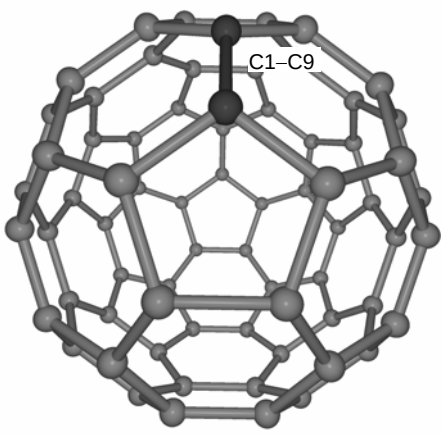
Description of 105 C–C bonds of the D_{5h}-C_{70}:**1** IPR isomer divided into 8 non-equivalent sets

C–C bond [1]	*Ring junction*	*Type* [2]	*Bond lengths (Å)*	θ_p (º) [3]	*MBO* [4]
1,9/a,b	6:6	pyracylene, ***A***	1.399	11.92	1.334
7,8/c,c	6:6	pyracylene, ***A***	1.393	11.49	1.332
21,40/d,e	6:6	***B***	1.421	9.43	1.246
21,22/d,d	6:5	corannulene, ***D***	1.438	10.28	1.219
23,24/e,e	6:6	pyrene, ***C***	1.470	8.60	1.167
6,7/b,c	6:5	corannulene, ***D***	1.448	11.73	1.140
1,2/a,a	6:5	corannulene, ***D***	1.451	11.85	1.138
7,22/c,d	6:5	corannulene, ***D***	1.446	10.88	1.138

Schlegel diagram showing the numbering system for D_{5h}-C_{70}:**1** (a) and structure with the C1–C9/Ca–Cb bond marked (b)



(a) Schlegel diagram of D_{5h}-C_{70}:**1**



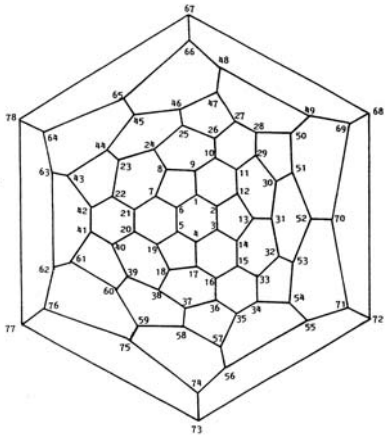
(b) Structure of D_{5h}-C_{70}:**1**

A.5 $D_{3h'}$-C_{78}:**5**

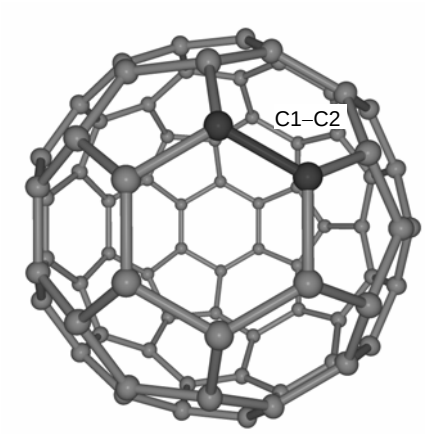
Description of the 117 C–C bonds of the $D_{3h'}$-C_{78}:**5** IPR isomer divided into 13 non-equivalent sets

C–C bond [1]	*Ring junction*	*Type* [2]	*Bond lengths (Å)*	θ_p (º) [3]	*MBO* [4]
1,2	6:6	pyracylene, ***A***	1.392	11.67	1.392
27,28	6:6	pyracylene, ***A***	1.372	10.47	1.373
22,23	6:5	corannulene, ***D***	1.414	10.49	1.293
7,21	6:6	***B***	1.419	9.63	1.283
23,24	6:6	***B***	1.423	9.56	1.221
8,24	6:6	***B***	1.424	9.48	1.214
10,26	6:6	***B***	1.436	9.65	1.205
7,8	6:5	corannulene, ***D***	1.443	10.39	1.195
10,11	6:6	pyrene, ***C***	1.470	8.63	1.163
1,6	6:5	corannulene, ***D***	1.443	11.67	1.158
1,9	6:5	corannulene, ***D***	1.446	11.15	1.129
22,42	6:5	corannulene, ***D***	1.451	10.57	1.111
23,44	6:5	corannulene, ***D***	1.470	10.31	1.090

