Composti Policiclici Aromatici
e forme allotropiche del carbonio

COMPOSTI AROMATICI POLICICLICI

Quando il carbone viene riscaldato a 1000 °C in assenza di aria subisce una scissione termica. In queste condizione evapora una miscela di prodotti volatili chiamati catrame di carbone. L'ulteriore distillazione frazionata del catrame di carbone fornisce i seguenti composti:

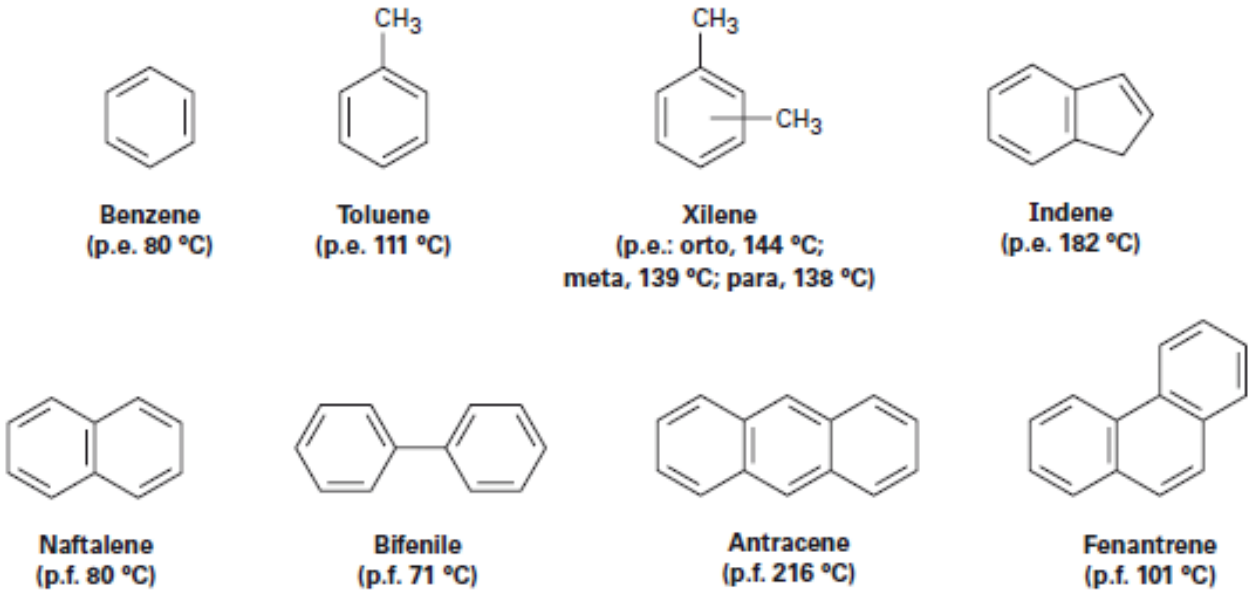
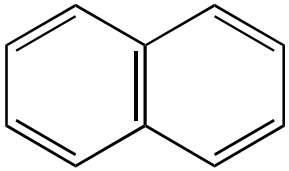


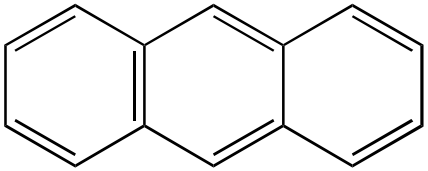
Figura 15.1 Alcuni idrocarburi aromatici presenti nel catrame di carbone.

COMPOSTI AROMATICI POLICICLICI

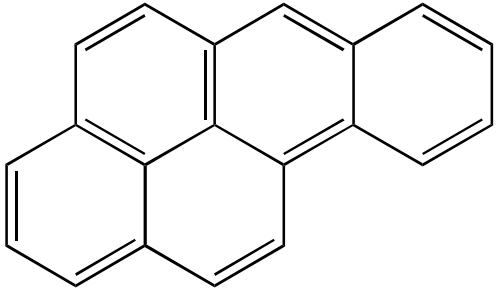
Il concetto generale di aromaticità può essere esteso anche ai composti aromatici policiclici.



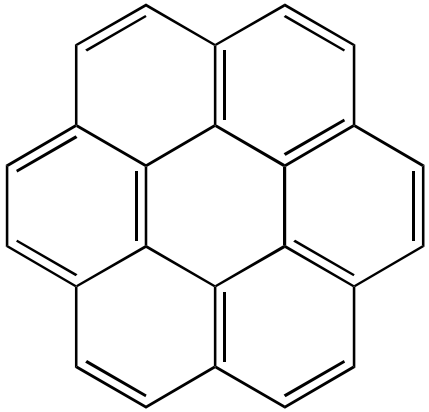
naftalene



antracene

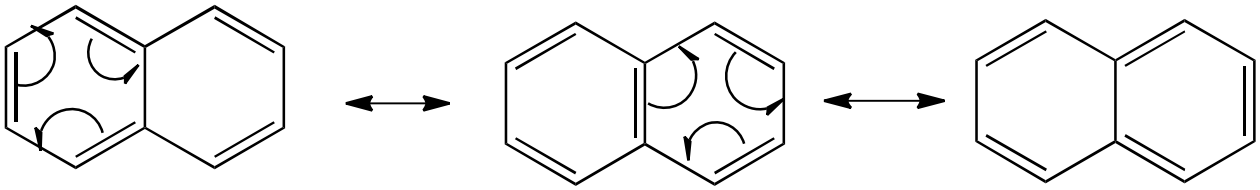


benzo[a]pirene



coronene

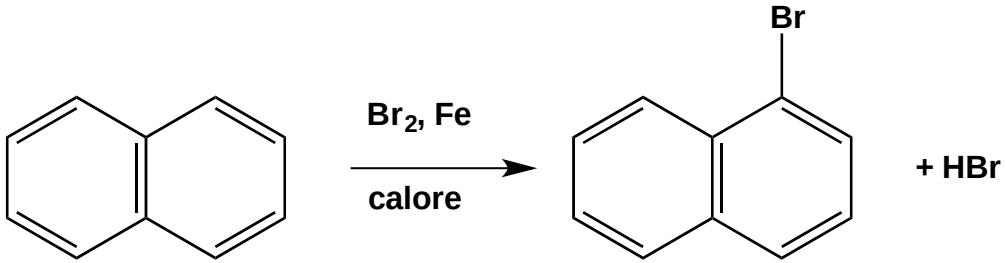
il naftalene ha 3 forme di risonanza



il calore di idrogenazione mostra una energia di stabilizzazione aromatica di 250 kJ/mol (60 kcal/mol)

COMPOSTI AROMATICI POLICICLICI

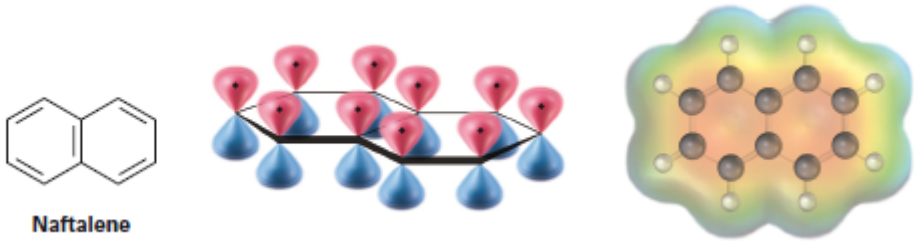
reattività: il naftalene reagisce lentamente con elettrofili fornendo prodotti di sostituzione (sostituzione elettrofila aromatica) e non addizione al doppio legame.



1-bromonaftalene (75%)

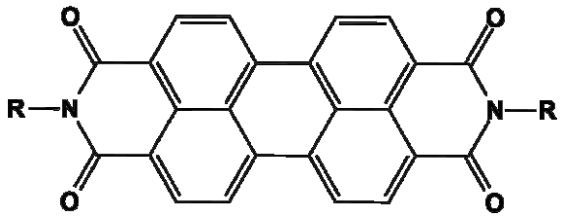
gli elettroni sono delocalizzati su entrambi gli anelli

Figura 15.10 Il disegno degli orbitali e la mappa di potenziale elettrostatico del naftalene mostrano che i dieci elettroni π sono completamente delocalizzati su entrambi gli anelli.



COMPOSTI AROMATICI POLICICLICI

Perché sono interessanti questi composti

Es. 

