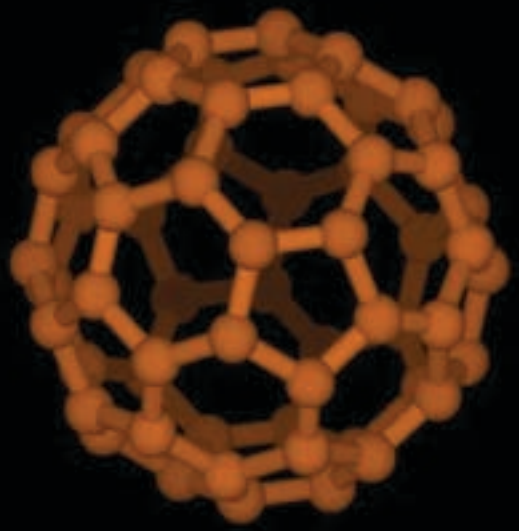
Synthesis, reactivity and applications of fullerenes



Carbon atoms are essential for life on our planet. They are the fundamental constituents of proteins, carbohydrates, fatty acids, nucleic acids (DNA e RNA)

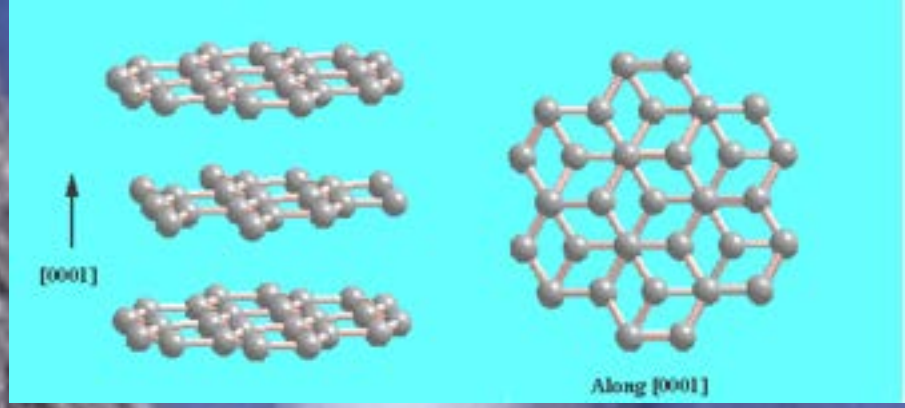
- C - C - C - C - C - C - C - C -

Allotropic forms of carbon

(different cristalline structure)

Before 1985

In the solid state only two fundamental structures were known: ***graphite*** and ***diamond***

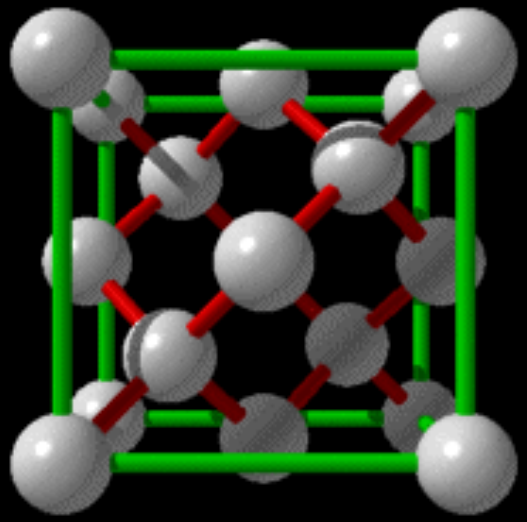


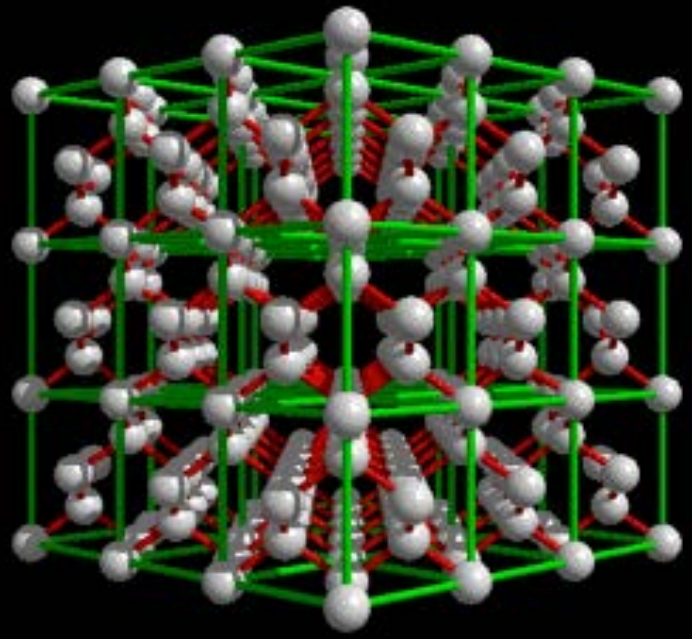
Graphite is a good electrical conductor, is greasy and finds wide use as lubricant; it is soft and black, with a weak metallic brightness

C

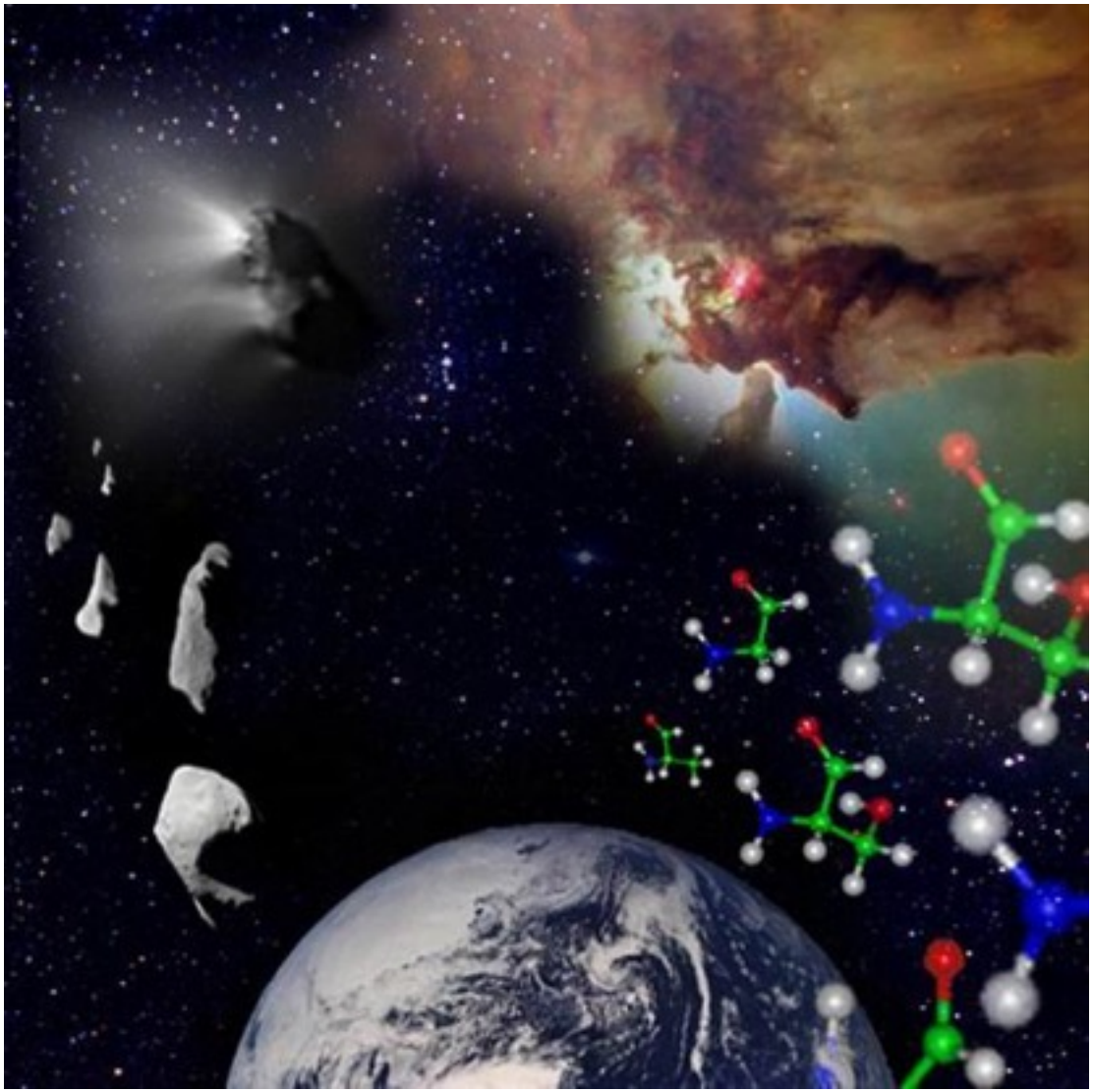
© 2002 RGB Ltd www.elementsofphotography.com