Schlegel diagram showing the numbering system for $D_{3h'}$-C_{78}:**5** (a) and structure with the C1–C2 bond marked (b)



(a) Schlegel diagram of $D_{3h'}$-C_{78}:**5**



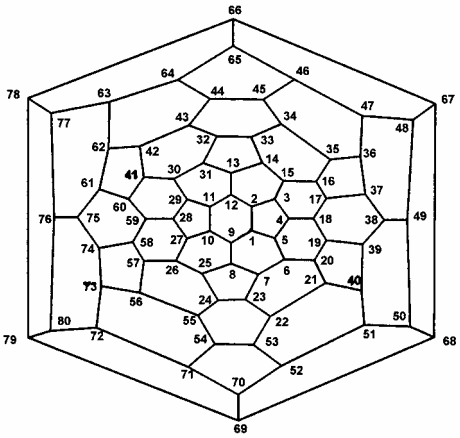
(b) Structure of $D_{3h'}$-C_{78}:**5**

A.6 I_h-C_{80}:**7**

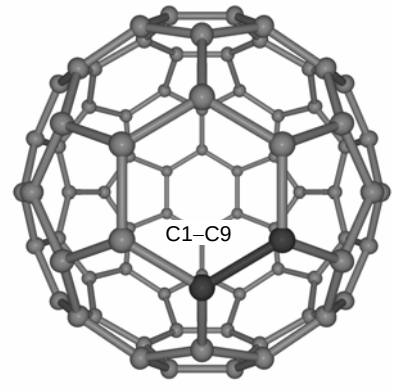
Description of the 120 C–C bonds of the I_h-C_{80}:**7** IPR isomer divided into 2 non-equivalent sets [5]

C–C Bond [1]	*Ring junction*	*Type* [2]	*Bond lengths (Å)*	θ_p (°) [3]	*MBO* [4]
1,9/66	6:6	***B***	1.428	9.62	1.209
1,2/65	6:5	corannulene, ***D***	1.438	10.58	1.194

Schlegel diagram showing the numbering system for I_h-C_{80}:**7** (a) and structure with the C1–C9 bond marked (b)



(a) Schlegel diagram of I_h-C_{80}:**7**



(b) Structure of I_h-C_{80}:**7**

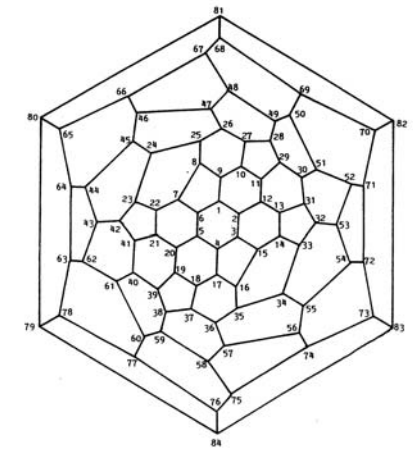
A.7 D_2-C_{84}:**22**

Description of the 126 C–C bonds of the D_2-C_{84}:**22** IPR isomer divided into 32 non-equivalent sets