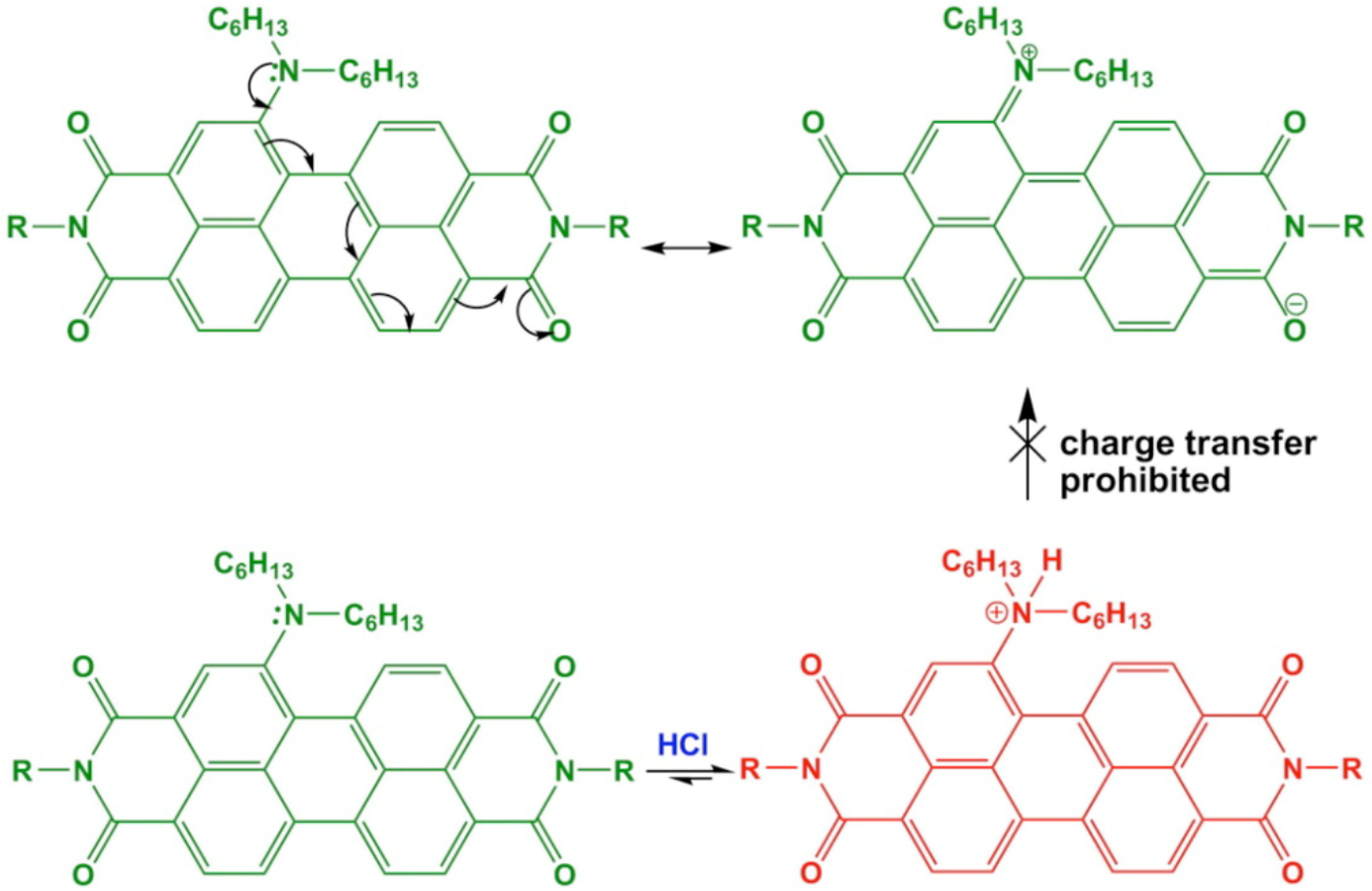
Organic Dyes

General structure of a **perylene bisimide** molecule (PBI).

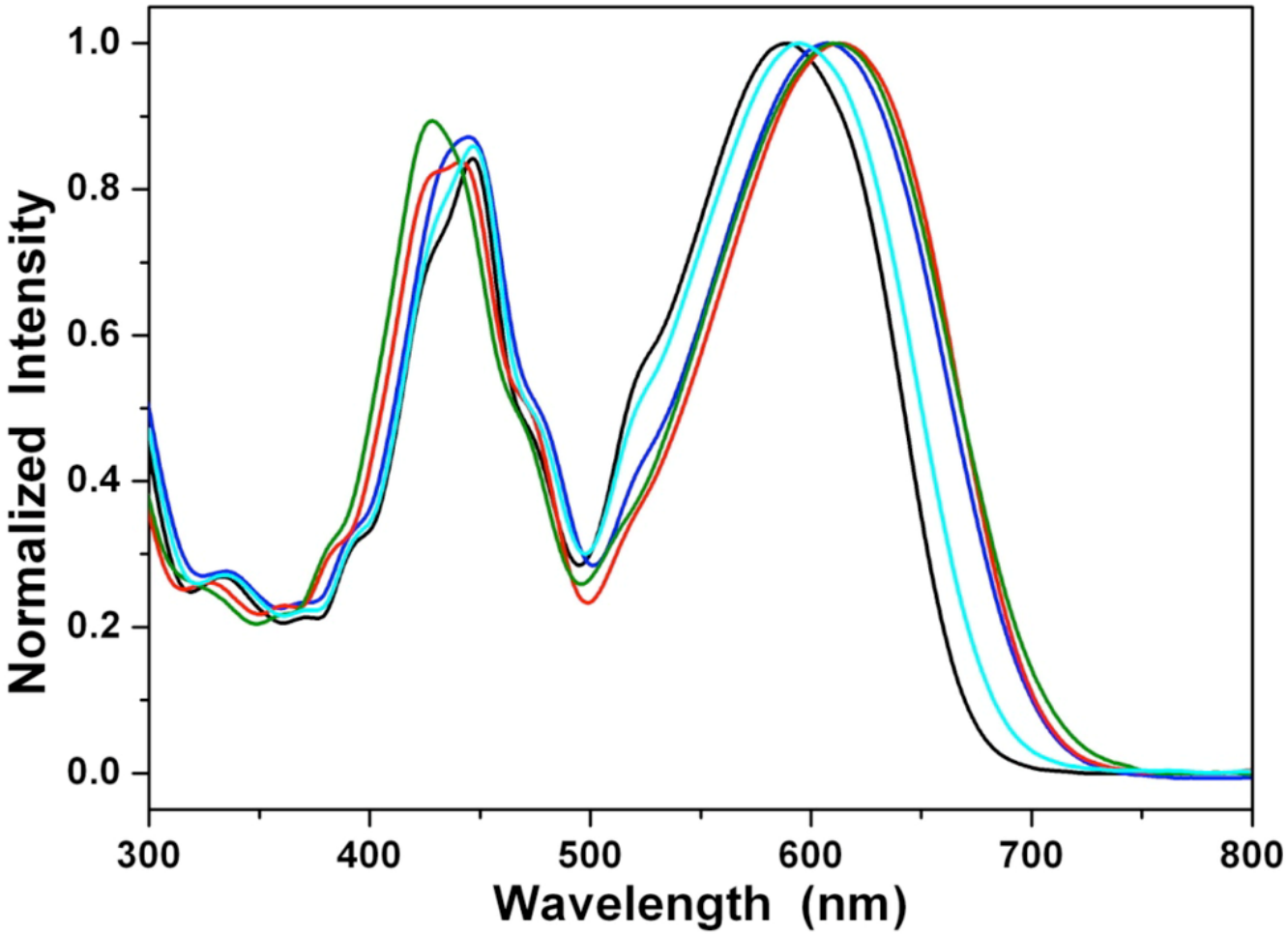
These polycyclic aromatic molecules have been considered for their exceptional features: they have (i) a strong absorption in the visible region ($400 < \lambda < 700$ nm) with a nearly unity quantum yield, (ii) a high thermal and oxidative stability, (iii) high electron mobility, (iv) sustainable costs of the raw materials, and (v) supramolecular self-assembling properties leading to the formation of functional architectures, due to the π-stacking between neighbouring molecules. In addition, due to the easy tunability of the HOMO and LUMO levels, PBIs has been already used in the field of organic electronics since they exhibit n-type semiconducting properties (reach of electrons).

COMPOSTI AROMATICI POLICICLICI

These molecules show intense green color in both solution and solid state and are highly soluble in dichloromethane and even in nonpolar solvents, such as hexane