Tridimensional structure of diamond



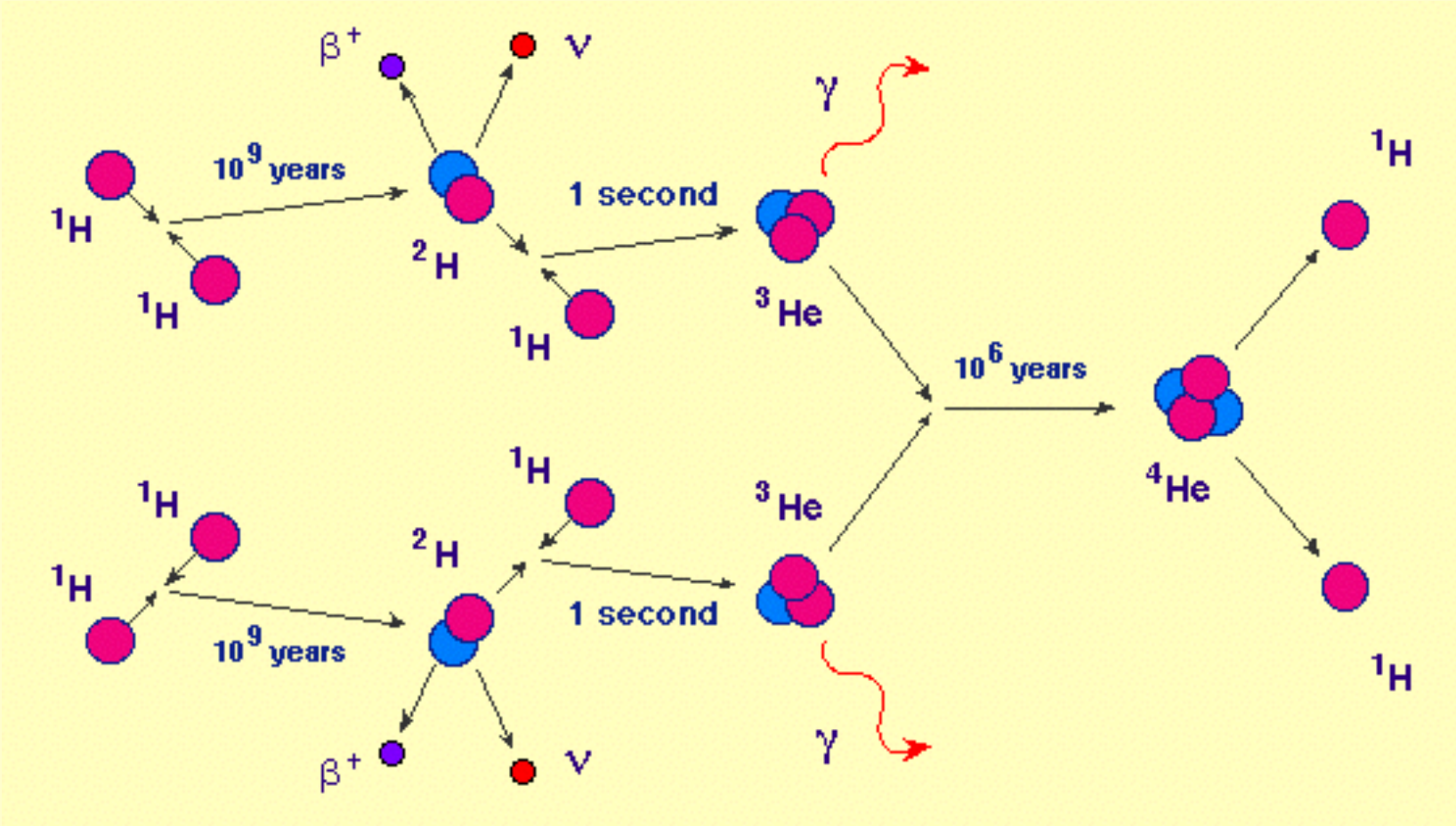


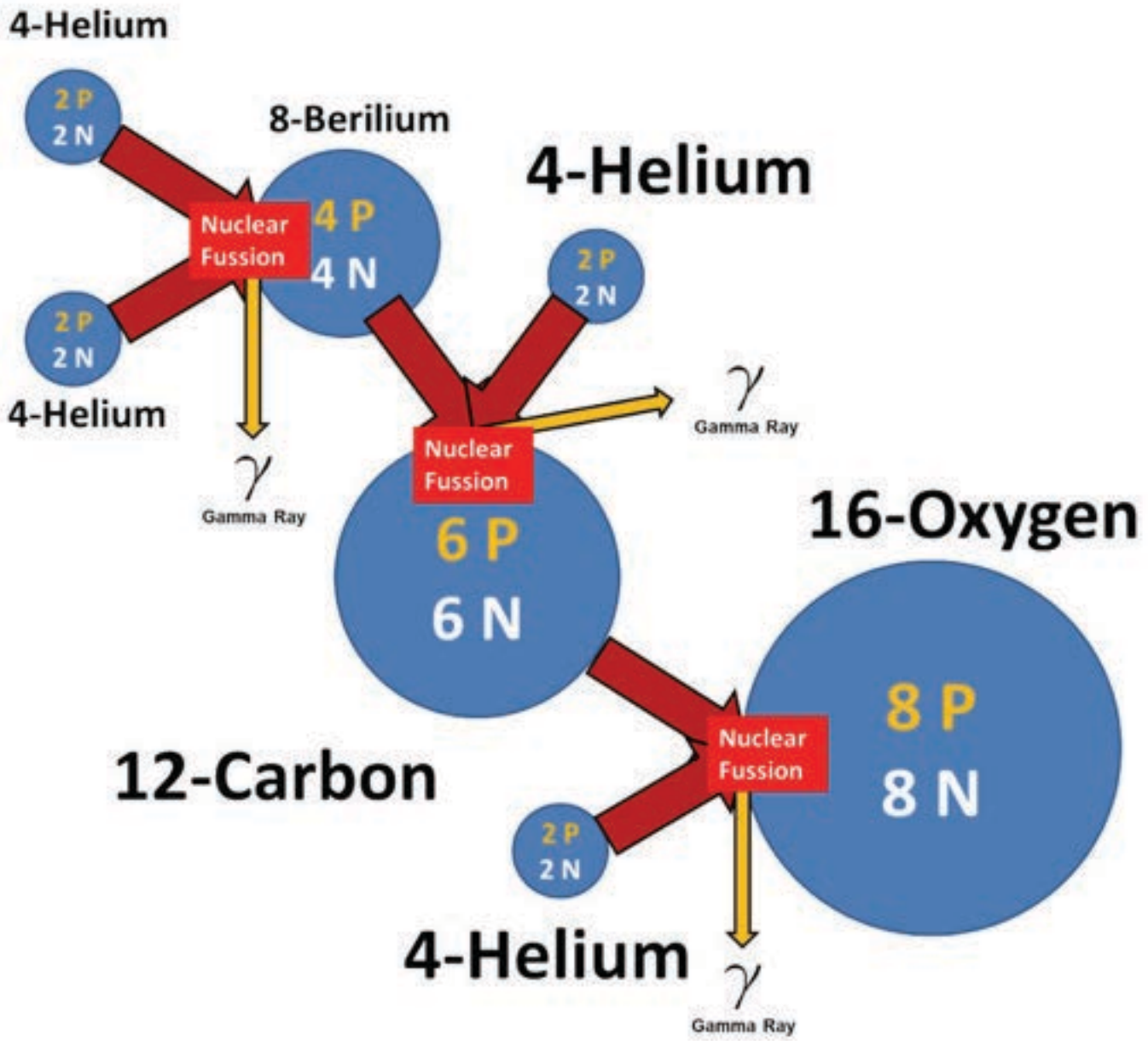




many molecoles observed in the space
are based on carbon



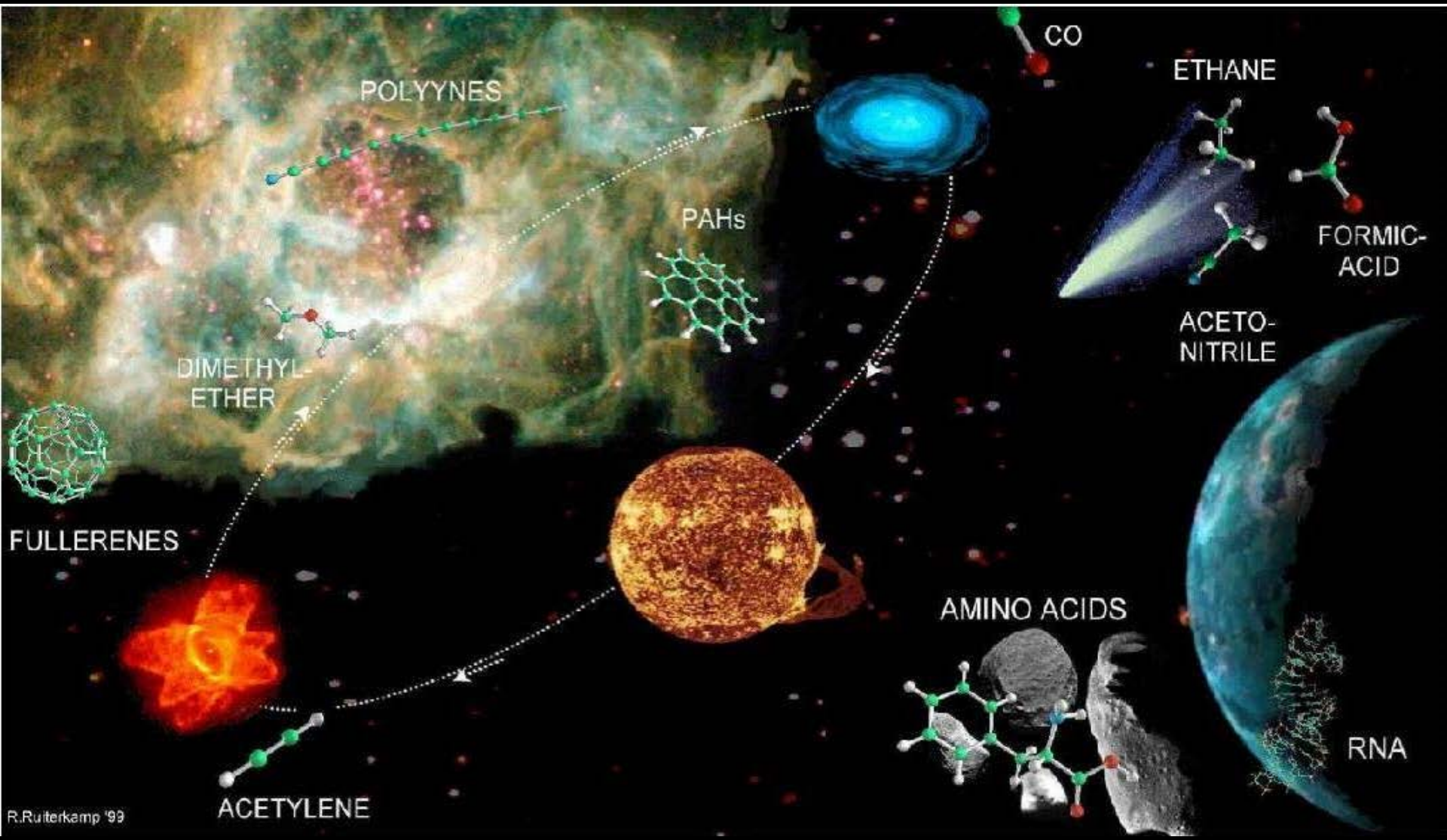

β+
ν
γ
1H
10^9 years
1 second
2H
3He
10^6 years
4He
1H
1H
1H
1H
2H
1 second
3He
10^9 years
β+
ν
γ
1H
1H



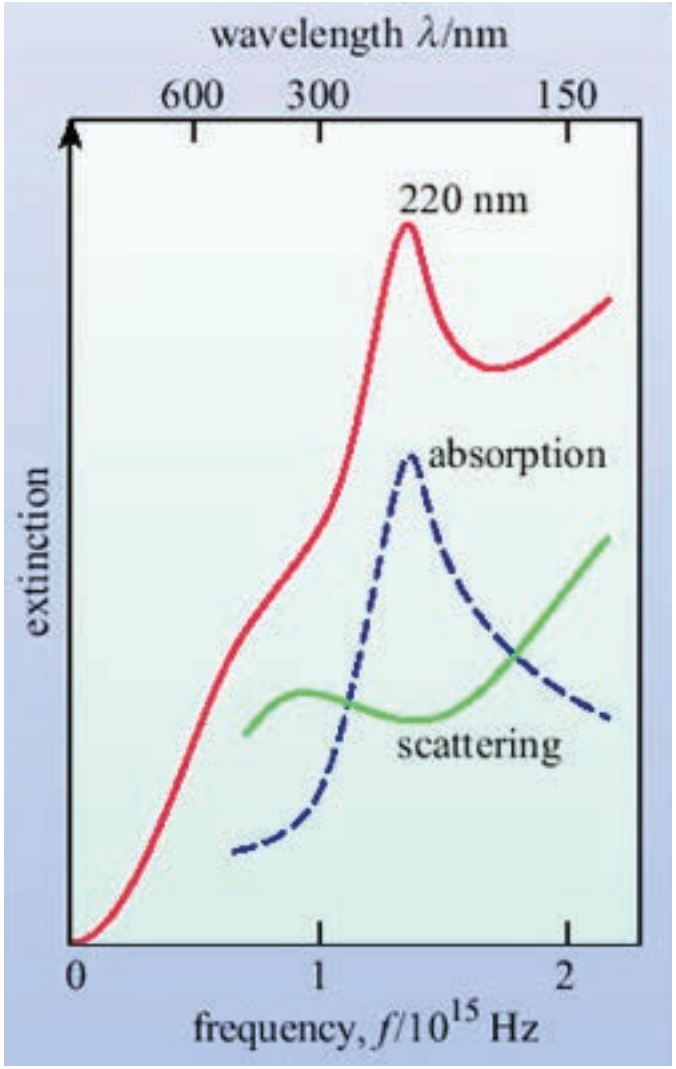
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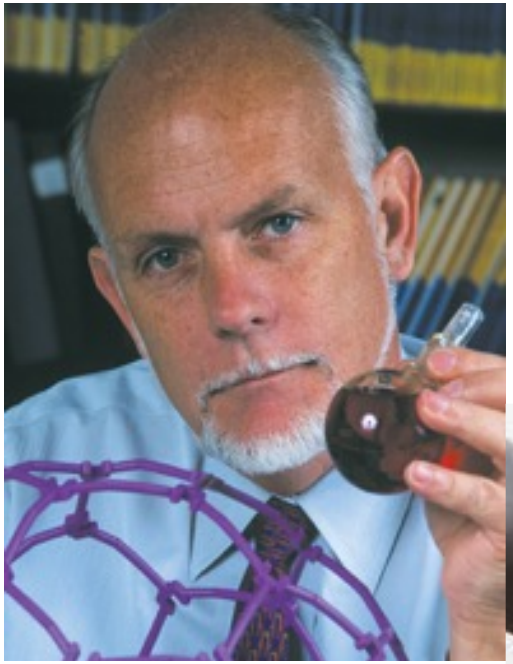
(poly-ynes)

http://www.everythingselectric.com/elements-formation/


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

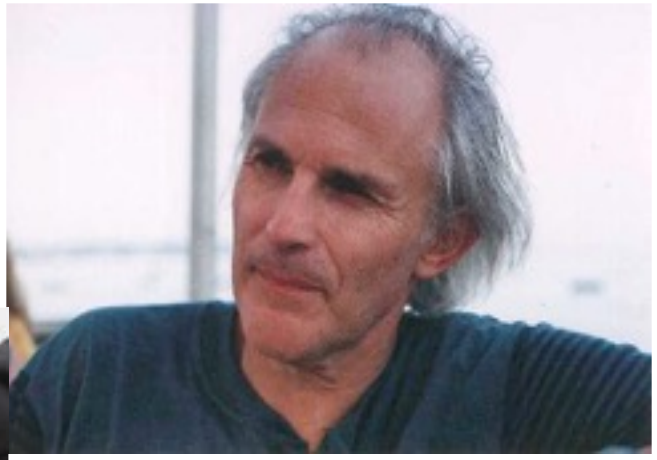
Spectrum of Interstellar Dust



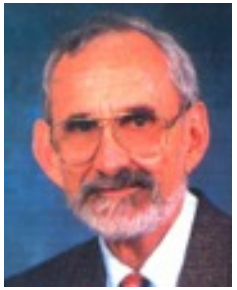


R. Smalley
Rice U, USA

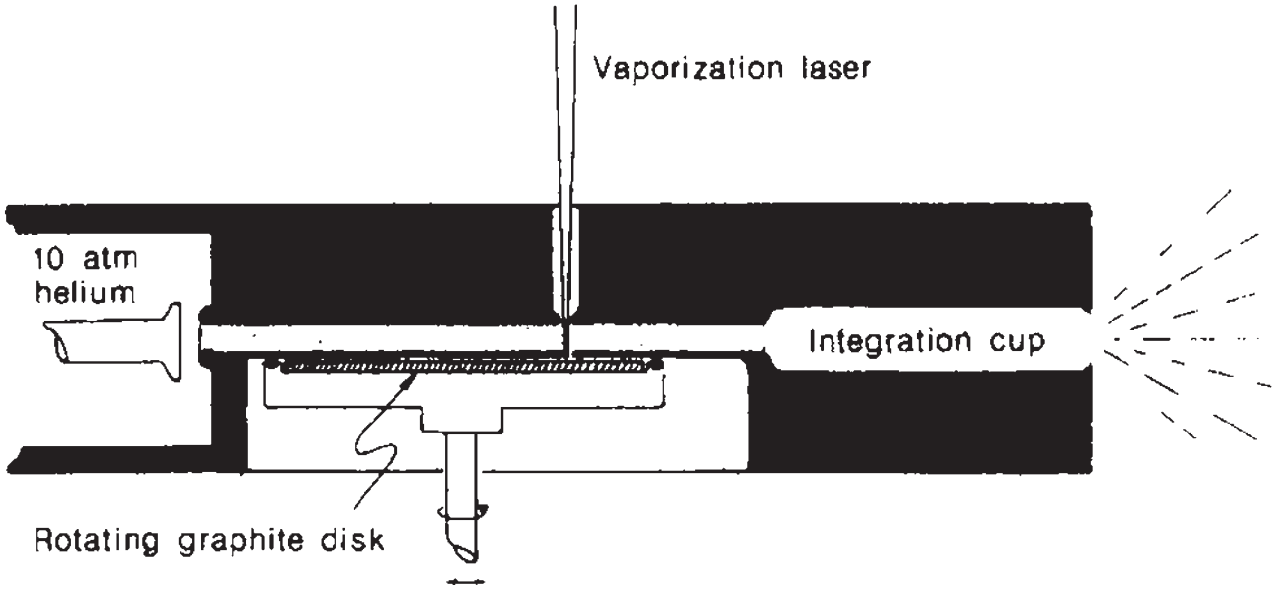




H. Kroto
U Sussex, UK



R. Curl
Rice U, USA



C_{60}: Buckminsterfullerene

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

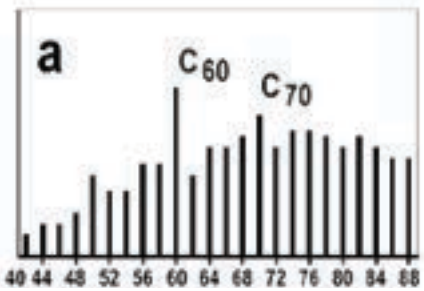
Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77251, USA

During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells[1], graphite has been vaporized by laser



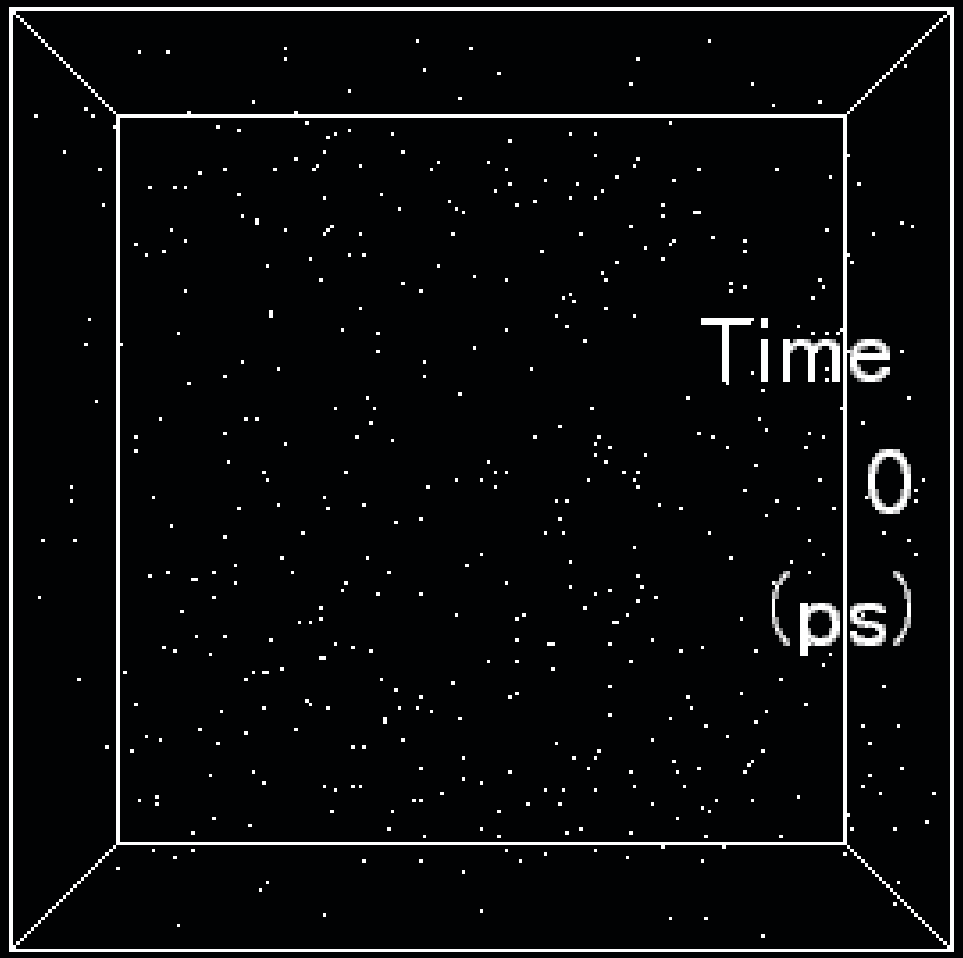
Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C_{60} molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.