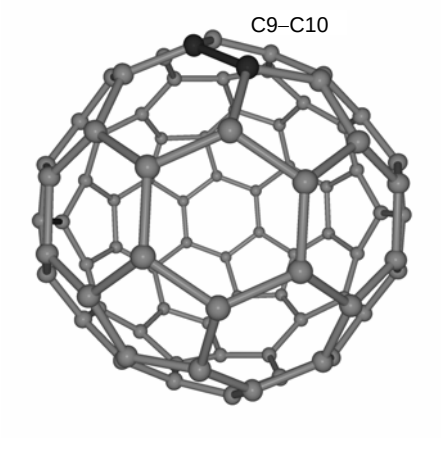
C–C bond [1]	*Ring junction*	*Type* [2]	*Bond lengths, Å*	θ_p (°) [3]	*MBO* [4]
9,10	6:6	pyracylene, ***A***	1.373	10.73	1.362
32,53	6:6	pyracylene, ***A***	1.369	10.71	1.347
7,22	6:6	pyracylene, ***A***	1.377	10.91	1.326
23,24	6:6	***B***	1.418	9.31	1.321
8,25	6:6	***B***	1.418	9.27	1.318
12,13	6:6	***B***	1.416	9.67	1.266
11,29	6:5	corannulene, ***D***	1.425	10.38	1.249
2,3	6:6	***B***	1.421	9.59	1.261
26,47	6:6	***B***	1.409	8.82	1.255
27,28	6:5	corannulene, ***D***	1.427	10.28	1.243
30,31	6:6	***B***	1.427	9.34	1.252
3,4	6:5	corannulene, ***D***	1.426	10.54	1.239
39,40	6:6	***B***	1.414	8.88	1.253
26,27	6:6	***B***	1.426	9.38	1.248
1,2	6:6	***B***	1.423	9.59	1.248
11,12	6:6	***B***	1.423	9.69	1.244
13,31	6:5	corannulene, ***D***	1.430	10.73	1.226
7,8	6:5	corannulene, ***D***	1.431	10.86	1.178
24,25	6:6	pyrene, ***C***	1.463	7.67	1.190
14,33	6:5	corannulene, ***D***	1.431	10.94	1.169
2,12	6:6	pyrene, ***C***	1.469	8.64	1.154
24,45	6:6	pyrene, ***C***	1.466	7.76	1.152
25,26	6:6	pyrene, ***C***	1.465	7.81	1.155
31,32	6:5	corannulene, ***D***	1.443	10.74	1.138

Continue					
23,42	6:5	corannulene, ***D***	1.445	10.84	1.128
10,27	6:5	corannulene, ***D***	1.439	10.80	1.130
10,11	6:5	corannulene, ***D***	1.444	10.78	1.125
8,9	6:5	corannulene, ***D***	1.449	10.76	1.121
1,9	6:5	corannulene, ***D***	1.450	10.63	1.124
13,14	6:5	corannulene, ***D***	1.452	10.80	1.122
28,29	6:5	corannulene, ***D***	1.454	9.79	1.110
3,15	6:5	corannulene, ***D***	1.453	10.73	1.111

Schlegel diagram showing the numbering system for D_2-C_{84}:**22** (a) and structure with the C9–C10 bond marked (b)