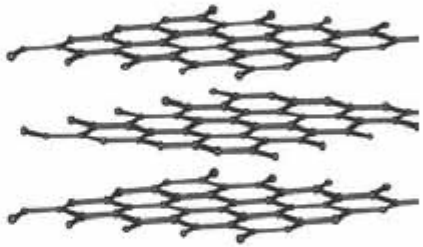
COMPOSTI AROMATICI POLICICLICI

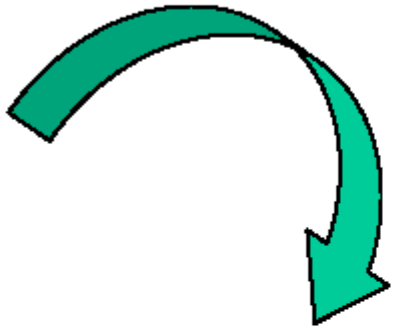


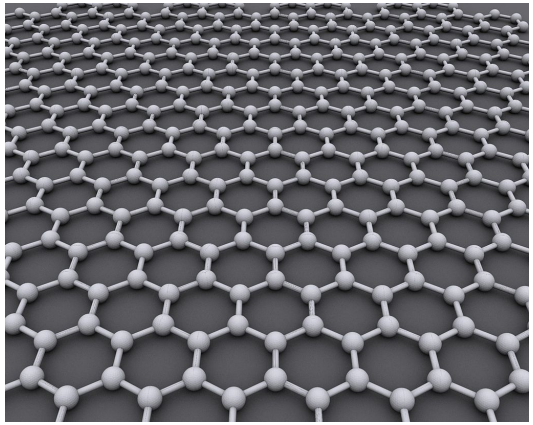
UV-Vis spectra in different solvents

FORME ALLOTROPICHE DEL CARBONIO

Forme allotropiche del carbonio





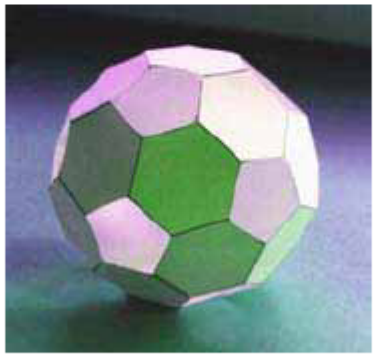


Grafene

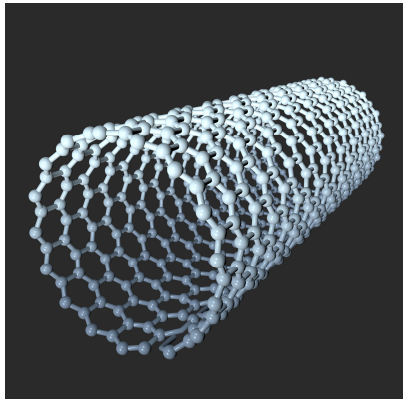
Diamante

Grafite

materiale noto per
la sua durezza



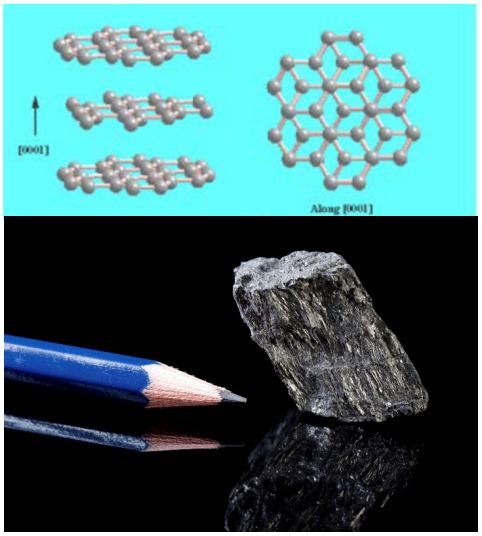
Fullerene



Nanotubi di carbonio

1970 { Eiji Osawa la teorizza
R.W.Henson la propone

GRAPHITE

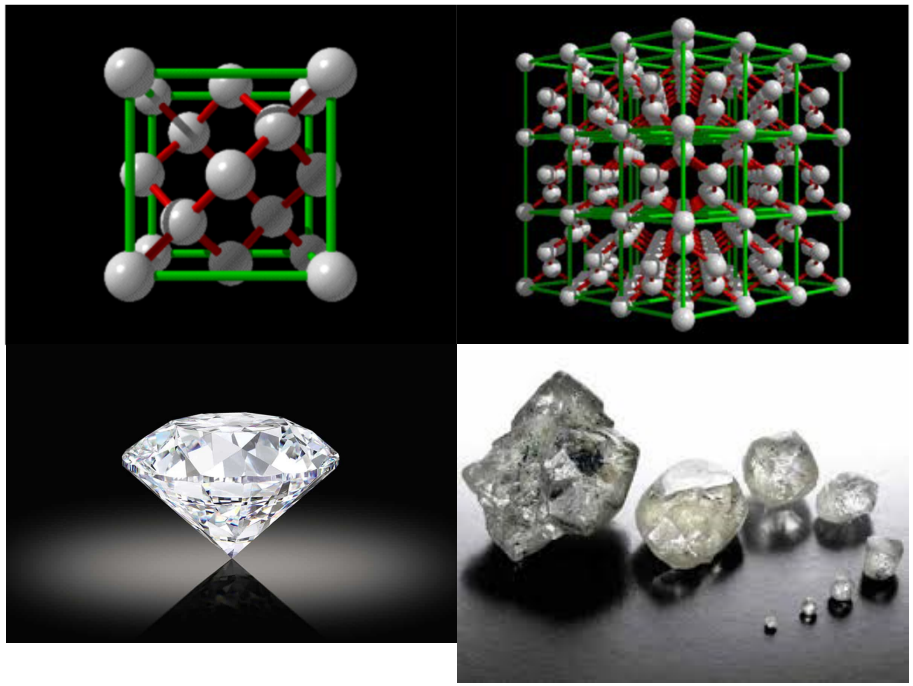


Graphite is a good electrical conductor, is greasy and finds wide use as lubricant; it is sol and black, with a weak metallic brightness.

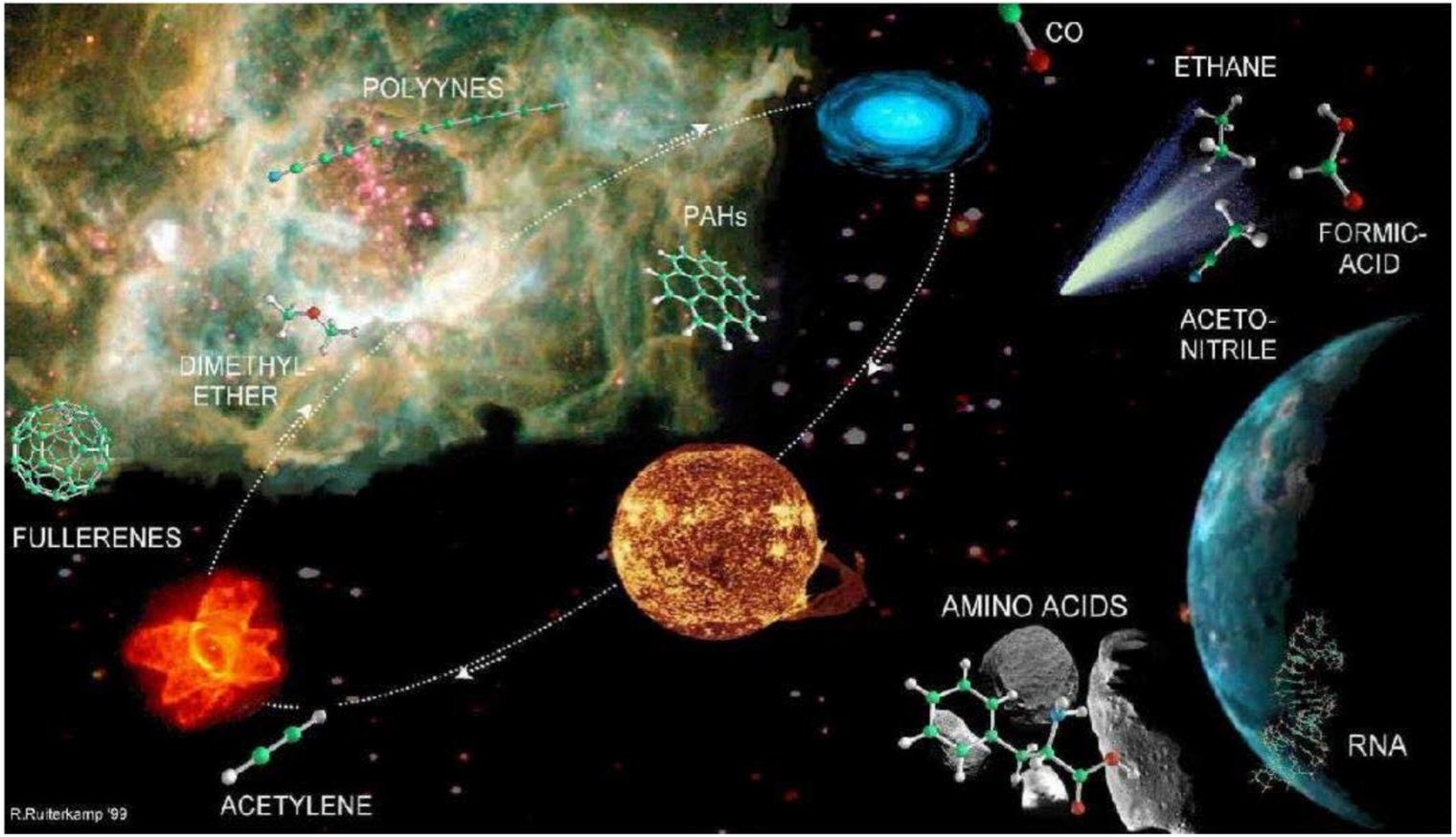
si forma alla temperatura di 1.200 ° C

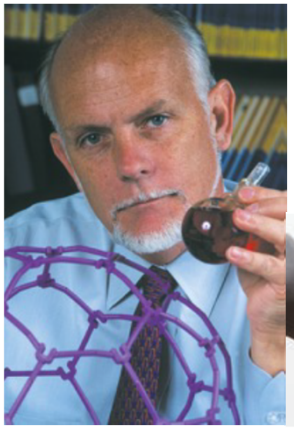
DIAMOND

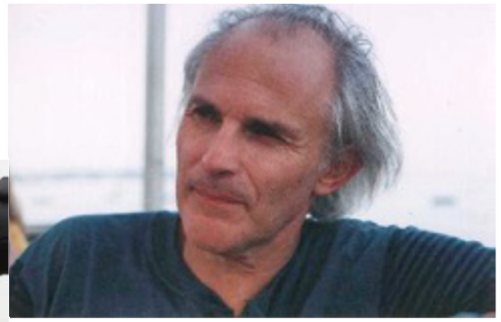
Tridimensional structure of diamond



si forma a temperature
comprese fra i 900 °C ed i 1.200 °C e pressione di circa 50 kbar


CO
ETHANE
POLYYNES
PAHs
FORMIC-
ACID
ACETO-
NITRILE
DIMETHYL-
ETHER
FULLERENES
AMINO ACIDS
RNA
ACETYLENE
R.Ruiterkamp '99