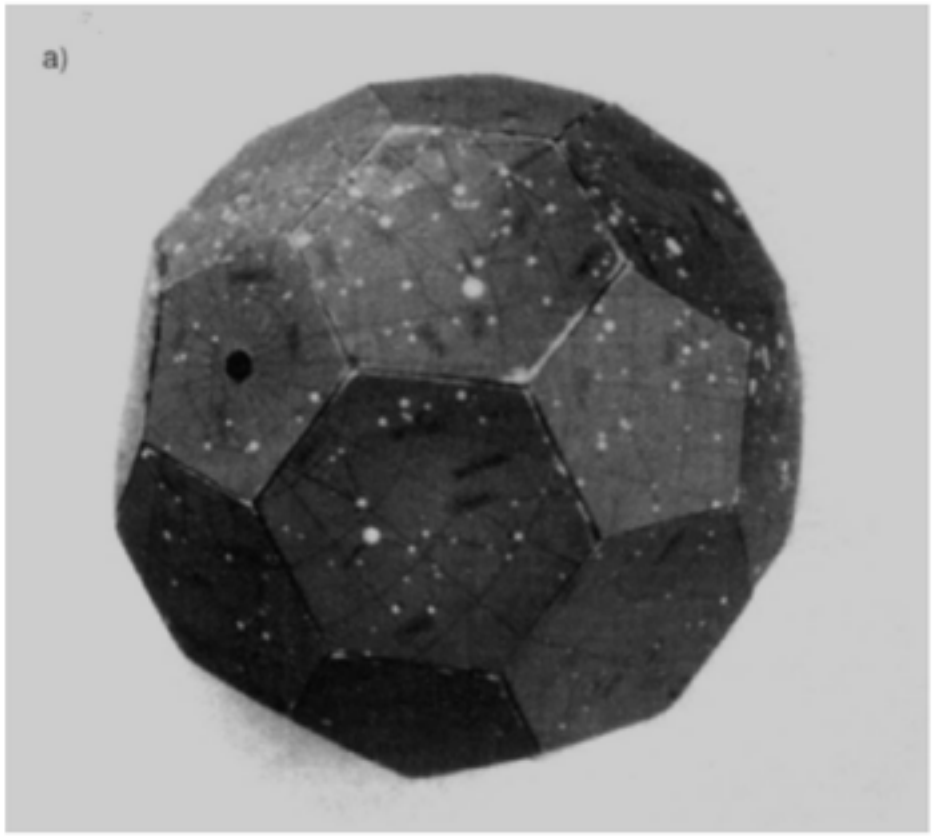
Mass spectra of the black powder obtained from carbon vapors



Number of carbon atoms

Angew. Chem. Int Ed Engl 1997. 36. 1578-1593


Time
0
(ps)



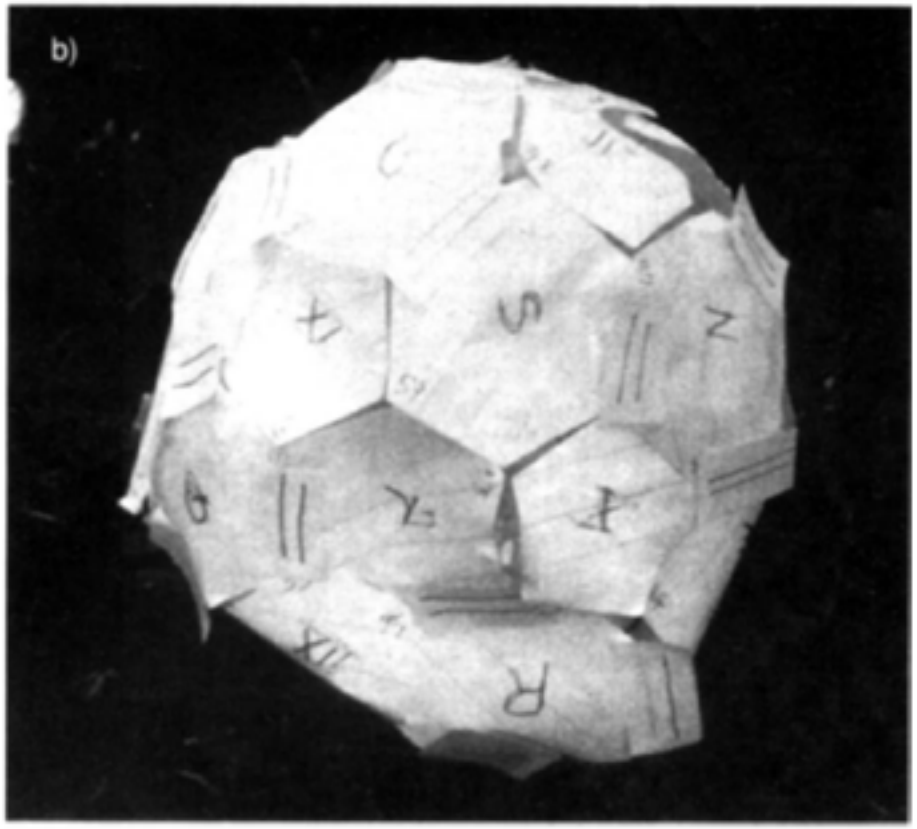
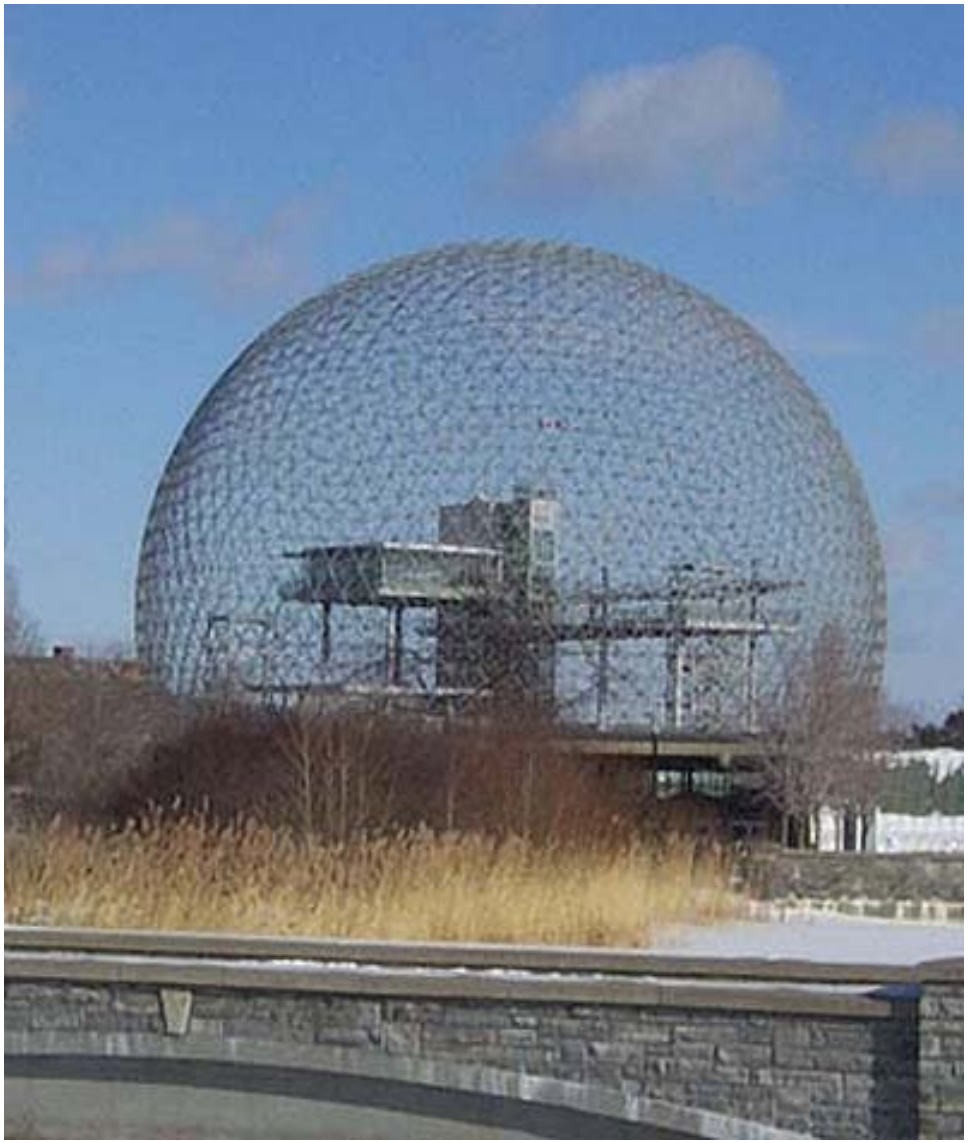
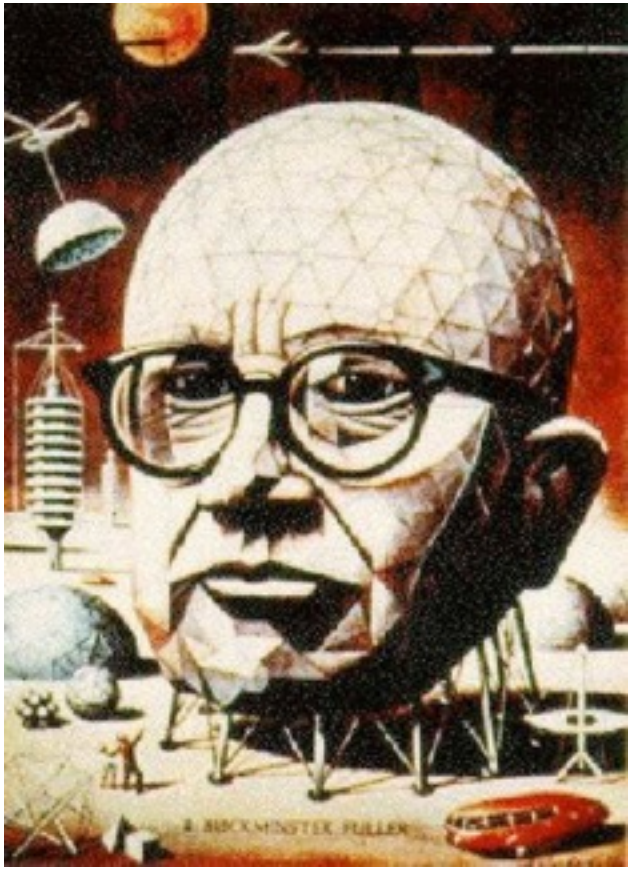


Figure 11. The two card models that played key roles in the positing of the truncated icosahedral structure of C_{60}. a) Stardome map of the sky (Buckminster Fuller patented t-icosahedral, and other polyhedral world-map projections); b) prototype C_{60} made by Smalley. Both models are truncated icosahedra with 60 vertices, 12 pentagonal and 20 hexagonal faces.

Angew. Chem. Int Ed Engl 1997. 36. 1578-1593

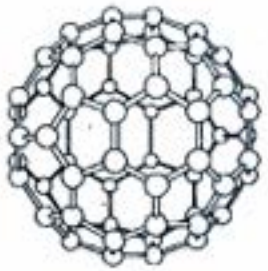




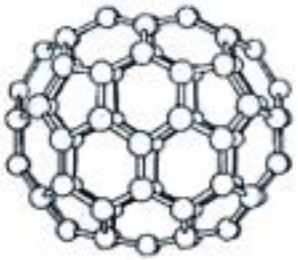
Expo '67 American Pavilion (now the Biosphère), by R. Buckminster Fuller, on Île Sainte-Hélène, Montreal