(a) Schlegel diagram of D_2-C_{84}:**22**



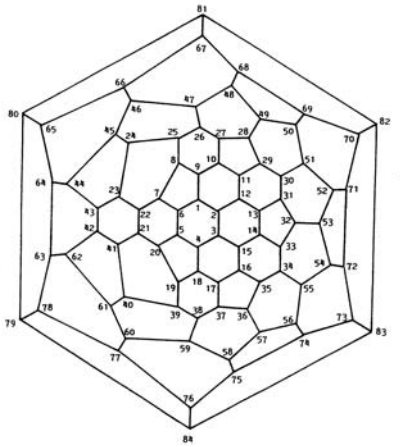
(b) Structure of D_2-C_{84}:**22**

A.8 D_{2d}-C_{84}:**23**

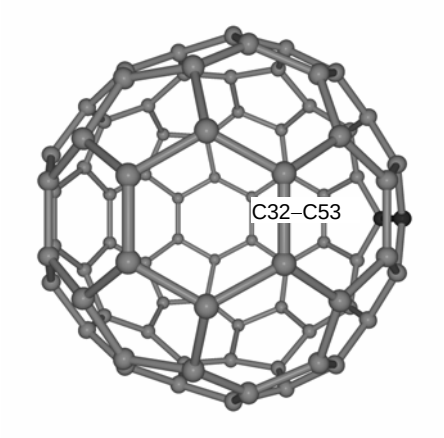
Description of the 126 C–C bonds of the D_{2d}-C_{84}:**23** IPR isomer divided into 19 non-equivalent sets

C–C bond [1]	*Ring junction*	*Type* [2]	*Bond lengths (Å)*	θ_p (°) [3]	*MBO*
32,53	6:6	pyracylene, ***A***	1.375	10.80	1.375
9,10	6:6	pyracylene, ***A***	1.369	10.68	1.352
5,6	6:6	pyracylene, ***A***	1.377	10.98	1.325
1,2	6:6	***B***	1.419	9.32	1.314
7,22	6:6	***B***	1.416	9.68	1.265
12,13	6:6	***B***	1.413	8.80	1.255
13,31	6:5	corannulene, ***D***	1.424	10.16	1.255
11,12	6:6	***B***	1.427	9.30	1.249
21,41	6:6	***B***	1.423	9.67	1.244
7,8	6:5	corannulene, ***D***	1.428	10.67	1.234
2,3	6:6	pyrene, ***C***	1.461	7.67	1.196
1,6	6:5	corannulene, ***D***	1.431	10.97	1.176
21,22	6:6	pyrene, ***C***	1.468	8.73	1.156
2,12	6:6	pyrene, ***C***	1.465	7.78	1.154
1,9	6:5	corannulene, ***D***	1.445	10.83	1.128
5,20	6:5	corannulene, ***D***	1.453	10.81	1.115
23,43	6:5	corannulene, ***D***	1.446	10.71	1.117
8,9	6:5	corannulene, ***D***	1.444	10.70	1.132
13,14	6:5	corannulene, ***D***	1.456	9.71	1.099

Schlegel diagram showing the numbering system for D_{2d}-C_{84}:**23** (a) and structure with the C32–C53 bond marked (b)



(a) Schlegel diagram of D_{2d}-C_{84}:**23**



(b) Structure of D_{2d}-C_{84}:**23**

REFERENCES AND NOTES

[1] Systematic numeric system from reference Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1993**, 813.
[2] See A.1 for a schematic representation of the different motifs: pyracylene ***A***, ***B***, pyrene ***C***, corannulene ***D***, pentalene ***E*** and ***F*** types.
[3] Average pyramidalization angle of each carbon atom in the carbon bond.
[4] Mayer Bond Order (MBO).
[5] Average values from a D_{2h} symmetry used in the calculation.