Richard E. Smalley
Rice U, USA

Harold W. Kroto
U Sussex, UK

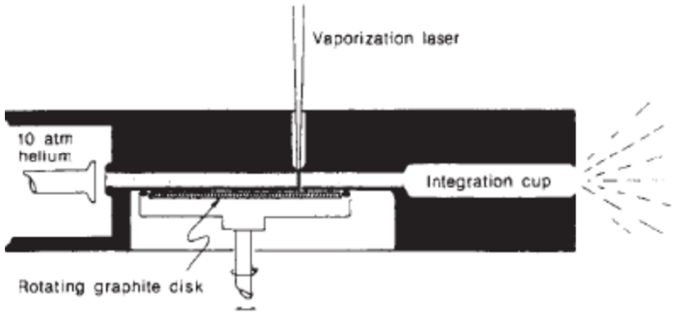
Robert F. Curl
Rice U, USA

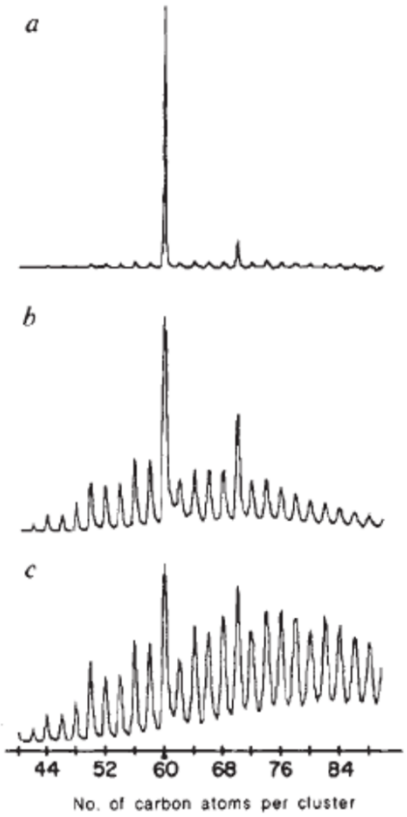
C_{60}: Buckminsterfullerene

H. W. Kroto*, J. R. Heath, S. C. O'Brien, R. F. Curl & R. E. Smalley

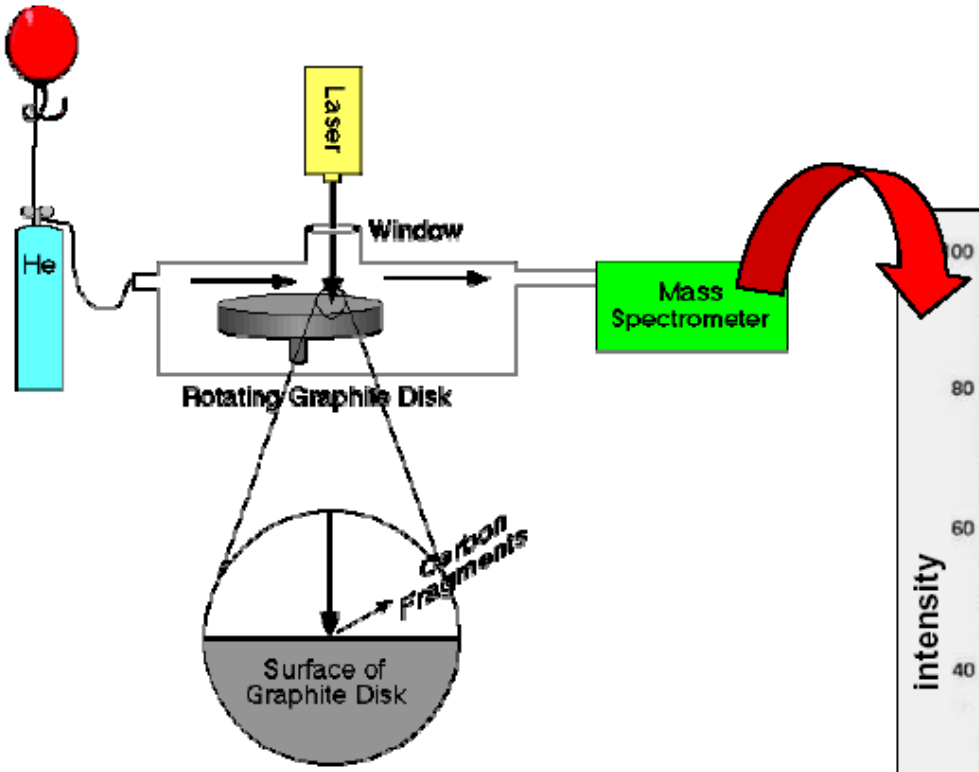
Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77251, USA

NATURE VOL. 318 14 NOVEMBER 1985



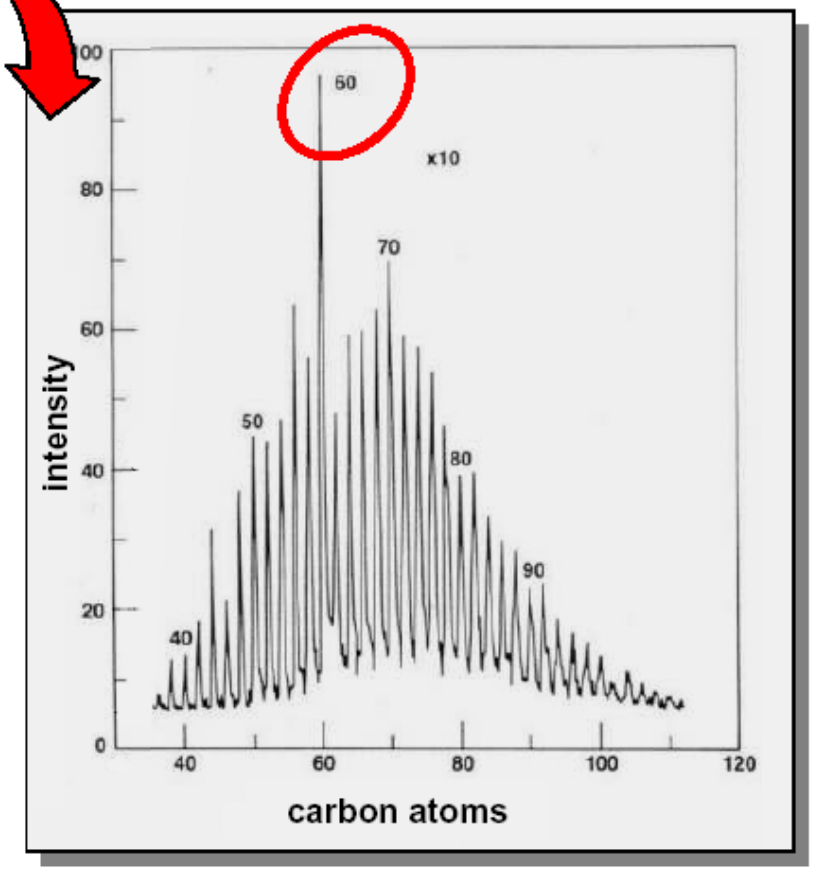


Fullerene: la scoperta

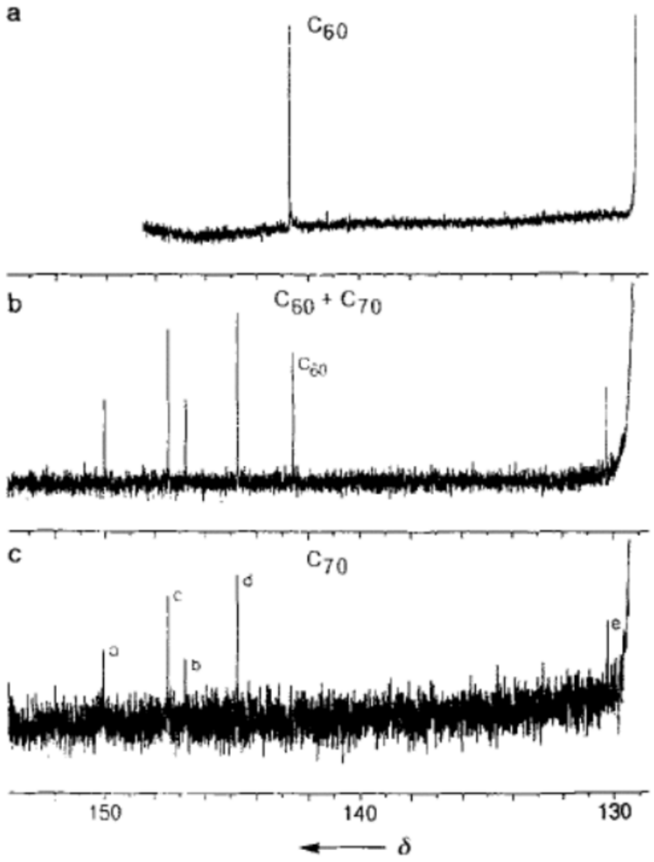


Nature **1985**, *318*, 162

M^+ = 720



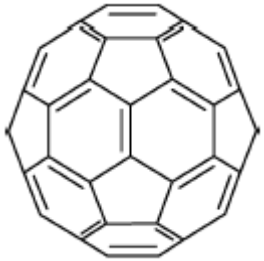
^{13}C NMR



struttura

Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C_{60} molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.