1985: FULLERENES are discovered

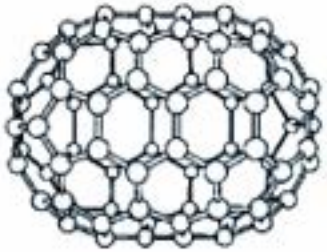
C60



C70



C80 isomer

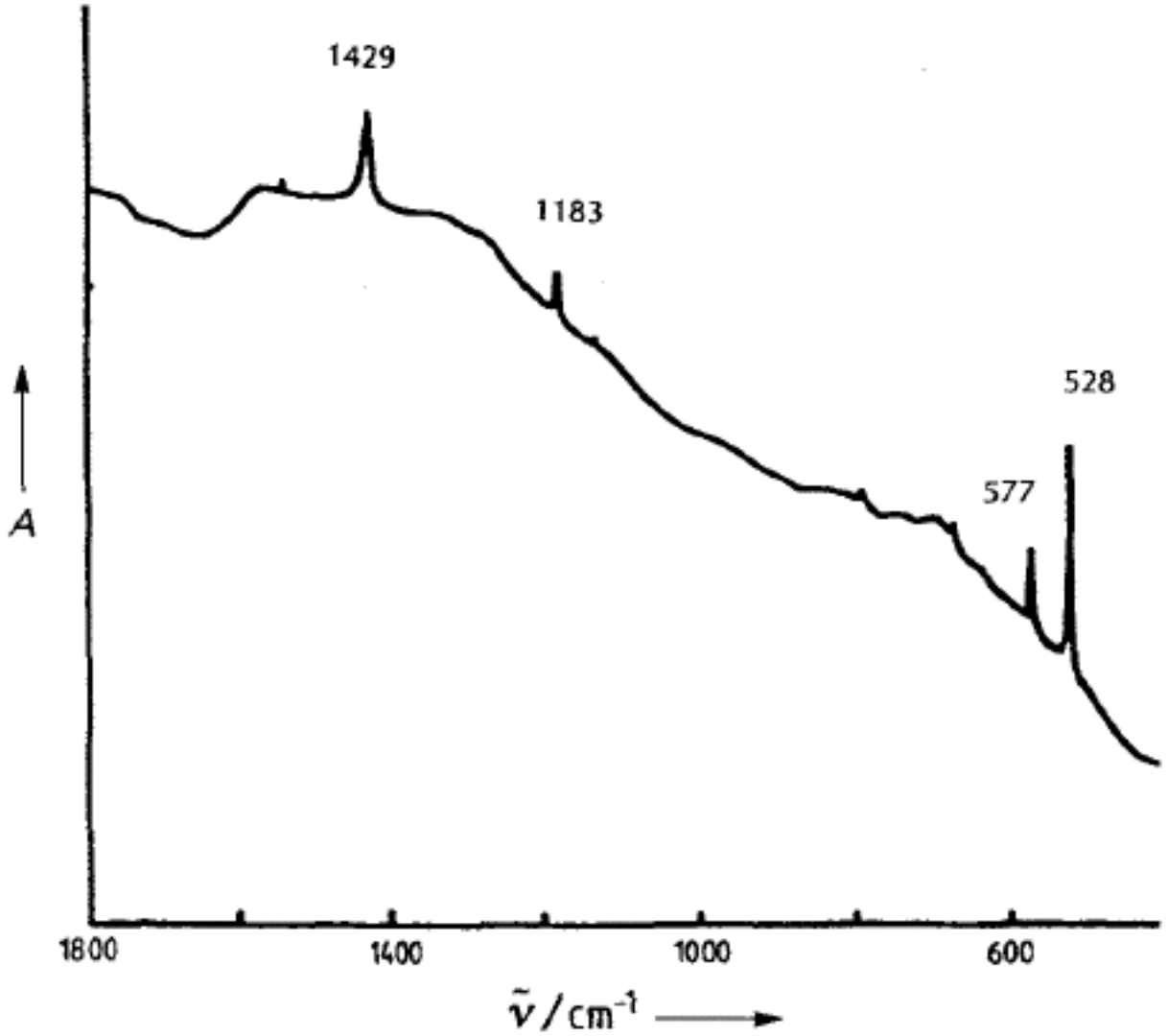


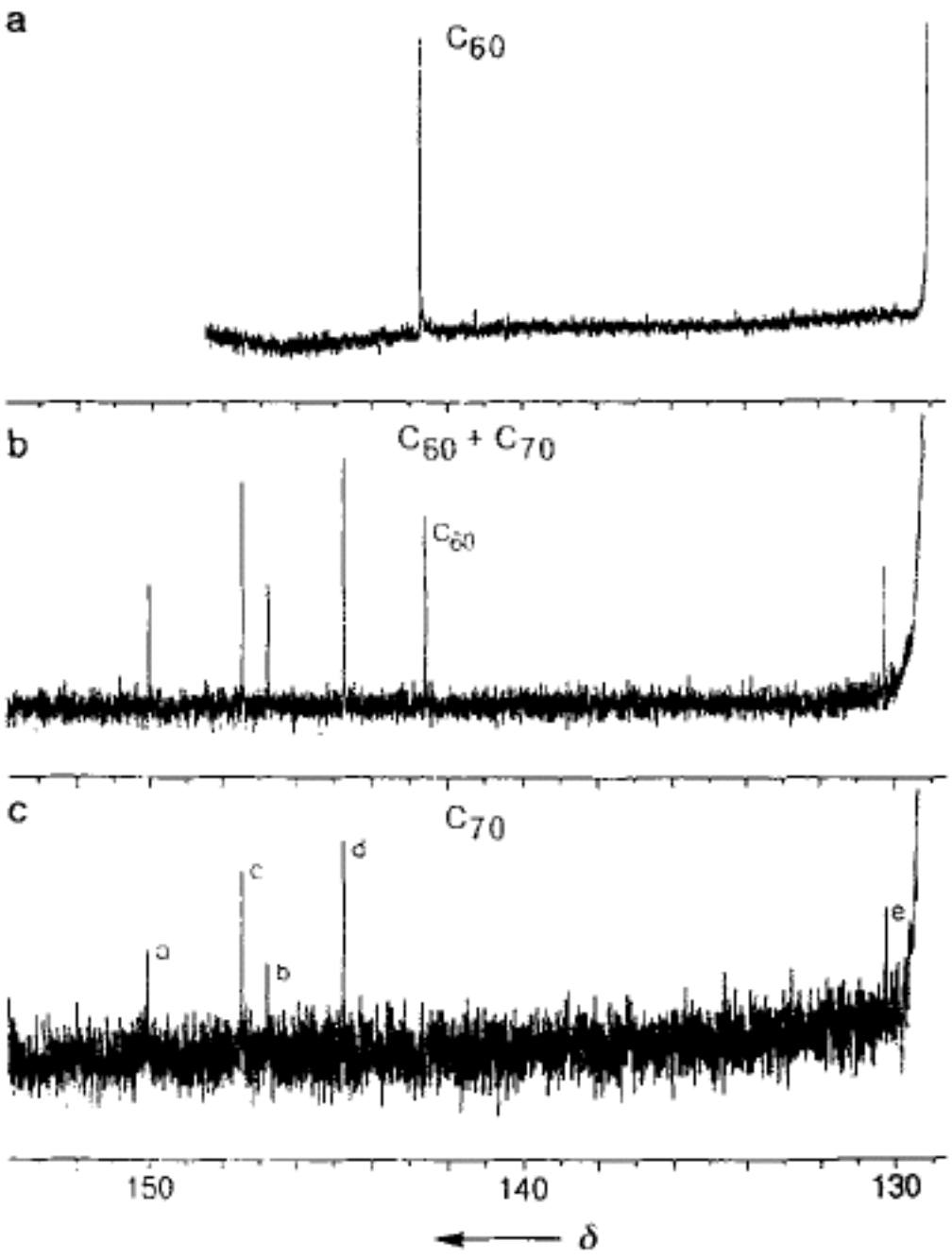
Solid C_{60}: a new form of carbon

W. Krätschmer*, Lowell D. Lamb†, K. Fostiropoulos* & Donald R. Huffman†

* Max-Planck-Institut für Kernphysik, 6900 Heidelberg, PO Box 103980, Germany
† Department of Physics, University of Arizona, Tucson, Arizona 85721, USA




1429
1183
528
577
A
1800
1400
1000
600
$\tilde{\nu}$ / cm^{-1}


a
C_{60}
b
C_{60} + C_{70}
C_{60}
c
C_{70}
a
b
c
d
e
150
140
130
δ

Fullerene timeline

1970

E. Osawa suggested the existence of a stable spherical molecule composed of 60 carbon atoms
(Kagaku *25*, 854)

1985

H. Kroto, R. Smalley, R. Curl (and the students J. Heath e S. O'Brien) discovered C_{60} fullerene
(Nature *318*, 162)

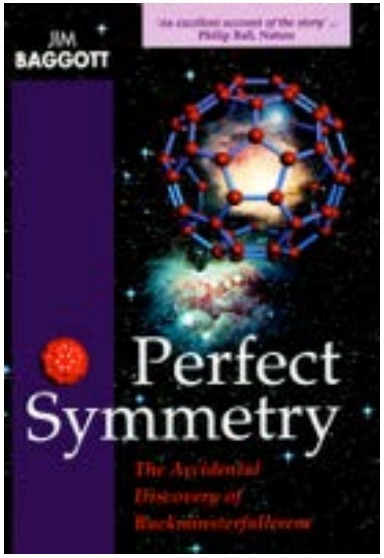
1990

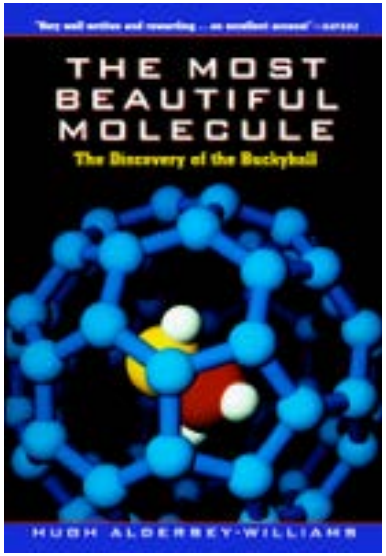
W. Krätschmer, L. Lamb, K. Fostiropoulos, D. Huffman produce macroscopic quantities of C_{60} e C_{70} using vaporization of graphite
(Nature *347*, 354)

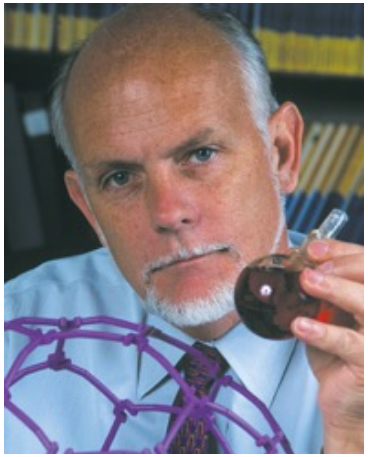
1996

The Nobel Prize for Chemistry is assigned to H. Kroto, R. Smalley e R. Curl

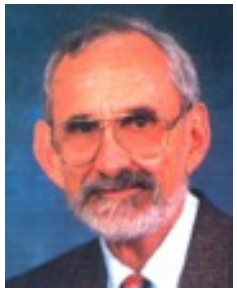
Buckminsterfullerene - C_{60}
The 1996 Nobel Prize for Chemistry



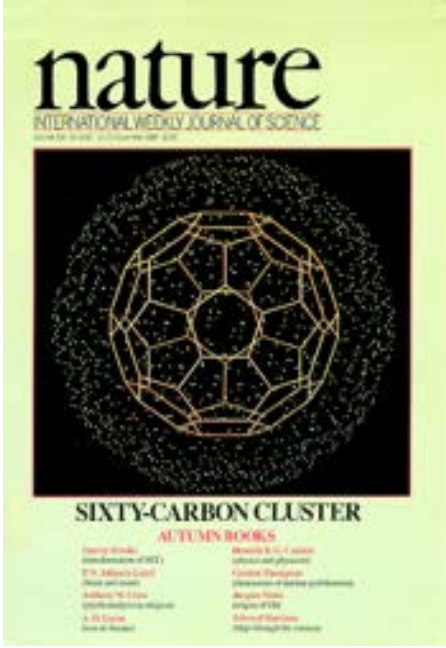


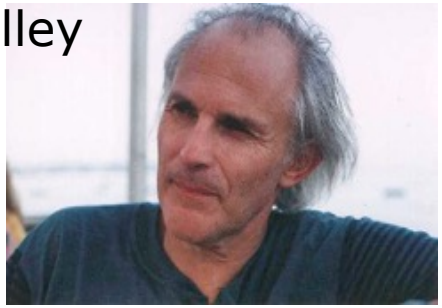


R. Smalley

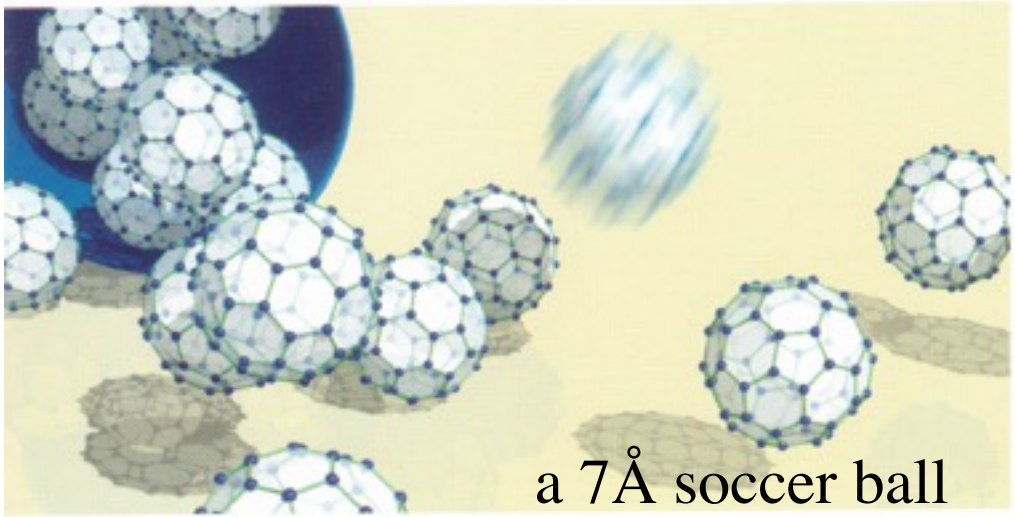


R. Curl





H. Kroto



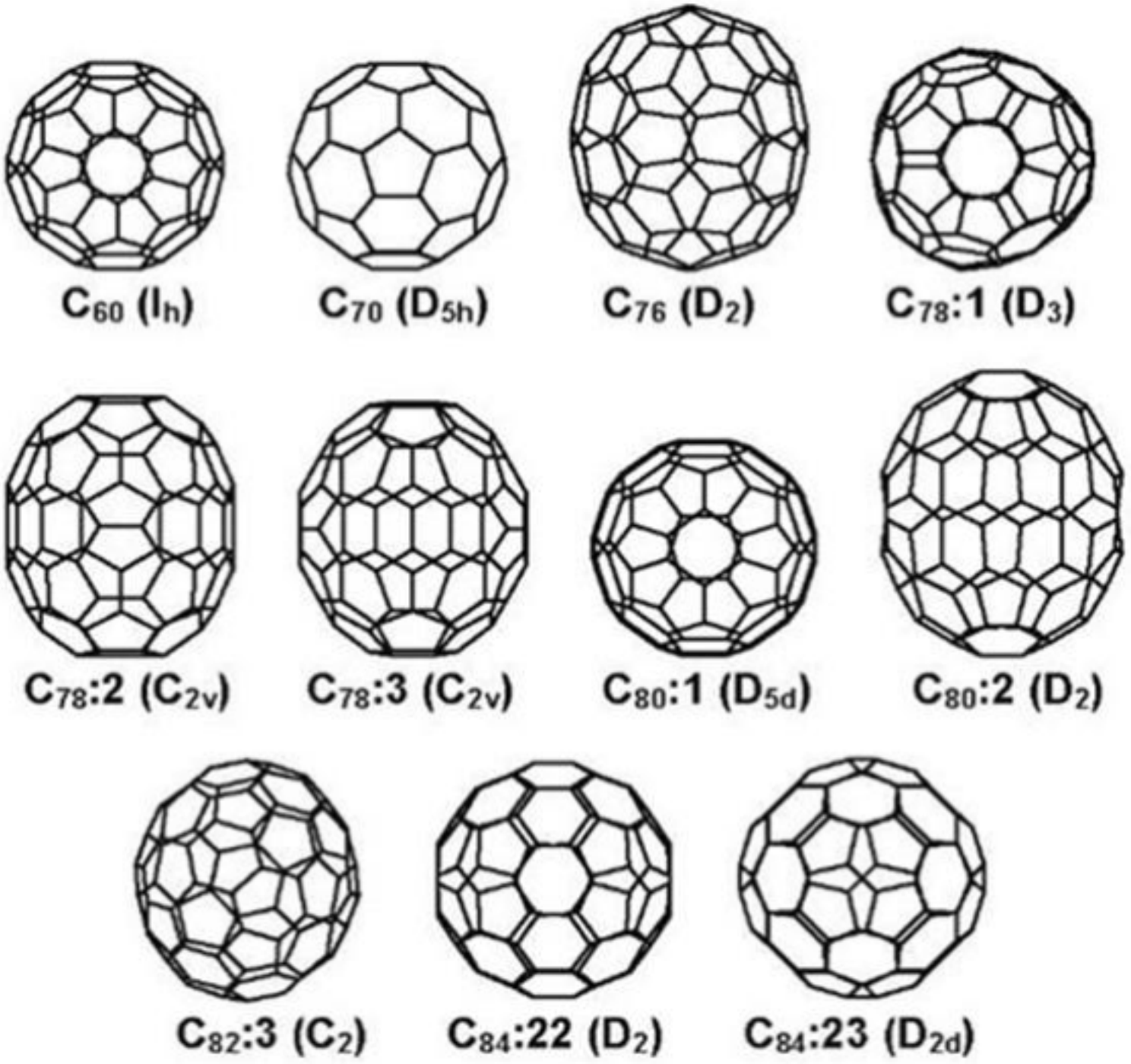
a 7Å soccer ball

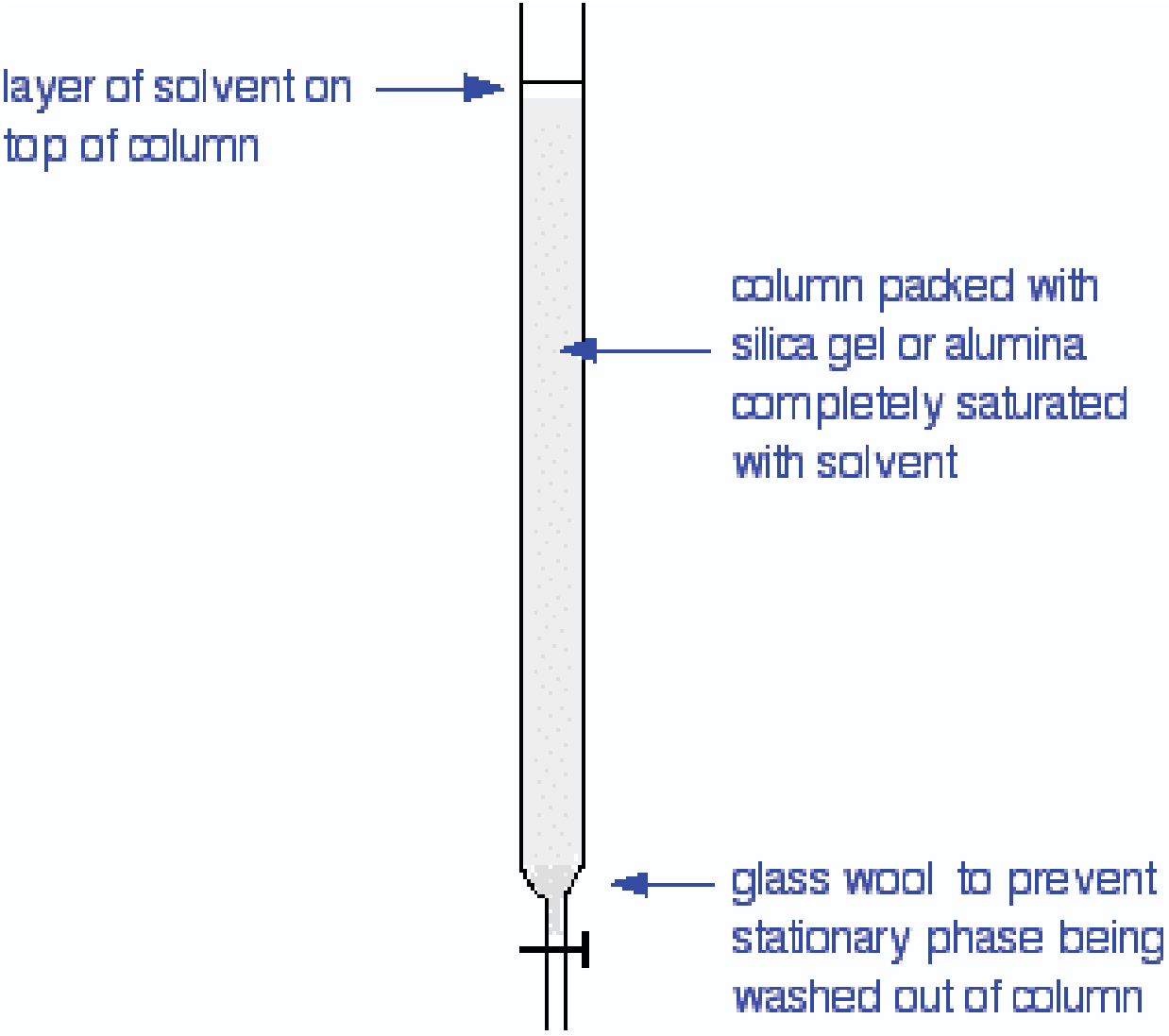




A fascinating new group of carbon molecules

Fullerenes: a whole new ball game


C_{60} (I_h)
C_{70} (D_{5h})
C_{76} (D_2)
C_{78}:1 (D_3)
C_{78}:2 (C_{2v})
C_{78}:3 (C_{2v})
C_{80}:1 (D_{5d})
C_{80}:2 (D_2)
C_{82}:3 (C_2)
C_{84}:22 (D_2)
C_{84}:23 (D_{2d})


layer of solvent on top of column
column packed with silica gel or alumina completely saturated with solvent
glass wool to prevent stationary phase being washed out of column