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agraïments

Tot gran viatge té una tripulació que surt a navegar faci mala mar o resplendeixi el sol més paradisíac. He d'agrair els que em van guiar inicialment en aquest viatge, quan jo ja era mariner sense vaixell esperant al port: la Rosa, el Ricart, el Joan, la Mar, l'Anna i especialment els capitans que m'embarcaren a la seva flota: en Josep Maria Poblet i en Carles Bo. Sempre recordaré amb nostàlgia la constància del primer i les mirades a l'horitzó del segon. A cada mariner se li assignava un vaixell i després d'un temps inspeccionant l'estribord i el babord tots acabàvem a la sala de màquines. La meva flota estava plena de vaixells, alguns ja portaven anys navegant i d'altres començaven, com jo. Tots els vaixells havíem salpat amb les veles esteses dins una mar immensa de color blau. Mentre navegàvem no ens veiem gaire però sempre recordarem les nits sota la embriagadora lluna a coberta o al camarot, al port, o alguna illa dita Sevilla i/o Barcelona o a la ciutat. Bons mariners sense dubte: el Xavi, el Jose, el Joan Miquel, el Jorge, l'Anaval, el Paco, l'Alfred, el Gerard, el Jesuset, l'Isa, l'Esther, l'Helena, la Susanna, el David, l'Elias i la Núria. Tots érem peculiars: alguns els hi agradava més muntar veles que navegar i d'altres tenien molta experiència en la navegació. Alguns passaven més temps a terra que a mar i d'altres sempre d'illa en illa. De tots ells en tinc un granet. Els mariners Elias i Núria eren del mateix escamot que el meu, de fet, vàrem salpar plegats. Quantes tempestes i alegries junts! Sempre teníem temps per anar a esvalotar el galliner del port! Ara crec que toca el de la ciutat, oi? Què faria un vaixell sense uns bons oficials de manteniment? Pregunteu-li al capità James S. Hook! Doncs, res. Quantes vegades ens han salvat d'un naufragi segur! El Jose, el Joan i l'Elisenda! Gràcies per mantenir els vaixells en bones condicions. D'altres portaven el paperam amb la cort (Yolanda) o bé revisaven el complex estilisme marcat per l'època (John). Quan portaves moltes dies de navegació sense tornar a port podies perdre't. A vegades era bo perdre't per la mar i deixar-te endur per alguna tempesta que de ben segur a algun lloc nou et portava. En aquestes escapades vaig acabar a tres illes força interessants: *Bath*, *Exeter* i *Sussex*. En cada illa vaig aprendre coses diferents. Ara penso que tothom hauria de tenir l'oportunitat de visitar-ne alguna, d'illa. No cal ser en *Robinson Crusoe* per fer-ho! La primera illa la vaig trepitjar molt cautelosament sense saber què i qui em

trobaria. Quin mariner seria jo sense les tècniques de navegació turques de *Bath*? Ebru, Yudum i Mete, molta sort *and see you later*! A l'illa de *Bath* vaig també forjar l'amistat amb un mariner de terra endins: el Pedret. *Una Pizza, please! We need a change*! A *Exeter* vaig fer una parada curta però profitosa, necessitava una mica de coco de platja: la Rosa, l'Helena i la Rakel em van acompanyar. Quines andorranes! Finalment en l'última illa vaig conèixer els natius. Fins i tot em van allotjar. Una forta abraçada per la càlida acollida de la família de la Doreen: Hugh, Suzanne, Ethan, Owain i Lydia. *I was like a brother*! *Thank you*! Tot i les aventures dignes d'un *Indiana Jones*: Arribada d'un *keimpa* a Sussex, a la recerca de les bases perdudes de Newcastle, el congrès fantasma d'Exeter, el projecte *Hirsch-Erlangen*: si tu no vols jo vinc, ful·lerens a *Methyl Tydfil* i la *Hadrian's Wall*?, el pis cinquè, *London* la no-capital, els trens sense rumb per la hispània ulterior, per què tres catalans no es troben a la mateixa hora i el mateix lloc?, el *Sherlock Holmes* de Lewes, de *James Bond* a l'Opera de *Glyndebourne*, creuer pel mississipí baètic ... i un llarg etcètera al final sempre vaig tornar a casa. Així doncs, tot mariner té uns dies a alta mar i altes a terra ferma. A terra ferma aprofitava per copsar l'opinió que sovint la llunyania de la mar no em deixava veure. Quant he après de la Montse, la Neus de Tarragona, el Carles i la Cruset de Reus, el Pedret de Montbrió, el Benito de Valls, el Pepe de Cambrils, el Xiquelo de la Ràpita, el Saki de l'Hospi, el Toni d'Orta, la Brezo de Tarragona, la Salla dels Omells de na Gaia, el Saura de Llorenç, el Nino de Bellvei, el Norber de l'Arboç i el Jaume de Santes Creus. Alguns eren amb mi al port a l'inici del viatge. Moltes gràcies a tots! Un que sempre trobava quan tornava era el Gerard. Gràcies per sempre ser-hi! Jo era d'aquells que quan sortia del port i anava a la ciutat, sempre tenia temps per anar a esvalotar-la. Quines estones més maques amb la gent de EL MARGE i el SEP: el Mariano, la Rosa, la Sílvia, el Joan, el Jaume de la Bisbal, l'Andreu i el Joan del Vendrell, la Laura de Masarbonés i el Marc de Llorenç. Els vostres granets mouen muntanyes. A casa del mariner però es coïa tot! A casa era on sempre tenia el refugi i tothom a qualsevol hora m'esperava o em feina la cassola. Quins pares! Sempre al peu del canó, més de terra que no pas de mar! Però il·lusionats que el fill anés a mar! I el meu germà sempre tant treballador fent niuet! Els meus cosins sempre m'esperaven quan tornava a casa amb el sarró: l'Albert i la Montse. Una abraçada a la meva àvia, la padrina, que em va veure