FULLERENE

C_{60} 

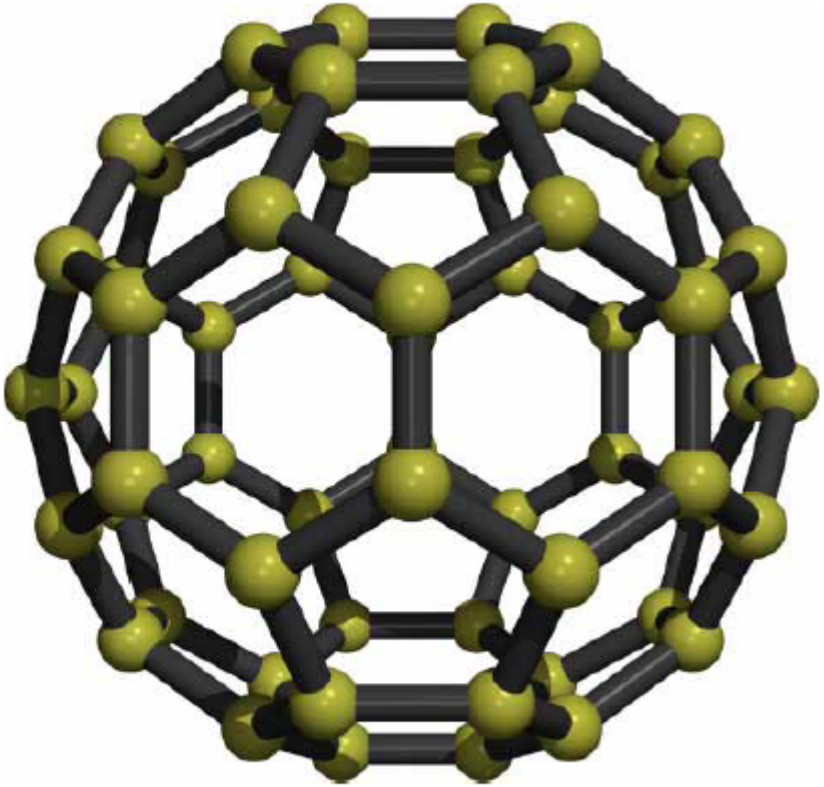
scoperto nel 1985 da Kroto, Smalley and Curl, *Nature* **1985**, *318*, 162

1996 Chemistry Nobel Prize

ROBERT F. CURL, Jr. , **SIR HAROLD W. KROTO** , and **RICHARD E. SMALLEY**

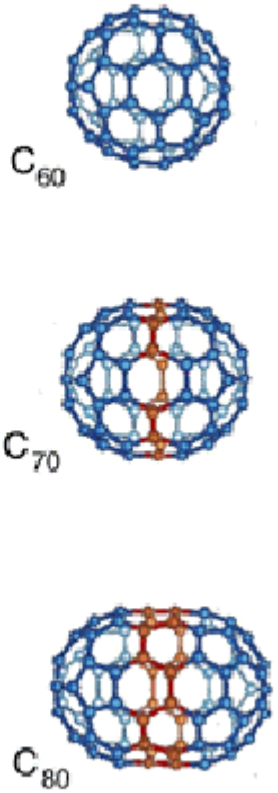
"for their discovery of fullerenes"

Fullereni

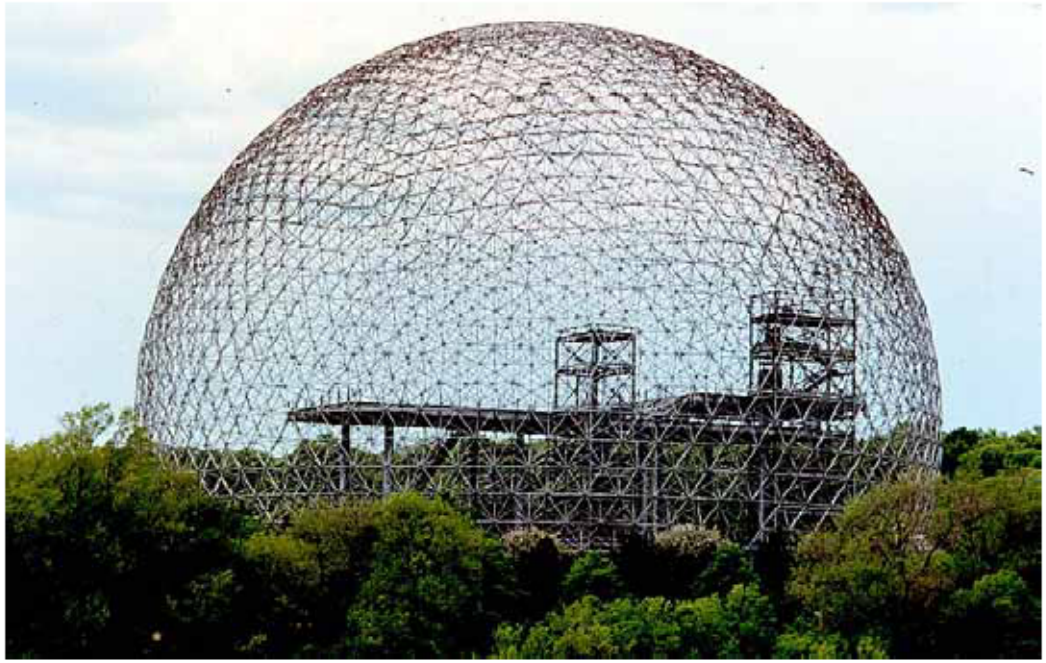


Buckminsterfullerene (C_{60})

truncated icosahedron (I_h symmetry)

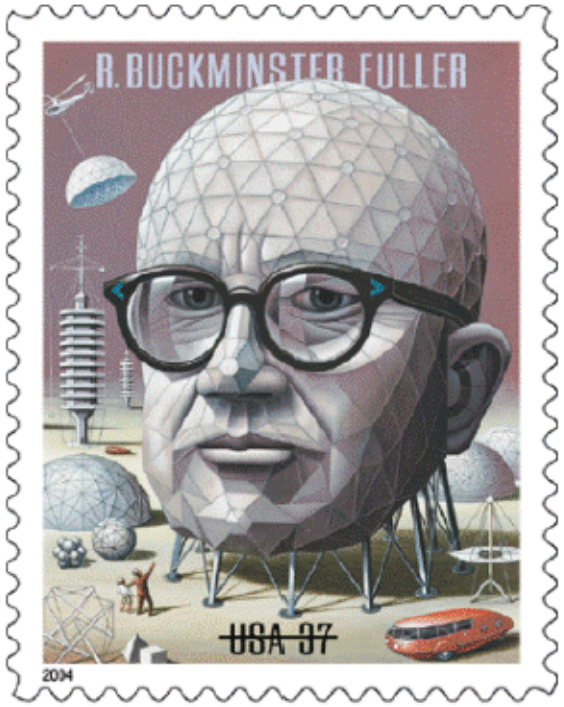


Buckminster Fuller



Geodesic Dome

Buckminster Fuller, US Pavilion for the 1967 International and Universal Exposition in Montreal



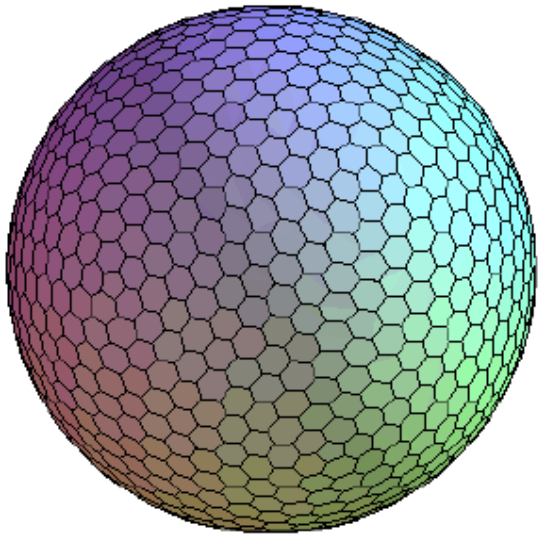
FULLERENE

Regola di Eulero

Un fullerene è un poliedro convesso con facce esagonali e pentagonali.

$$F - S + V = 2$$

Se uso solo esagoni F − S + V = 0. Affinché la formula di Eulero per i poliedri sia rispettata, occorre che diventi uguale a 2. In breve, occorre sostituire **12** esagoni con altrettanti **pentagoni**

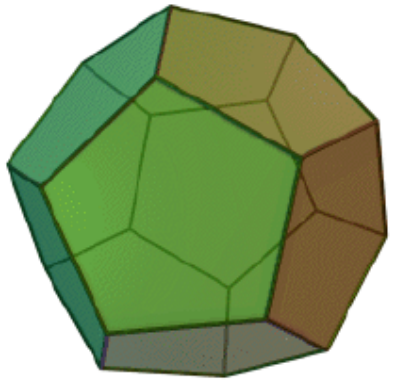


Il fullerene presenta 20 esagoni e 12 pentagoni

Facce 12

Spigoli 30

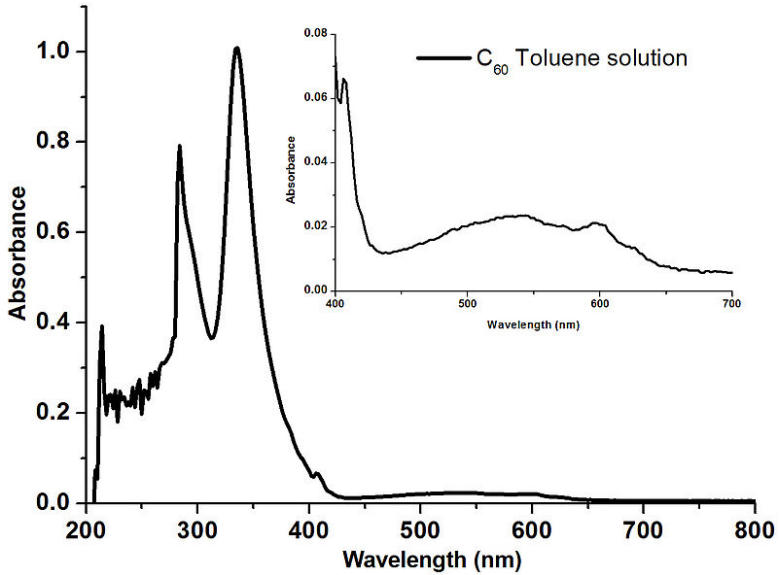
Vertici 20



FULLERENE

C_{60} properties

Proprietà di ottica non lineare:



Spettro UV-Vis del C_{60} in toluene

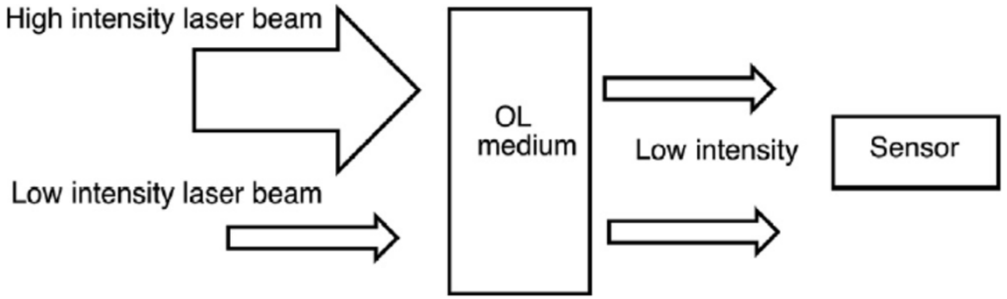
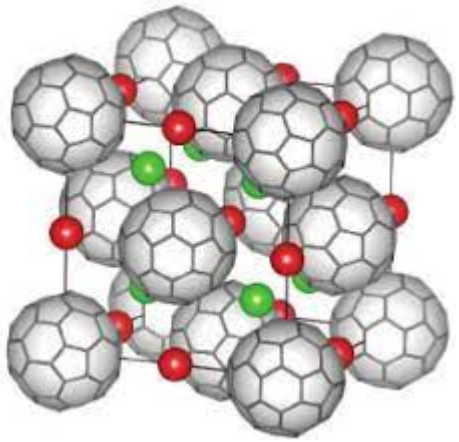


Fig. 1. Passive optical limiting for sensor protection with different laser intensities.

C_{60} properties

Superconduttore se dopato con metalli alcalini a T < 40 K



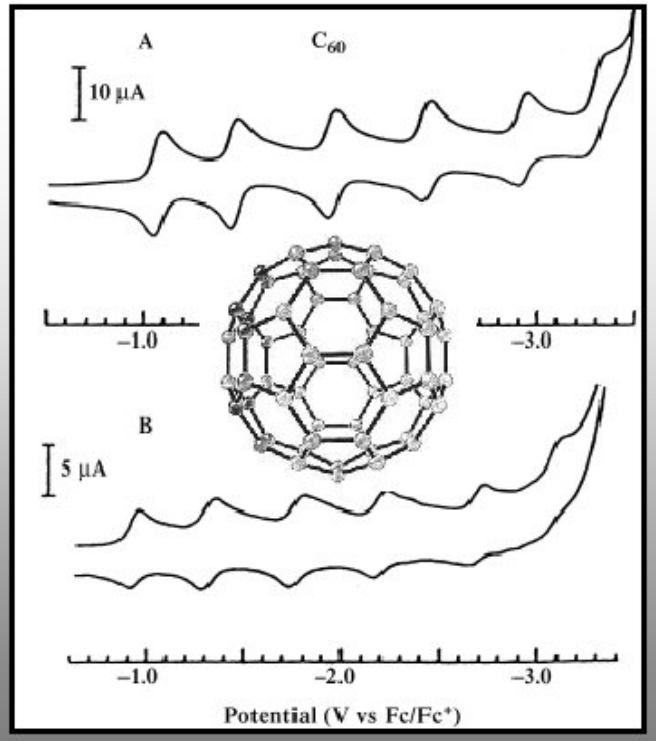
A_3C60

FULLERENE

C_{60} properties

proprietà elettrochimiche
può accettare fino a 6 elettroni

Cyclic voltammograms of C60 and C70 in a toluene solution



C_{60} properties

Organic Molecular Soft Ferromagnetism in a Fullerene C_{60}

PIERRE-MARC ALLEMAND, KISHAN C. KHEMANI, ANDREW KOCH, FRED WUDL, KAROLY HOLCZER, STEVEN DONOVAN, GEORGE GRÜNER, JOE D. THOMPSON

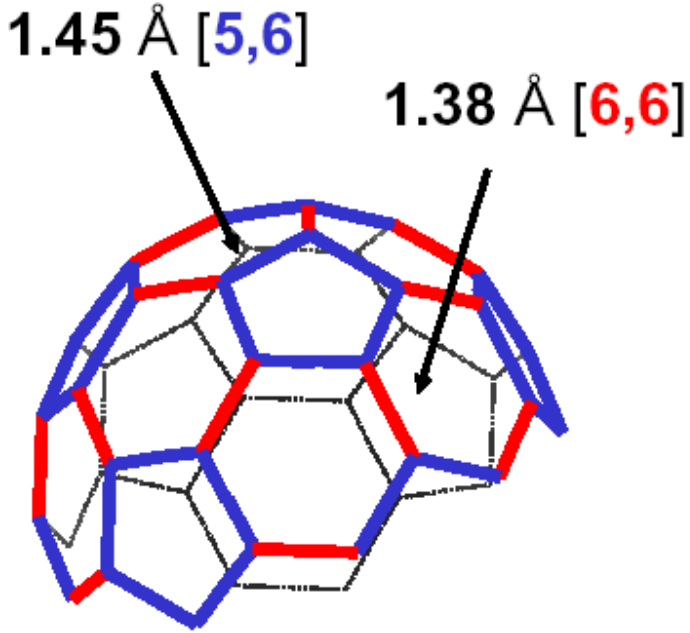
The properties of an organic molecular ferromagnet [$C_{60}TDAE_{0.86}$; TDAE is tetrakis(dimethylamino)ethylene] with a Curie temperature T_c = 16.1 kelvin are described. The ferromagnetic state shows no remanence, and the temperature dependence of the magnetization below T_c does not follow the behavior expected of a conventional ferromagnet. These results are interpreted as a reflection of a three-dimensional system leading to a soft ferromagnet.

Science, 1991

C_{60} properties

- X-Ray crystal structure determinations on C_{60} and on some of its derivatives have proved the existence of two different types of bonds: ‘short bonds’ or 6,6 junctions shared by two adjacent hexagons (ca. 1.38 A ° long) and ‘long bonds’, or 5,6 junctions, fusing a pentagon and a hexagon (ca. 1.45 A ° long).

Proprietà strutturali del C_{60}



ΔH_f = 10.16 Kcal/mol per C

(ΔH_f)graphite = 0 Kcal/mol

(ΔH_f)diamond = 0.4 Kcal/mol

The six-membered rings are **not aromatic** in that they contain alternating single and double bonds. 6,6-bonds are shorter than 5,6-bonds.

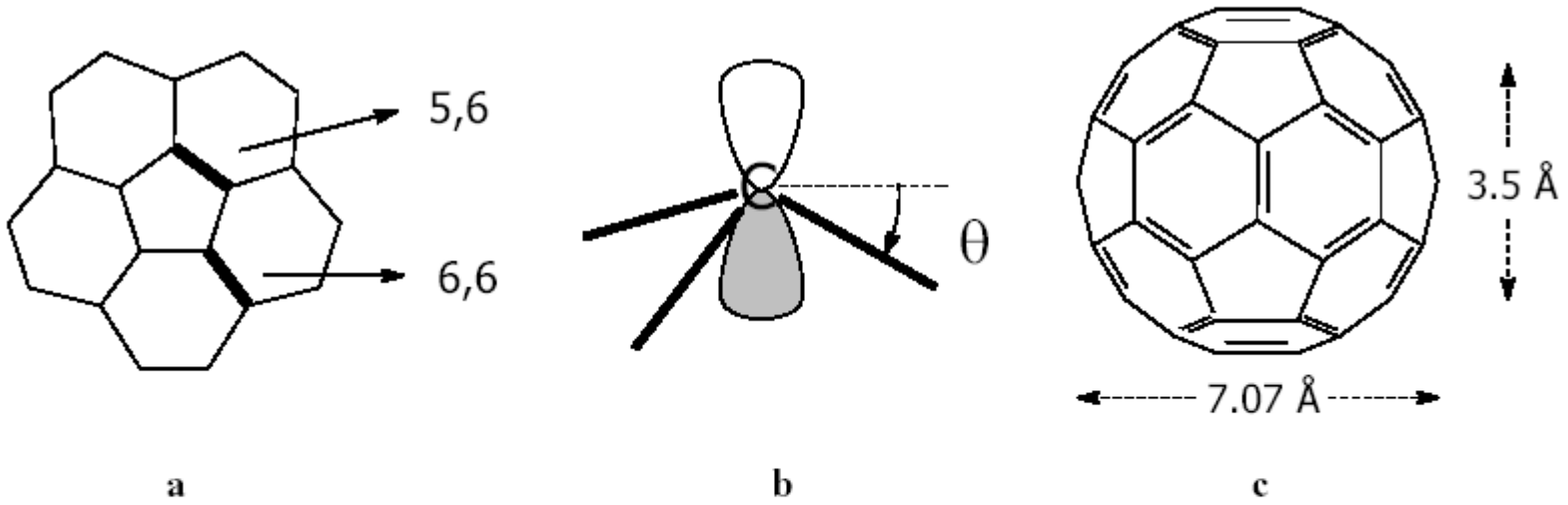
The overall buckyball structure has to be viewed as fused **1,3,5-cyclohaxatrienes** and **[5]radialenes**

spherical geometry causes **pyramidalization** of the unsaturated C-atoms. Strain Energy ≈ 80% H_f

- Haddon and Raghavachari, in *buckminsterfullerenes*, VCH, 1993
- H.D. Beckhaus et al. *Angew. Chem.* 1992, 31, 63)