J. Org. Chem. 1992, 57, 11, 3254-3256

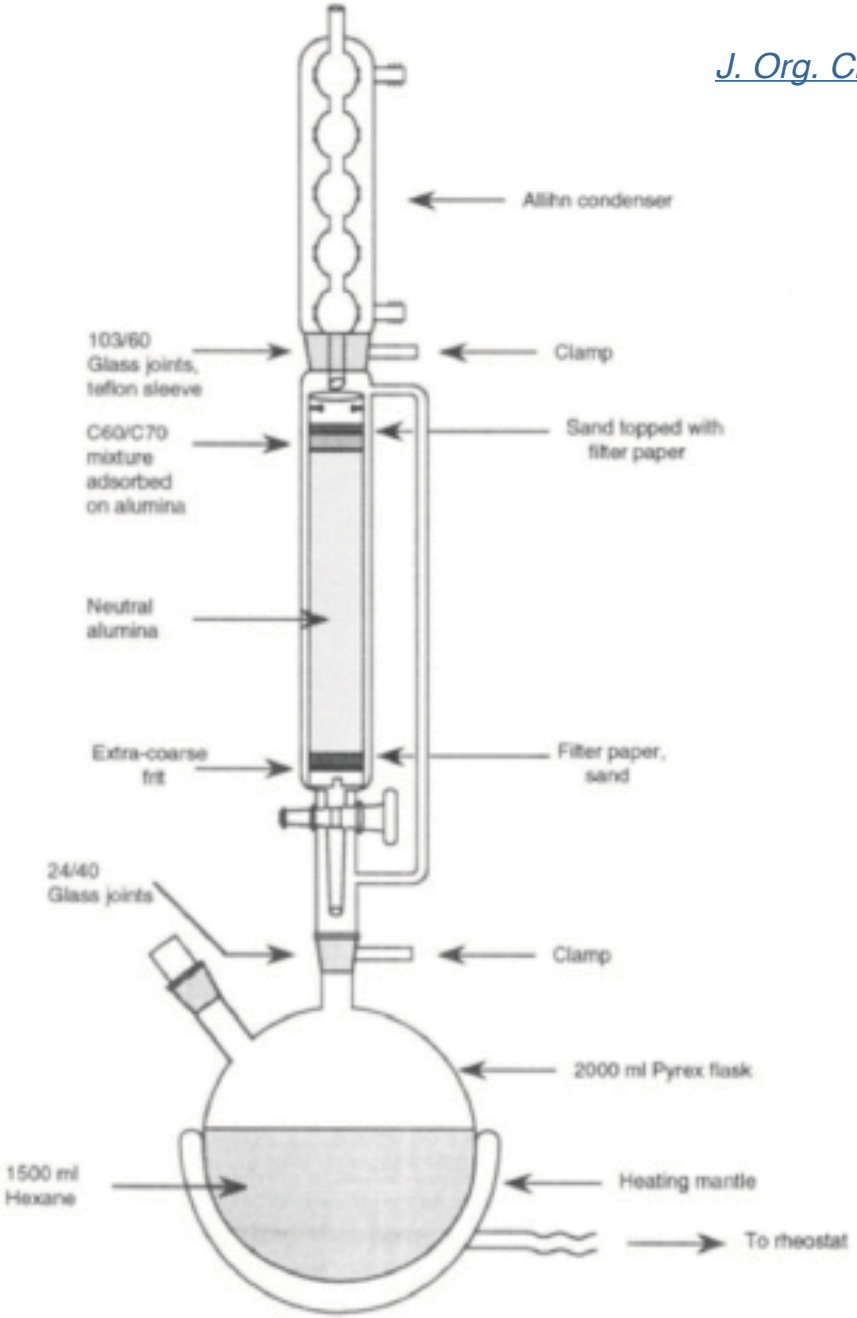


Figure 1. Schematic representation of the modified Soxhlet chromatography apparatus.

Purification of Gram Quantities of C_{60}. A New Inexpensive and Facile Method

Walter A. Scrivens, Peter V. Bedworth, and James M. Tour*

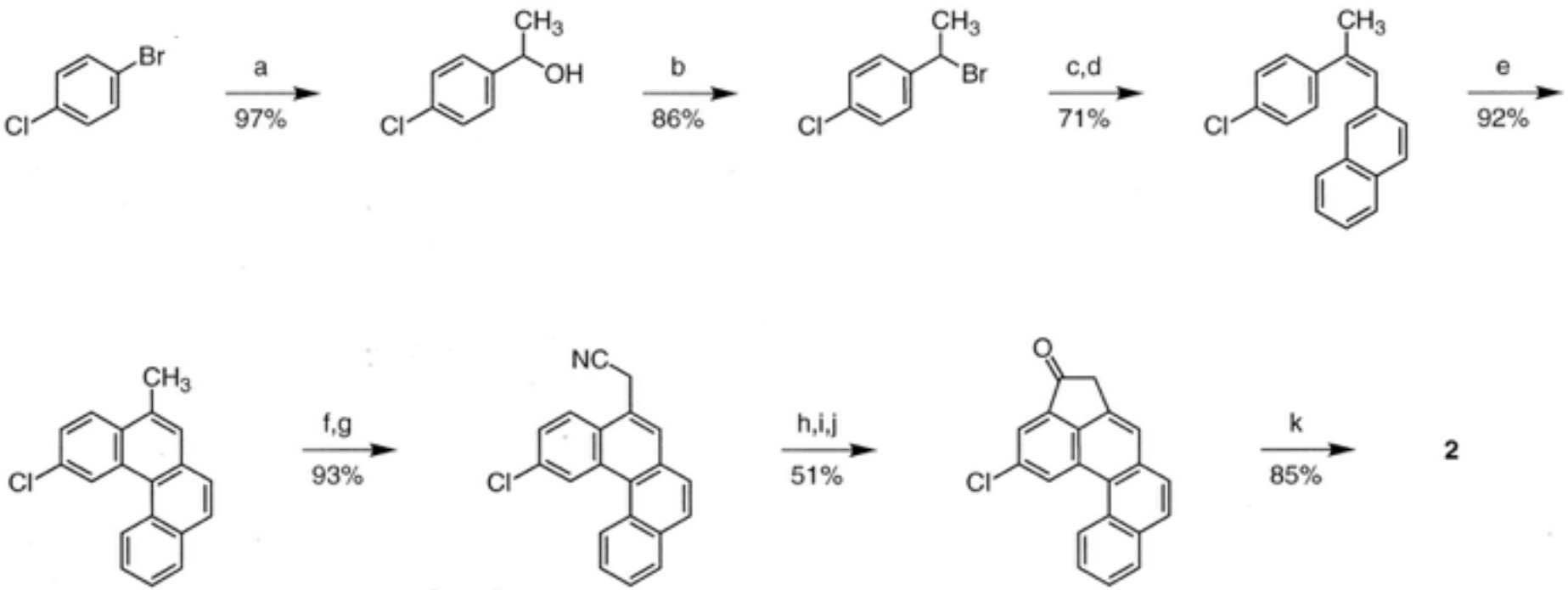
Department of Chemistry and Biochemistry
University of South Carolina
Columbia, South Carolina 29208

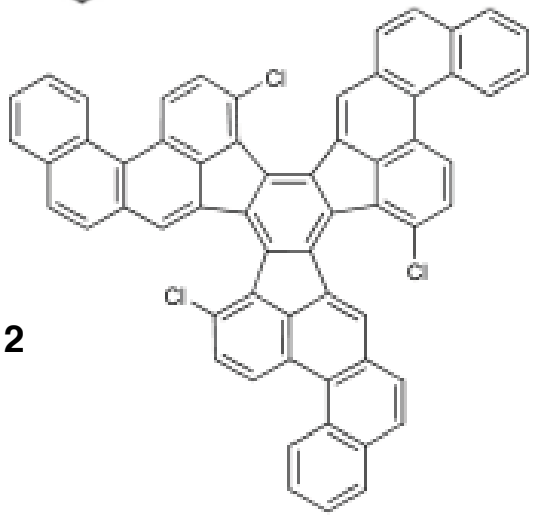
Received June 17, 1992

J. Am. Chem. Soc. 1992, 114, 7917-7919


C60

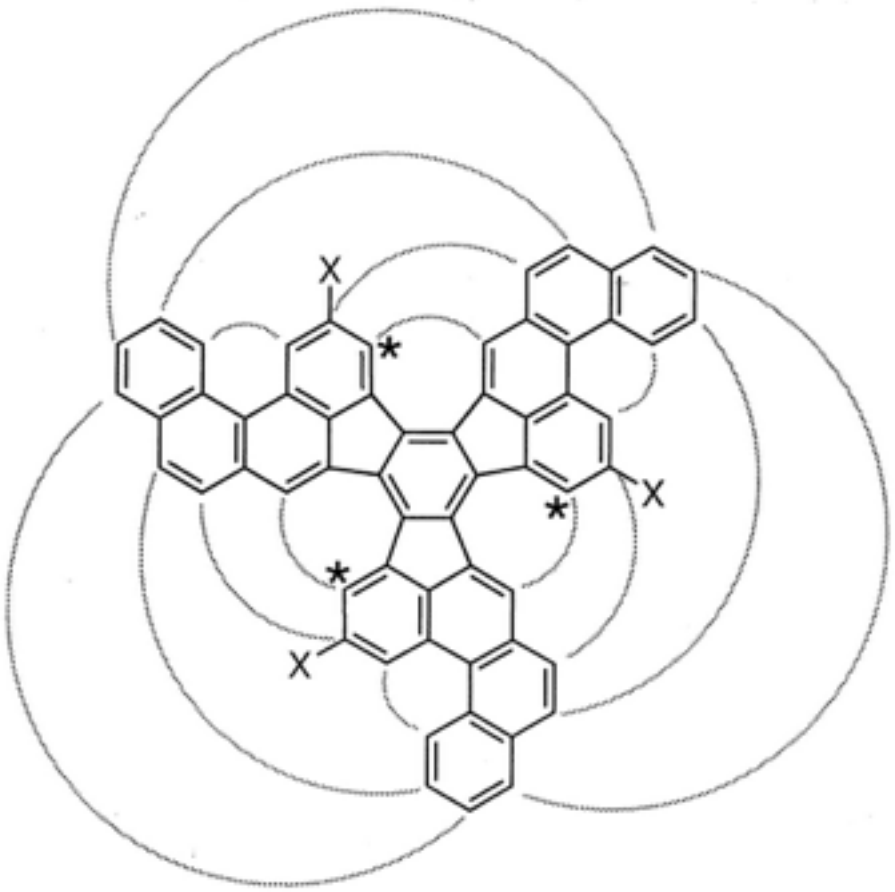
Total Synthesis of C_{60}





2

L. T. Scott et al. Science, Vol. 295, Issue 5559, pp. 1500-1503



1 X = H **2** X = Cl

Flash Vacuum Pyrolysis of **2**

1100 °C
0.01mm



C_{60}
Buckminsterfullerene

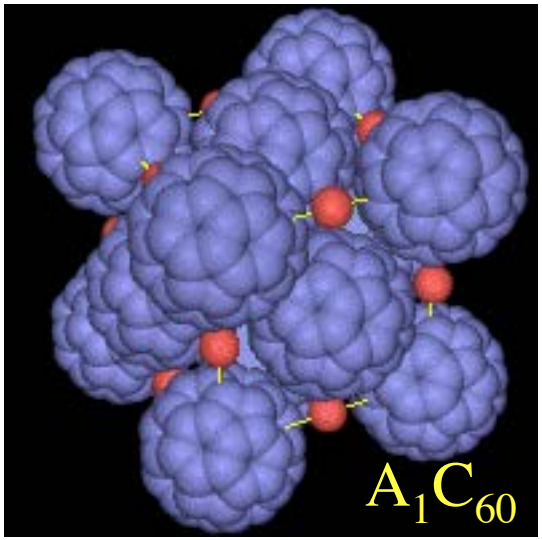
L. T. Scott et al. Science, Vol. 295, Issue 5559, pp. 1500-1503
Angew. Chem. Int. Ed. 2004, 43, Issue 38, pp. 4994-5007

Fullerenes: Some Potential Applications

-- High temperature superconductors

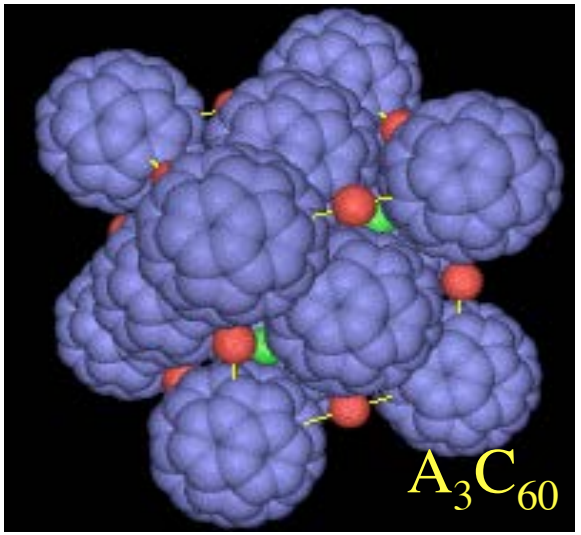
Materials Based on C_{60}, obtained through Doping with Alkali Metals (K, Li, Na, …)

Drastic changes of the electronic e/o crystalline structure



Face centered cubic

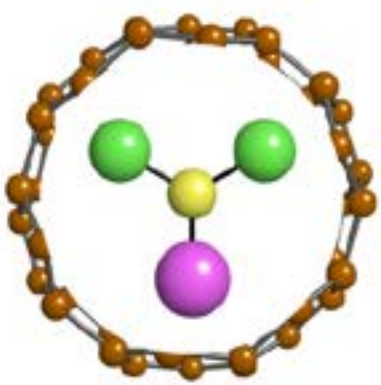
Metallic



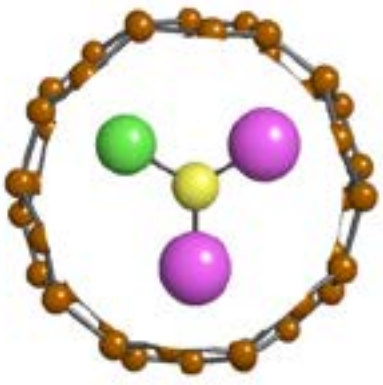
Superconductors at high temperature

(T_c < 40 K)

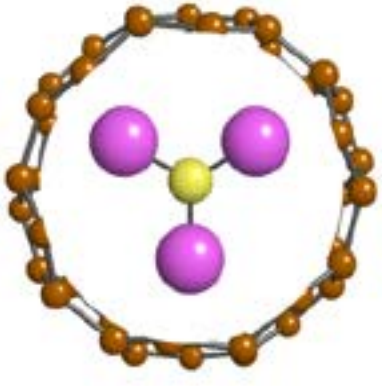
Can atoms be inserted inside the cage???