iniciar en aquest món i la meva tieta! I sobretot una mirada de futur als cosinets més xics: el Robert, la Marta, els dos Arnaus, l'Aida, la Núria, la Laia i al Roger. Endavant! Entre tant de tràfec, l'Elena m'ha revifat l'ésser humà tant el de muntanya com el de mar, una abraçada i a volar! Però, és clar, fins i tot la mar es pot fer petita si observes atentament allò que vols! A poc a poc vas agafant el rumb i substitueixes els cops de timó per unes bones veles. Jo vaig veure un dia un far molt i molt llunyà i allí em vaig dirigir. Vaig pujar-lo i aquí sóc: ben il·luminat amb unes bones vistes cap a un munt de fars i mars més! On és el proper viatge? i la resta de mariners? Mires enrere i veus el trajecte, ha valgut la pena el camí, oi! Moltes gràcies!

Octubre de 2004
La Bisbal del Penedès / La Masó
Campa xic / *Little* Campa

viatges

Estada al Departament de Química de la Universitat de Bath (Gran Bretanya). Juliol i agost del 2000. Tutor: Dr. Andrew Burrows. Síntesi de fosfines.

Participació en la XVIIena REUNIÓ DE LA XARXA DE QUÍMICA TEÒRICA DE CATALUNYA celebrada a Tarragona el 4 i 5 de juliol del 2001.

Participació i presentació del pòster: "A DFT study of Organometallic Derivatives of Fullerenes, Jordi Muñoz, Josep M. Campanera, Jordi Vázquez, Carles Bo and Josep M. Poblet" en el FIGIPS: MEETING IN INORGANIC CHEMISTRY celebrat entre el 15 i el 20 de juliol de 2001 a Barcelona.

Estada al Departament de Química de la Universitat d'Exeter (Gran Bretanya). Agost del 2001. Tutor: Dr. Craig Butts. Reaccions fotoquímiques de ful·lerens.

Participació i presentació de la comunicació. "Enllaç en els endohedres $Sc_3N@C_x$ x = 68, 78 i 80, Josep M. Campanera, Carles Bo, Marilyn M. Olmstead, Alan L. Balch i Josep M. Poblet" en la XVIIIena REUNIÓ DE LA XARXA DE QUÍMICA TEÒRICA DE CATALUNYA que tingué lloc a Barcelona els dies 8 i 9 de juliol de 2002.

Participació i presentació del pòster: "Bonding within the endohedral fullerenes $Sc_3N@C_x$ x = 68,78 and 80, Josep M. Campanera, Carles Bo, Marilyn M. Olmstead, Alan L. Balch and Josep M. Poblet" a l'ESPA2002: ELECTRONIC STRUCTURE: PRINCIPLES AND APPLICATIONS, celebrat a Sevilla de l'11 al 13 de Setembre de 2002.