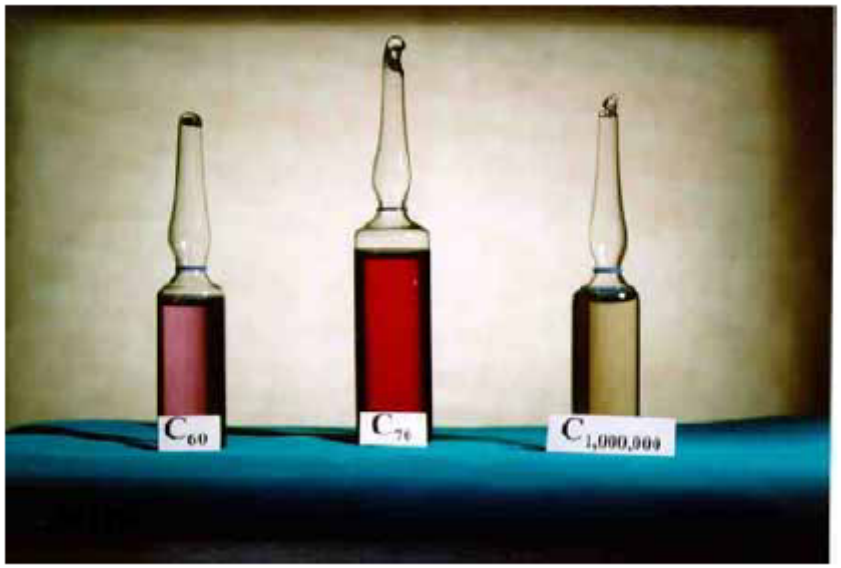
- A. Hirsch, Z. Chen, H. Jiao. *Angew. Chem.* **2000**, *39*, 3915.
- M. Bühl, A. Hirsch *Chem. Rev.* **2001**, *101*, 1119.

Proprietà strutturali del C_{60}

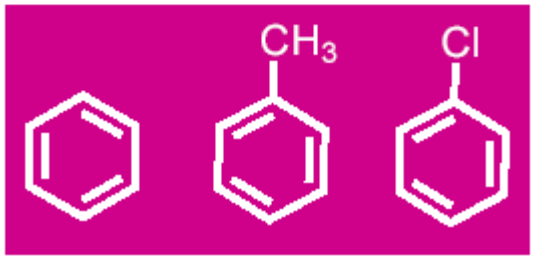


(**a**) legami 5,6 e 6,6 nel C_{60}; (**b**) angolo di piramidalizzazione θ; (**c**) diametro esterno (*edge-to-edge*) e interno del C_{60} (il diametro di Wan der Waals è circa 10.4 Å)

FULLERENE

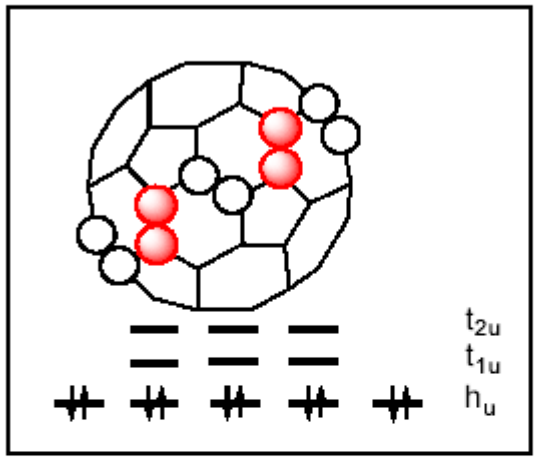


C_{60} solution in toluene



and CS_2

Reattività



C_{60} behaves essentially as a **strained electron-poor alkene**; addition chemistry is mainly driven by strain relief

fullerenes are very difficult to oxidize but are **readily reduced** (reactivity towards electron-rich reagents)

1,2-additions occur at 6,6-double bonds. In 1,2-adducts the bond- length alternation is totally preserved

the regioselectivity of addition reactions is governed by **avoidance of** products with **5,6 double bonds** in the lowest energy Kekulè structure (price tag of 8.5 kcal mol^{-1})

multiple addition to C_{60} is a complicated process governed by differences in bond order and LUMO coefficients at each site: many possible **regio-isomers**

FULLERENE

The **chemical transformations** that are possible with C60 could be classified in five main groups (figure 1.3):

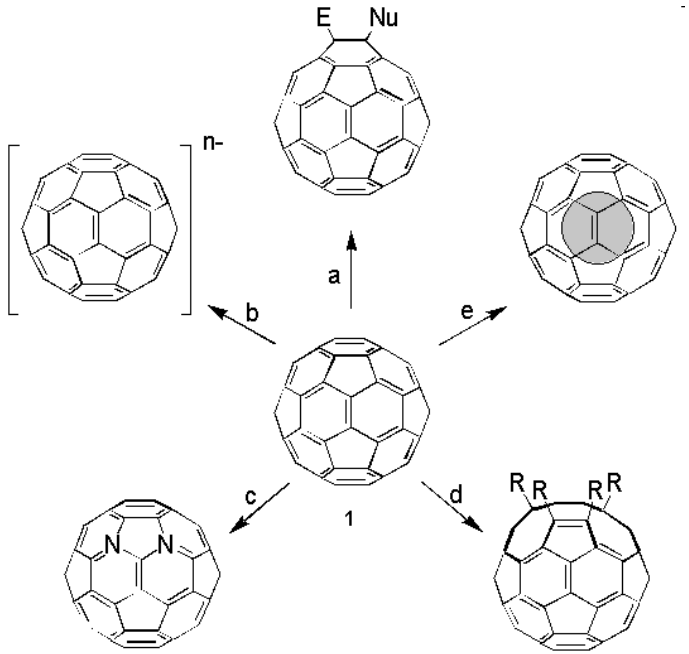
a) *Addition reactions*. Formation of exohedral compounds by addition of nucleophiles or radicals, cycloadditions, complexations with transition metals and others.

b) *Electron transfer reactions*. Chemical reduction of fullerenes can easily be achieved by reaction with electropositive alkali and alkaline earth metals or organic donor molecules.

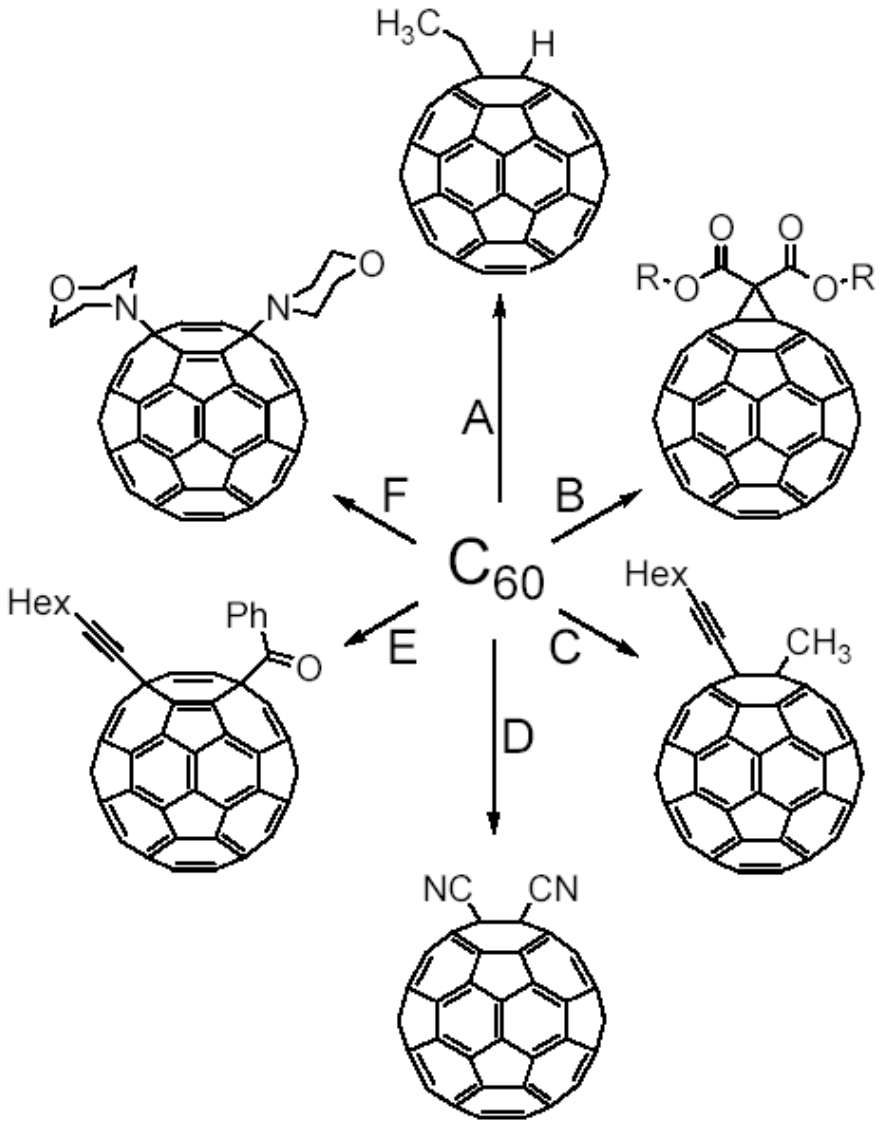
c) *Heterofullerenes*. Substitution of a carbon atom of the fullerene skeleton for a heteroatom, for example nitrogen or boron.

d) *Ring opening reactions*. Producing a hole in the C60 skeleton while breaking a discrete number of bonds.

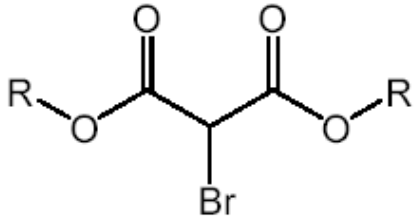
e) *Formation of endohedrals*. Introducing and trapping of atoms inside the spherical carbon cage.