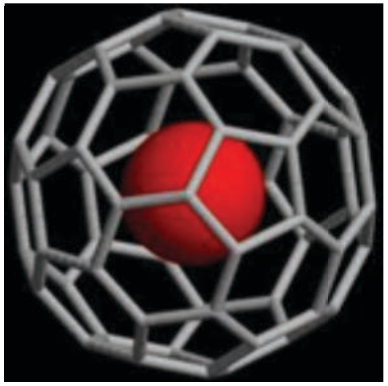
$ErSc_2N@C_{80}$



$Er_2ScN@C_{80}$



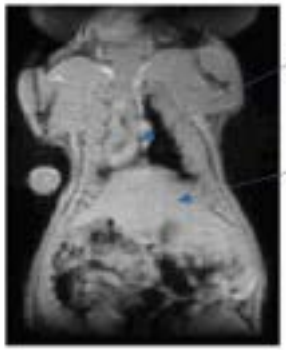
$Er_3N@C_{80}$

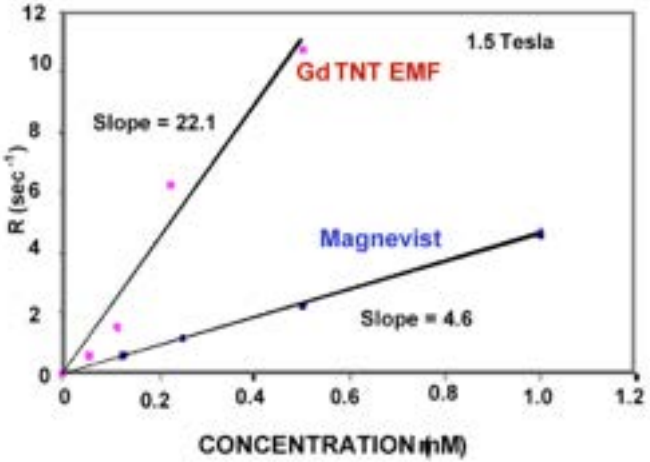


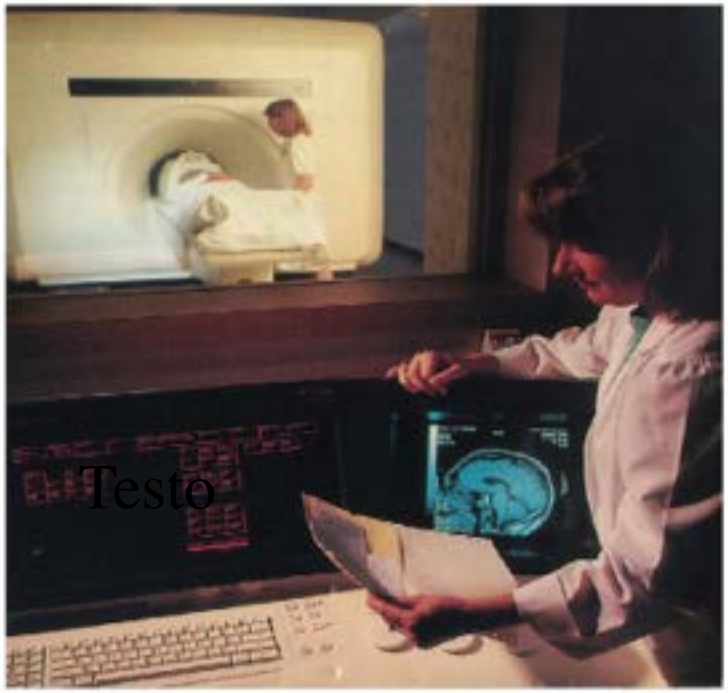
1 H																1 H	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112		114		116		118

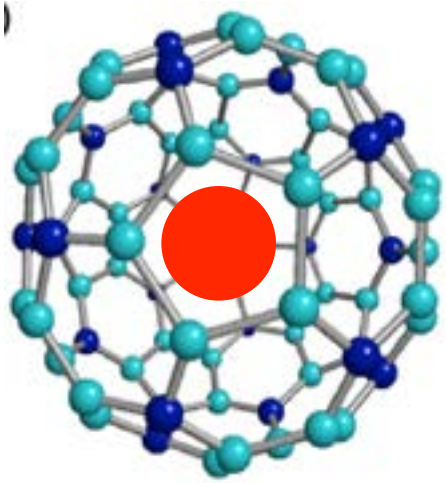
58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

MRI Contrast Agents



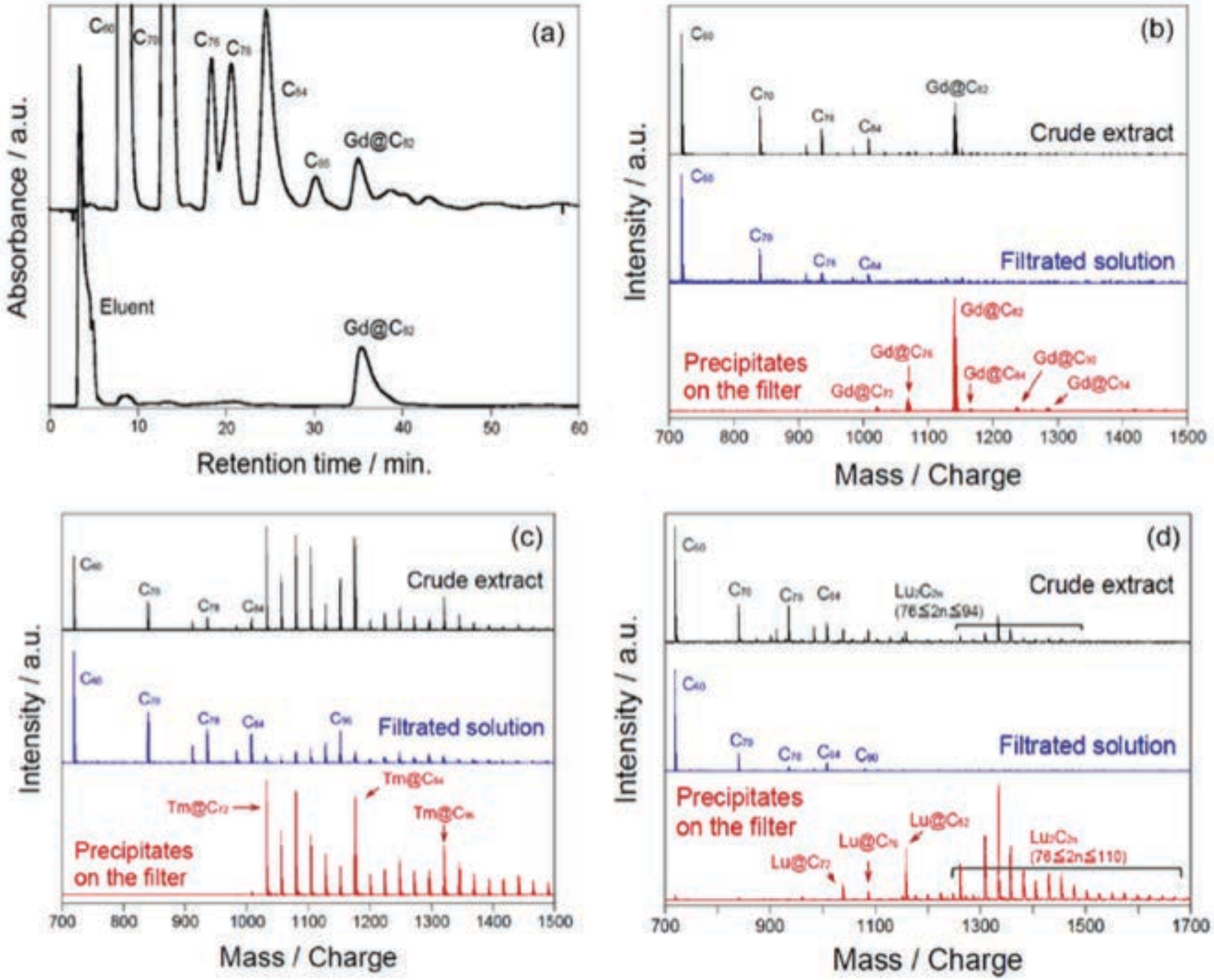




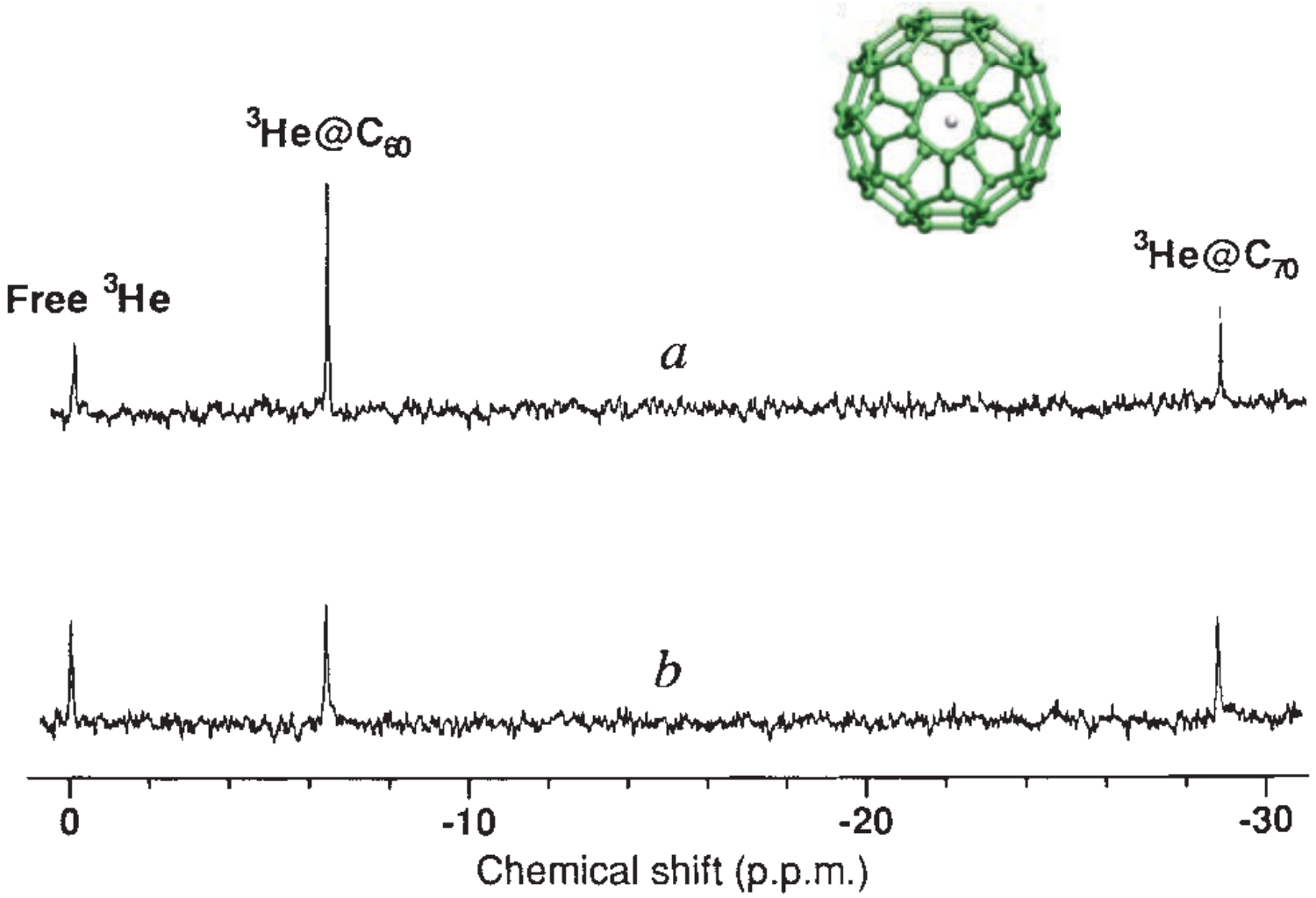


Shinohara *et al.* have reported significant increases (20-40) in the ^1H MRI T_1 spin-lattice relaxivity rates for $Gd@C_{82}(OH)_n$ when compared with commercial Gd-DTPA

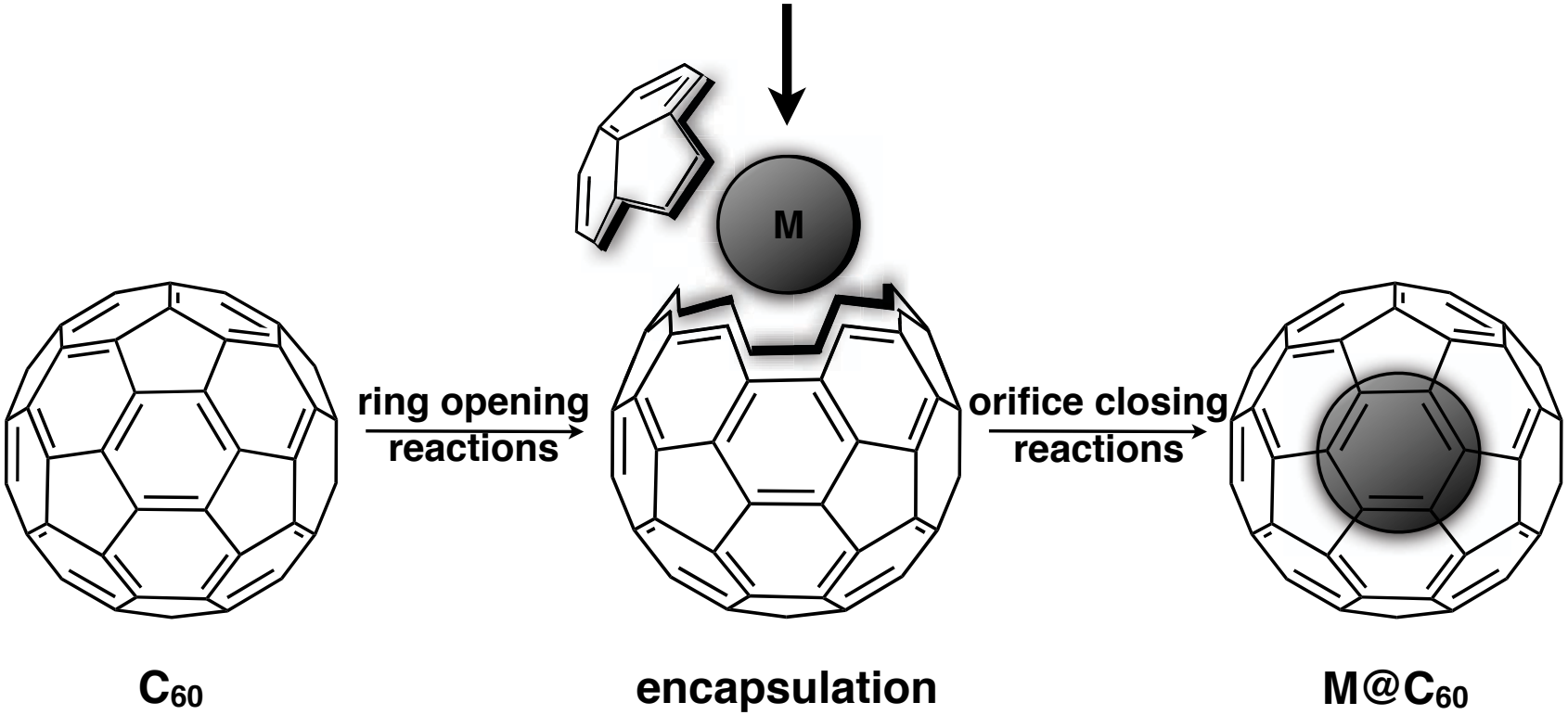
J. AM. CHEM. SOC. VOL. 125, NO. 14, 2003 **4391**


(a)
Absorbance / a.u.
Eluent
Gd@C82
Retention time / min.
(b)
Crude extract
Filtrated solution
Precipitates on the filter
Intensity / a.u.
Mass / Charge
(c)
Crude extract
Filtrated solution
Precipitates on the filter
Tm@C72
Tm@C84
Tm@C86
Intensity / a.u.
Mass / Charge
(d)
Crude extract
Filtrated solution
Precipitates on the filter
Lu@C72
Lu@C76
Lu@C82
Intensity / a.u.
Mass / Charge