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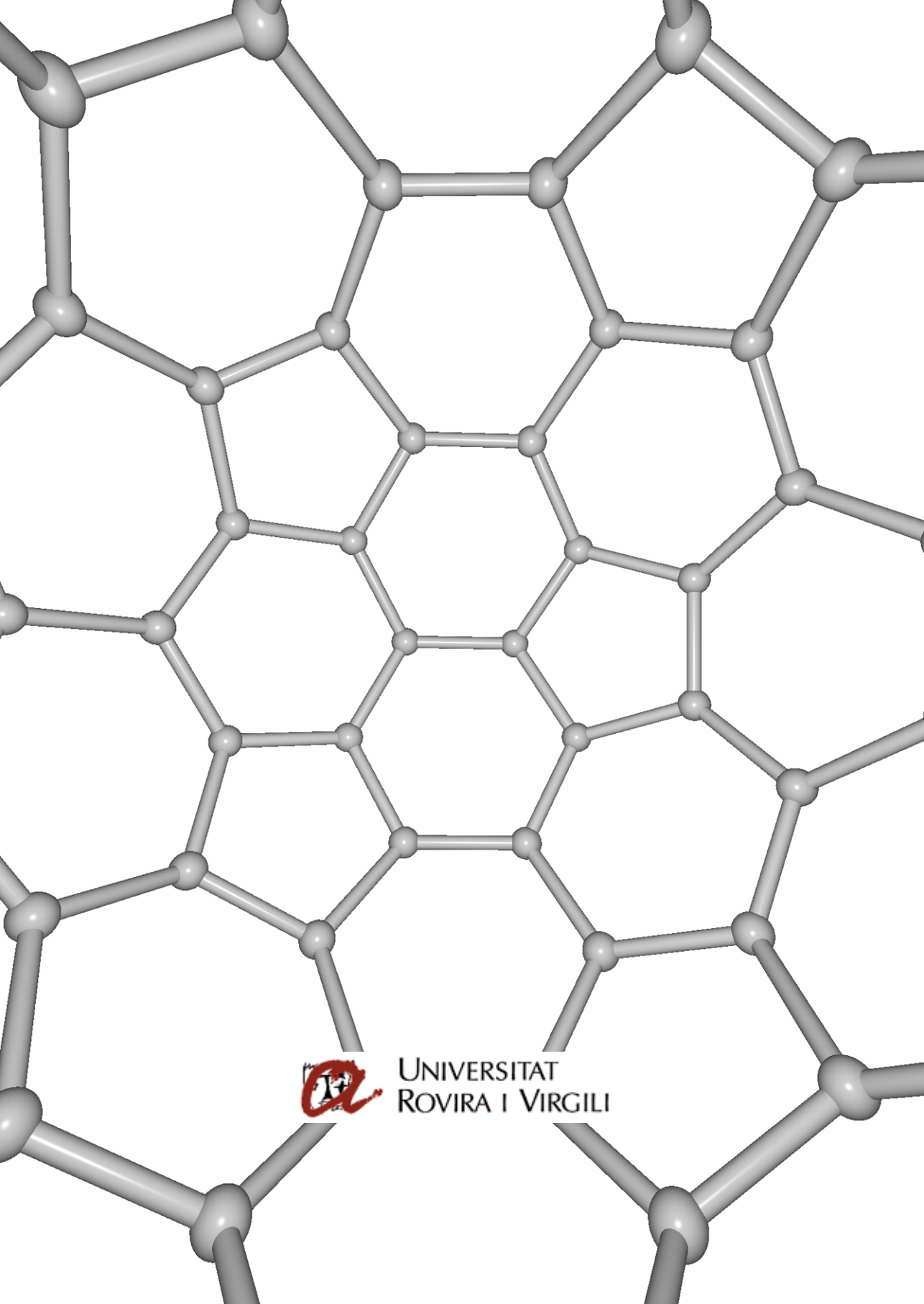

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