Addizioni nucleofile al C_{60}



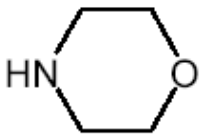
A EtMgBr, H^+

B  , NaH

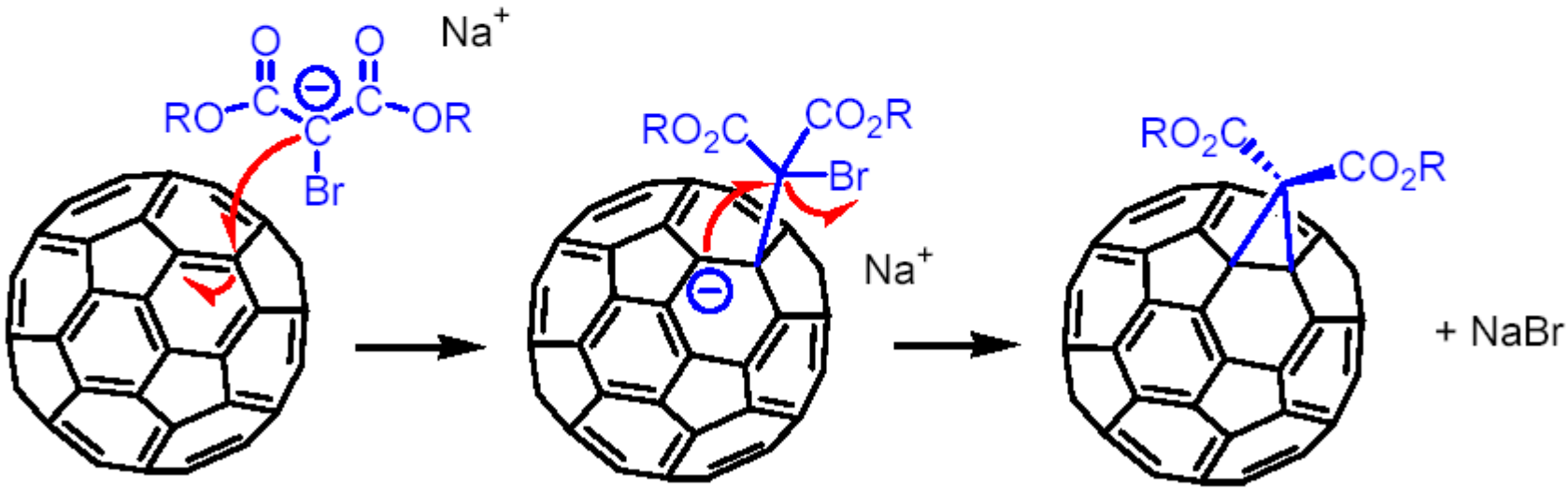
C Hex—≡—Li , MeI

D NaCN, TsCN

E Hex—≡—Li , PhCOCl

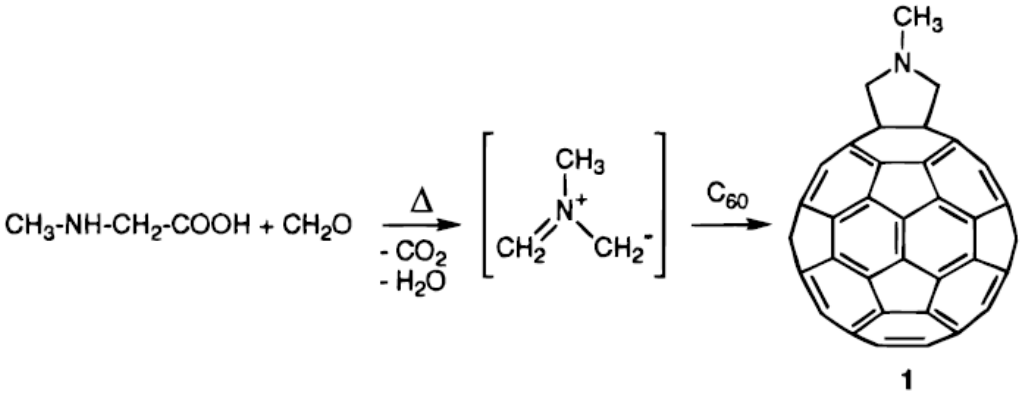
F 

Ciclopropanazione del C_{60} (metanofullereni)



1,3-dipolar cycloaddition of azomethineylides to C60

the Prato's reaction



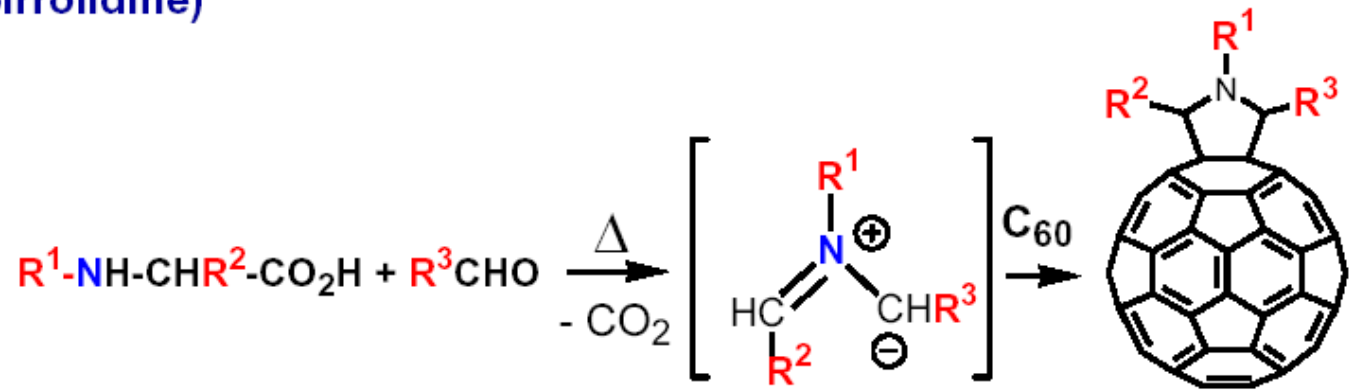
41% yield
82% on the consumed C60

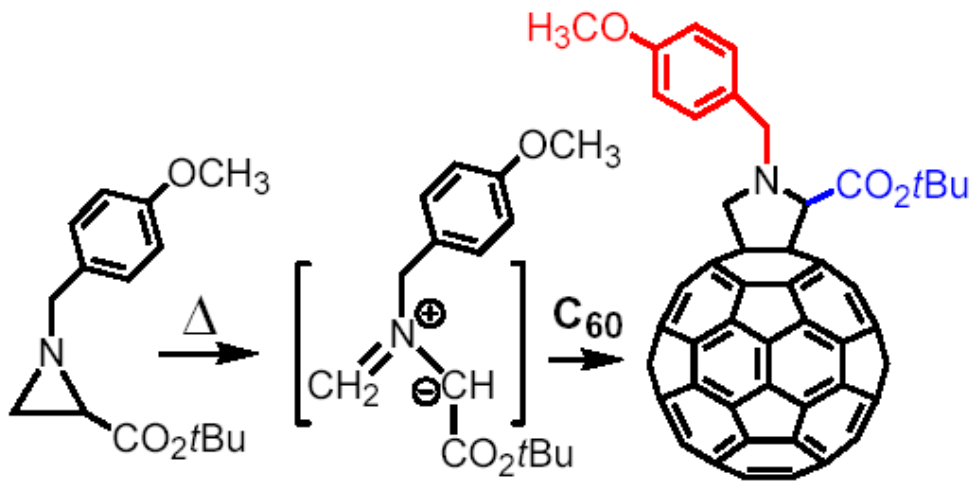
the reaction is site selective in that it affords exclusively the product of cycloaddition across a 6,6 ring junction of the fullerene

Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798–9799.

Cicloaddizione di ilidi azometiniche

(fulleropirrolidine)





M. Maggini, G. Scorrano, M Prato *J. Am. Chem. Soc.* **1993**, 9798
M. Prato, M. Maggini *Acc. Chem. Res.* **1998**, 519
X. Zhang, M. Willems, C. S. Foote *Tetrahedron Lett.* **1993**, 8187

FULLERENE

In the presence of large excesses of reagents, up to nine pyrrolidine rings can be introduced, as detected by MS analysis of the reaction crude.

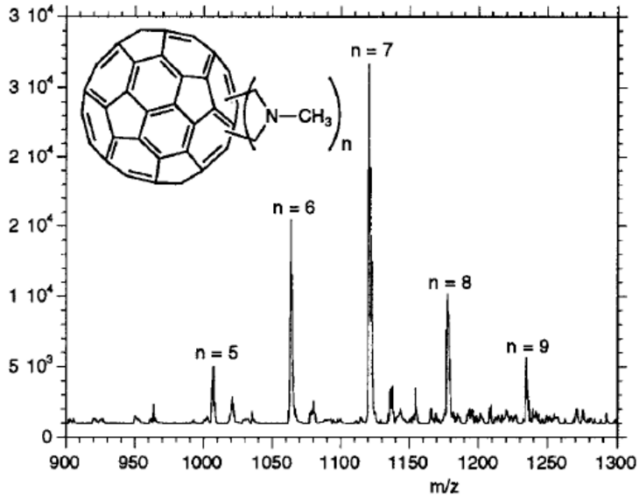


FIGURE 1. APCI-MS spectrum of the crude mixture obtained by heating a toluene solution containing C_{60}, 20 equiv of sarcosine, and 20 equiv of formaldehyde for 8 h.

Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798–9799.

C60 bis-adducts