Mixture of C60/C70 5 h @ 600 °C @ 2500 atm ^{3}He

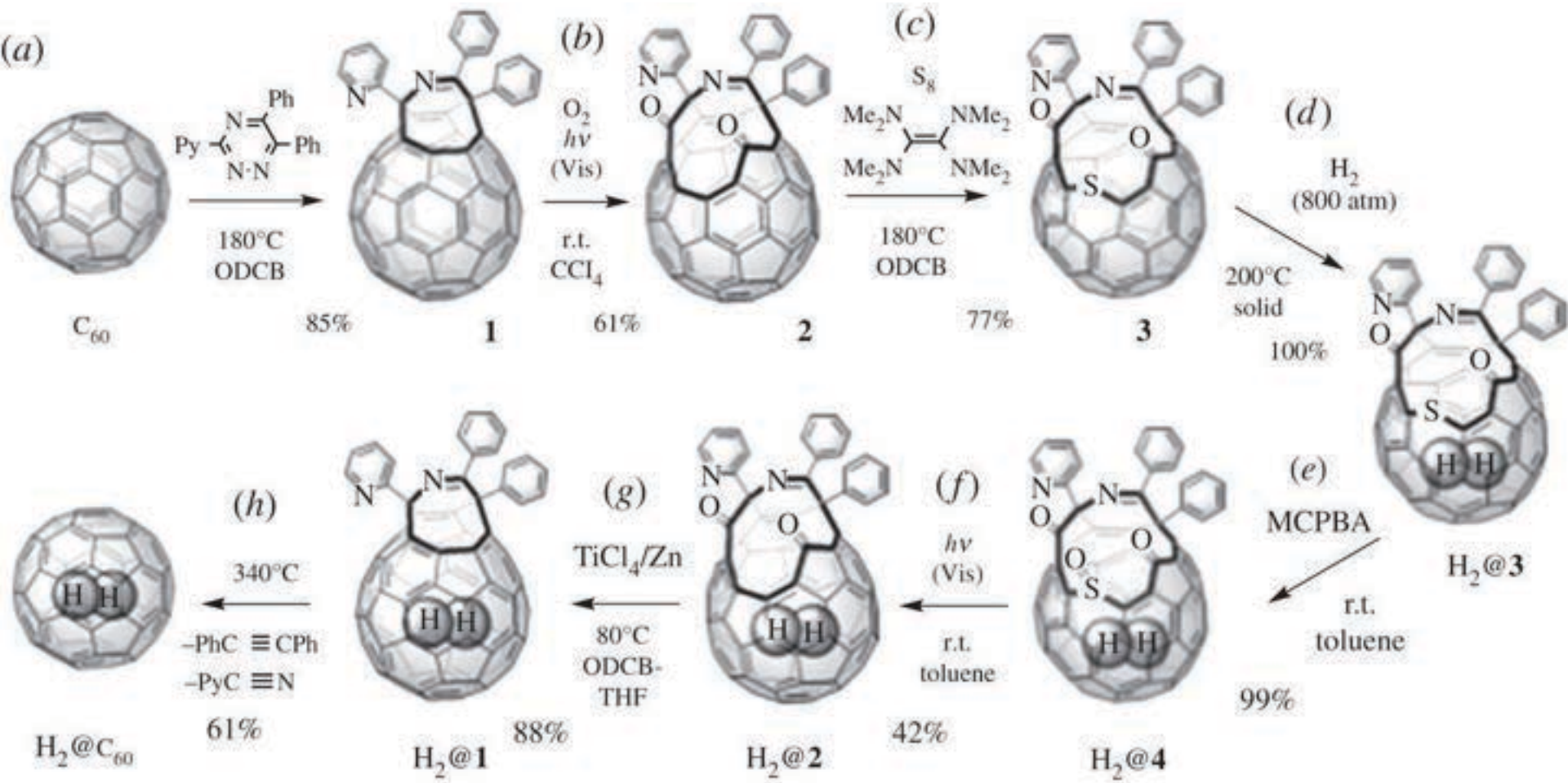


Science 1993, 259, 1428

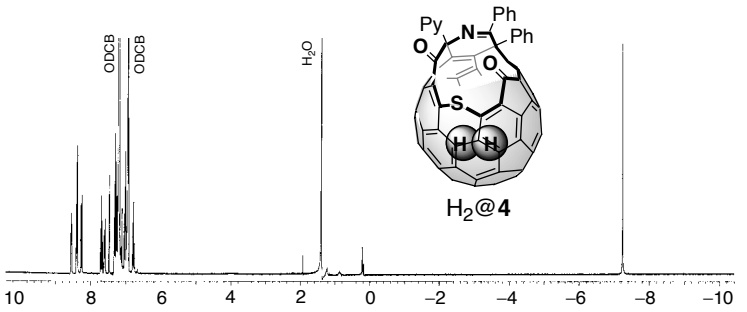


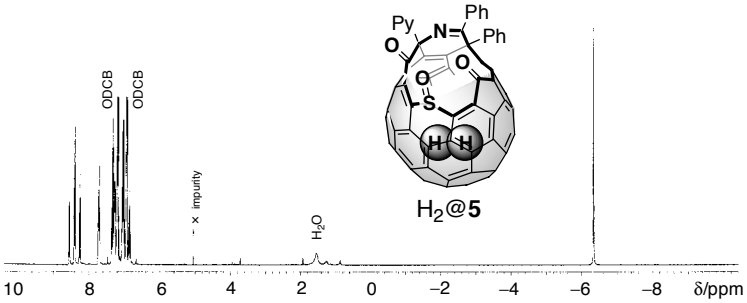
for a review, see: J. Mater. Chem., 2011, 21, 1305–1318

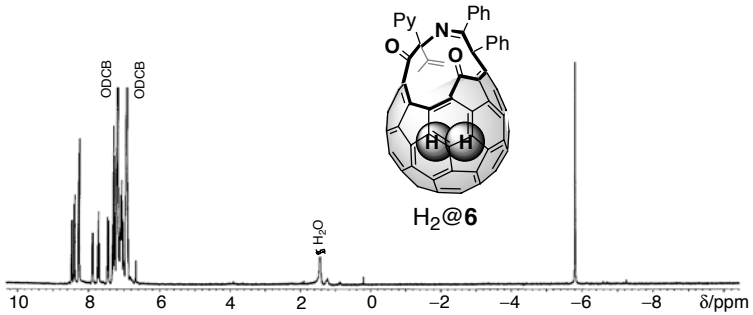
Molecular surgery of C60

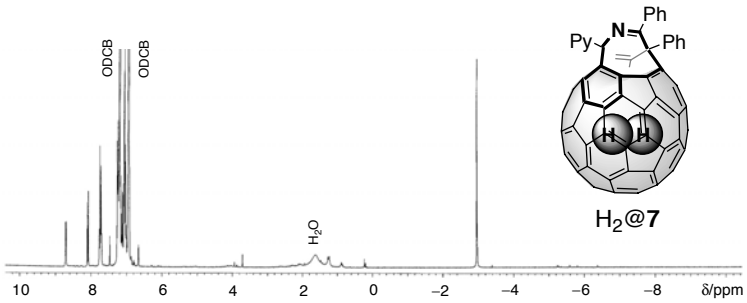


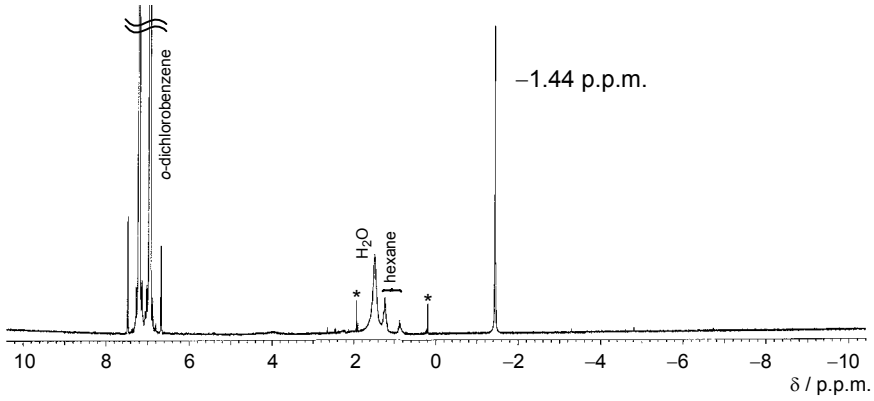
Science 2005, Vol. 307, Issue 5707, pp. 238-240





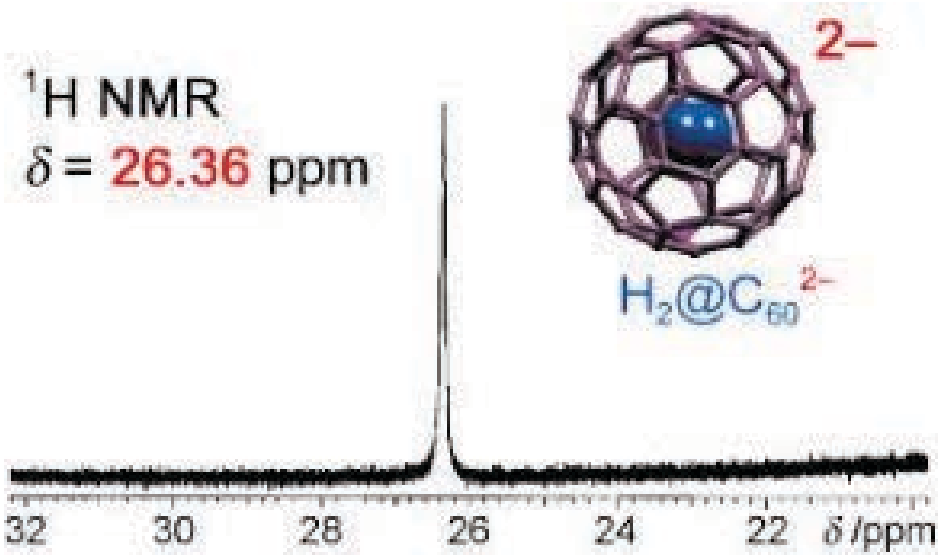






5.98 ppm upfield-shifted relative to the signal of dissolved free hydrogen

Murata & Komatzu
Science 2005, Vol. 307, Issue 5707, pp. 238-240



Angew. Chem. Int. Ed., 2008, 47, 2039-2041

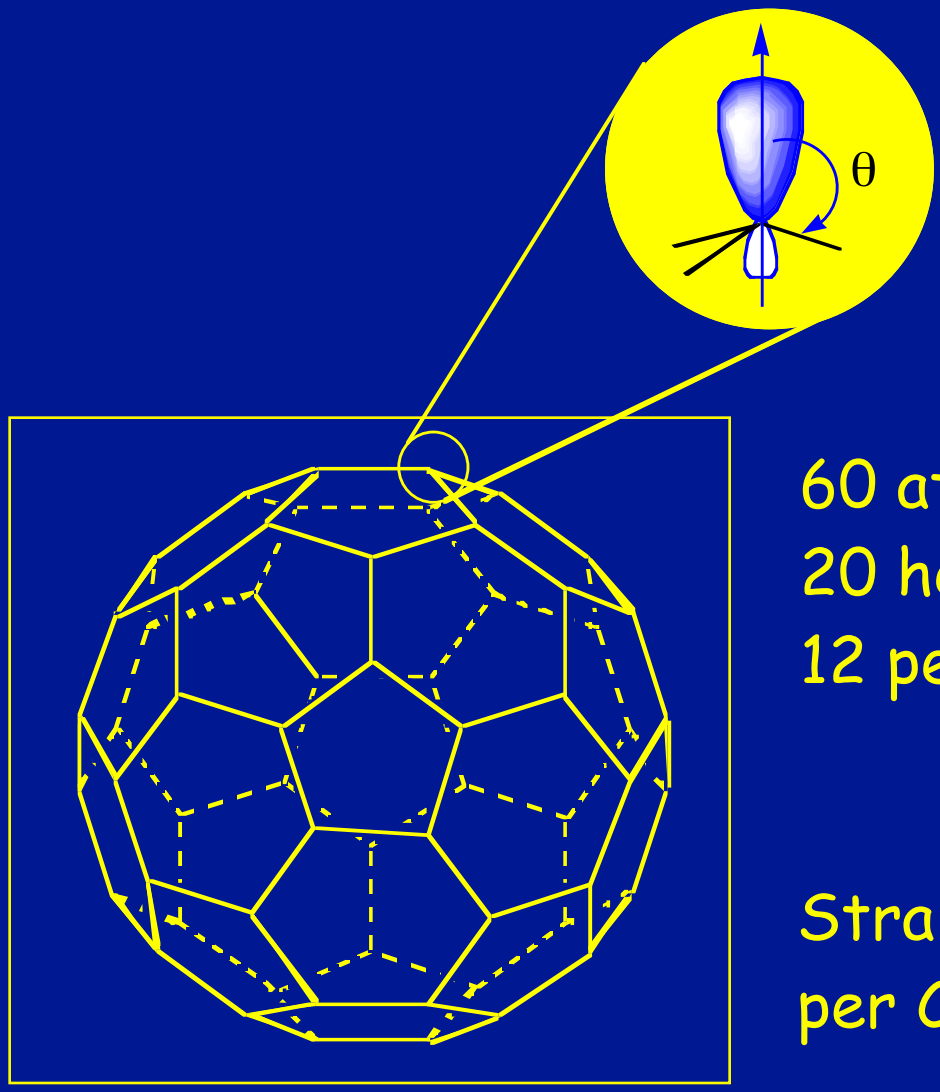
Potential Applications of Fullerenes

catalyst
lubricant
superconductor
organic magnet
production of:
- batteries
- diamond
- nanotubes
- electro- and photoluminescent materials
- electronic and optical devices
- toner for fotocopier
- photochromic glasses

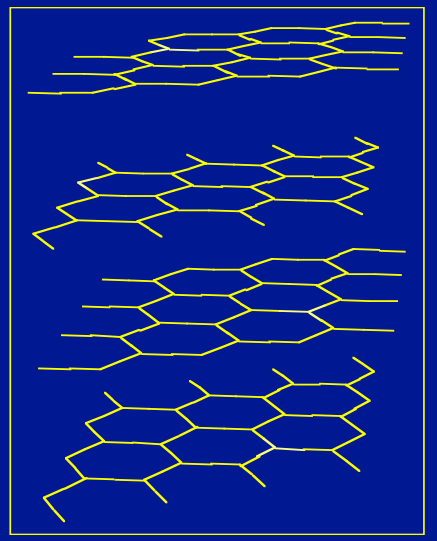
PHARMACO-BIOLOGICAL


Examples

[60]Fullerene is soluble curved graphite

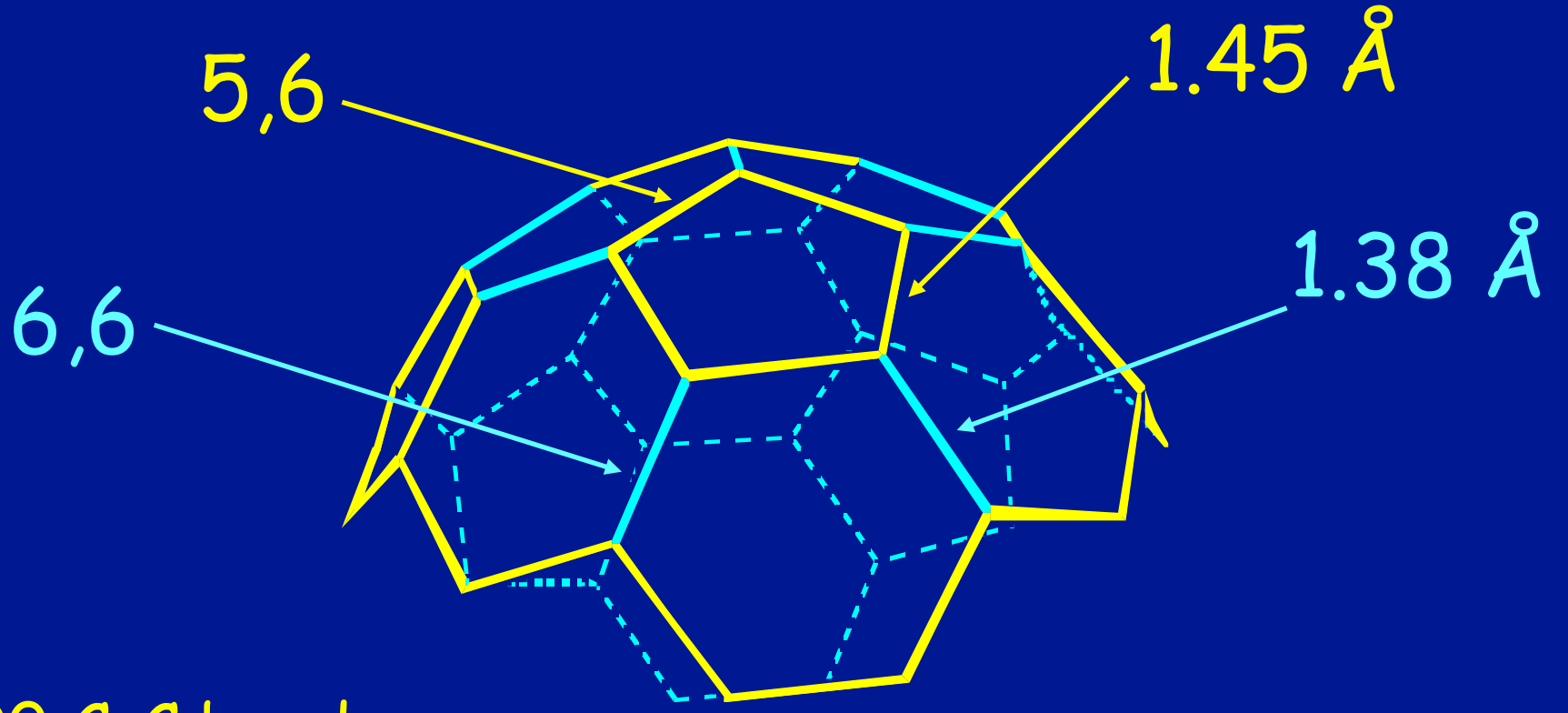


θ (101.6˚)
(R. C. Haddon)



60 atoms of C
20 hexagons
12 pentagons

Strain Energy = ca 8 Kcal/mol
per C atom (ca 80% H_f)



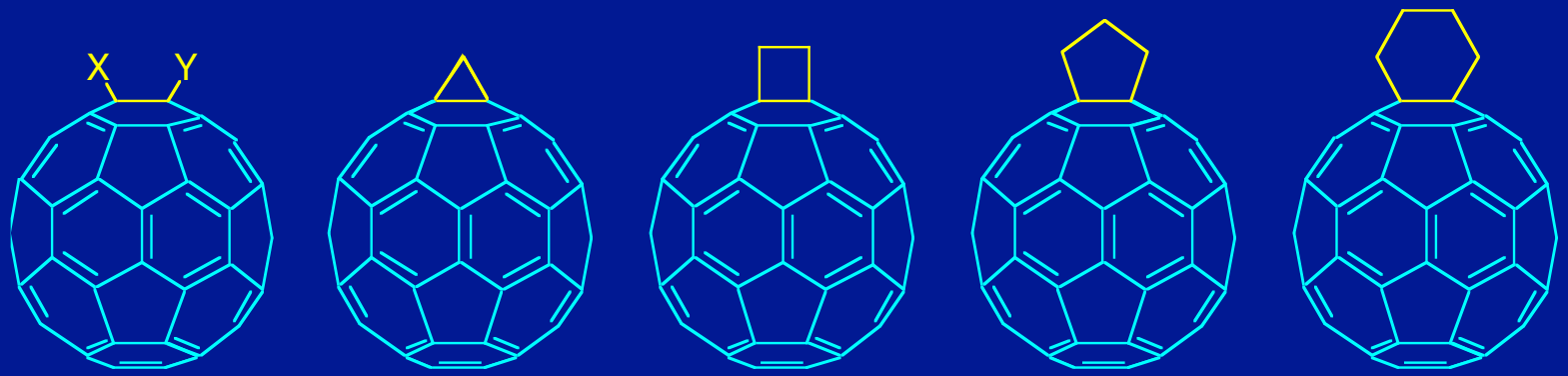
90 C-C bonds

30 "conjugated" double bonds

12,500 possible resonance structures

no delocalization → only 1 polyenic structure

different geometrical shapes can be built on the fullerene surface



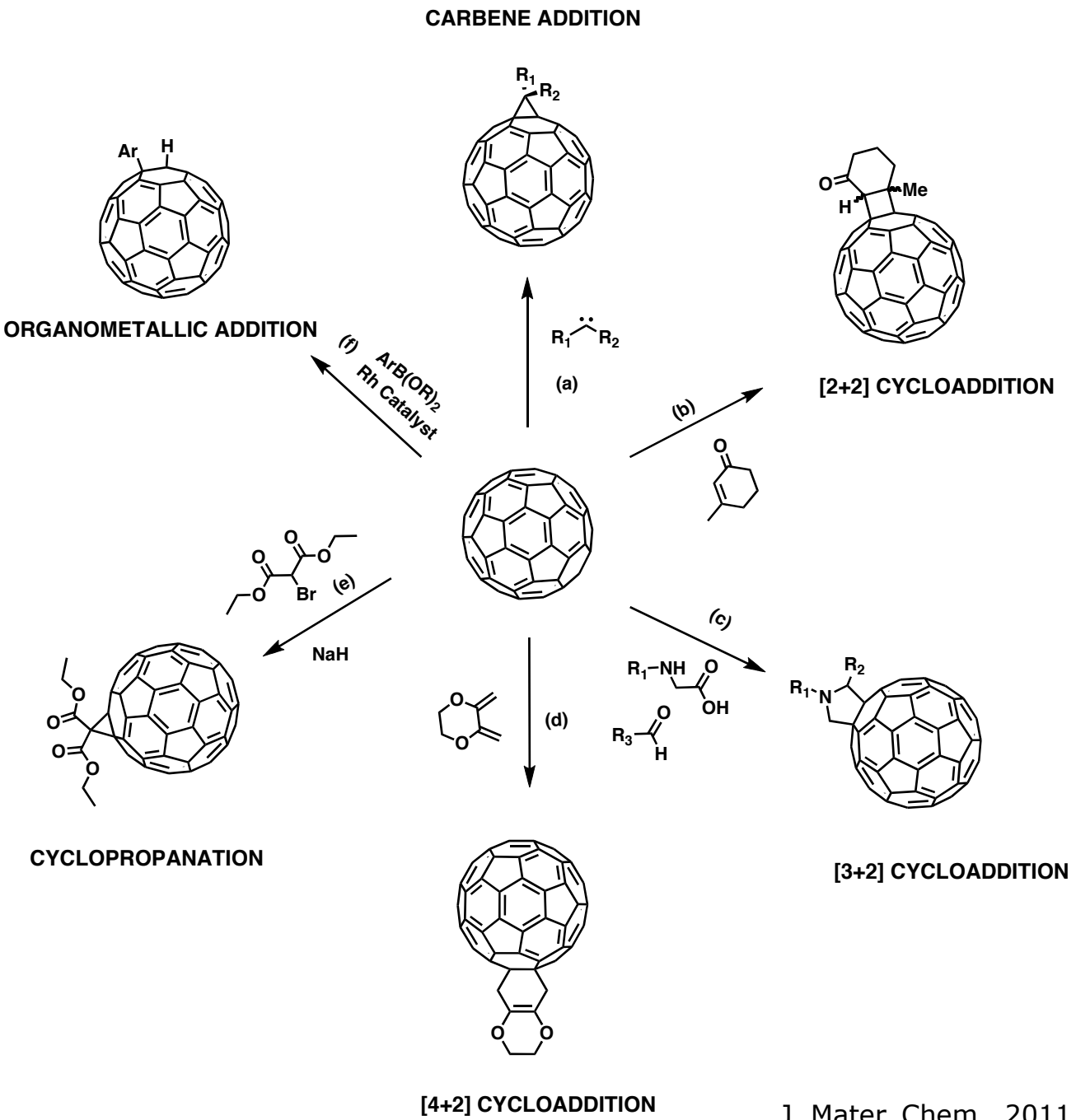
nucleophiles (Grignard, lithium)

carbenoids 1 + 2

[2 + 2]

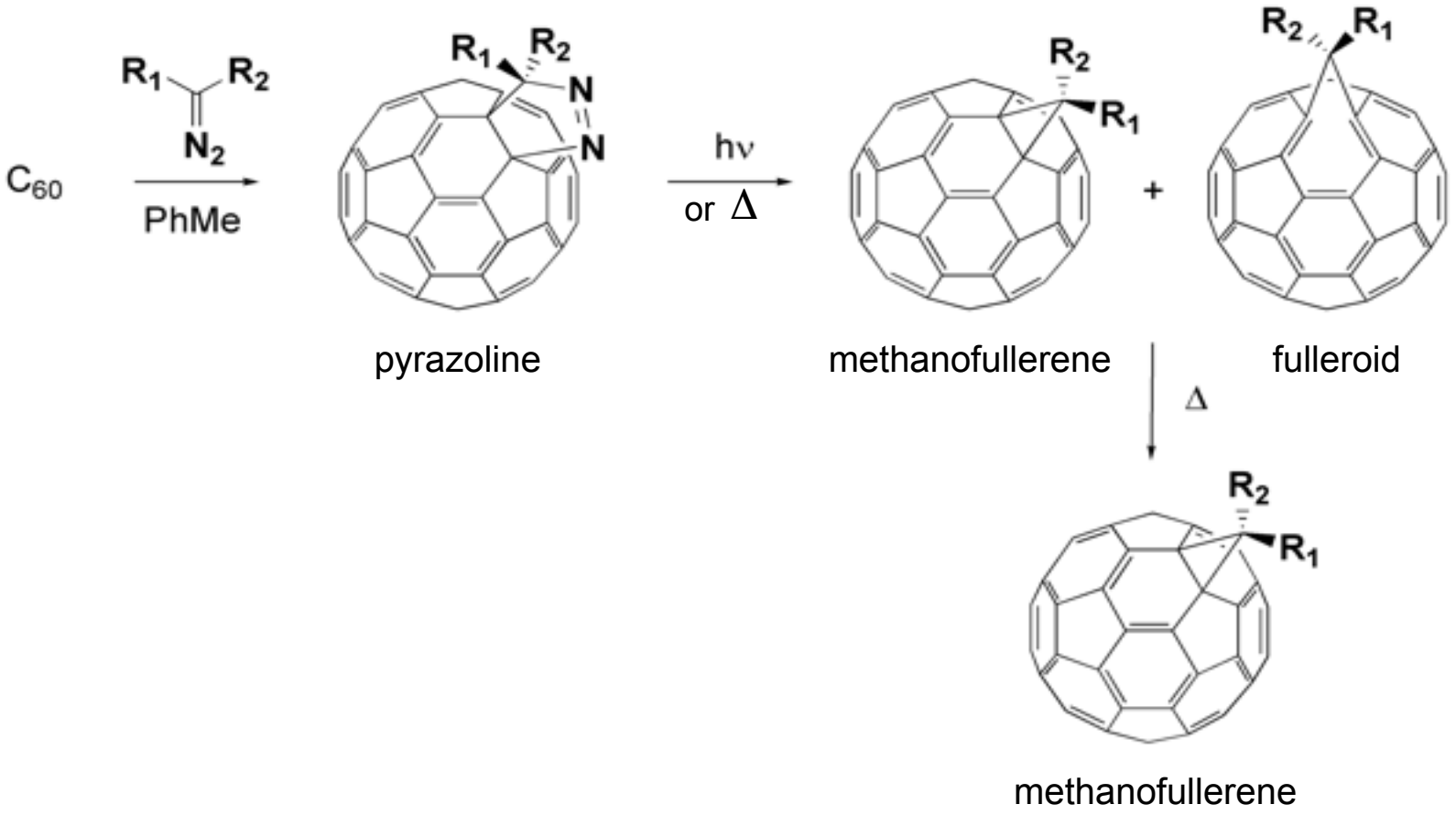
[3 + 2]

[4 + 2]



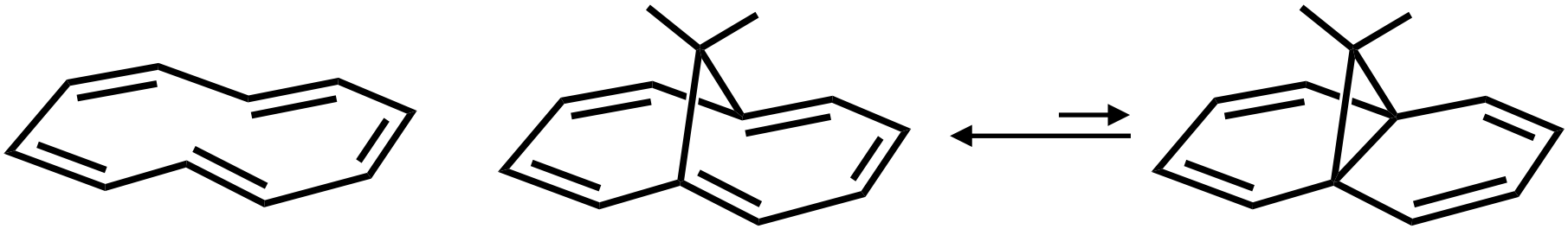
J. Mater. Chem., 2011, 21, 1305–1318

Cycloaddition reaction between diazo compounds and C_{60}



Wudl, F., et al, Science, 1991

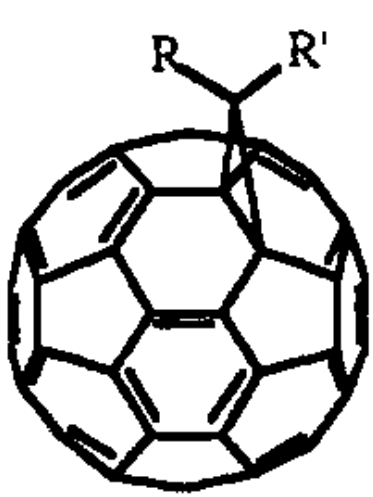
Chemistry of Annulenes



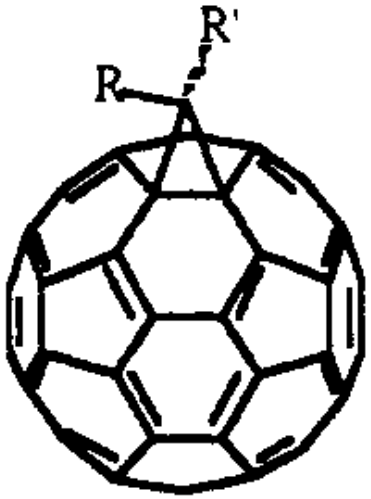
1

Theoretical calculations estimate the resonance energy of **1** as 50-90% that of benzene, 17.2 kcal/mol has been calculated on the basis of heats of hydrogenation.

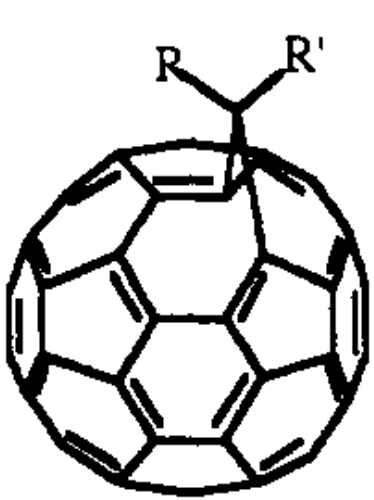
Vogel, Emanuel; Klug, W.; Breuer, A. "1,6-Methano[10]annulene". Organic Syntheses. 54, 11



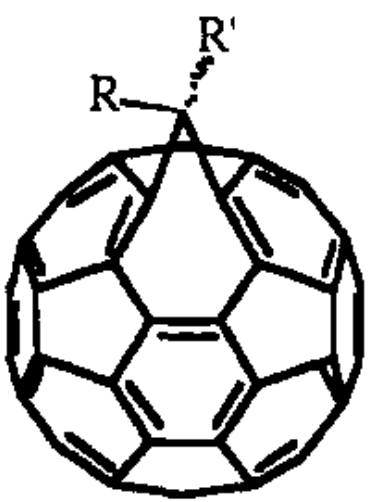
1



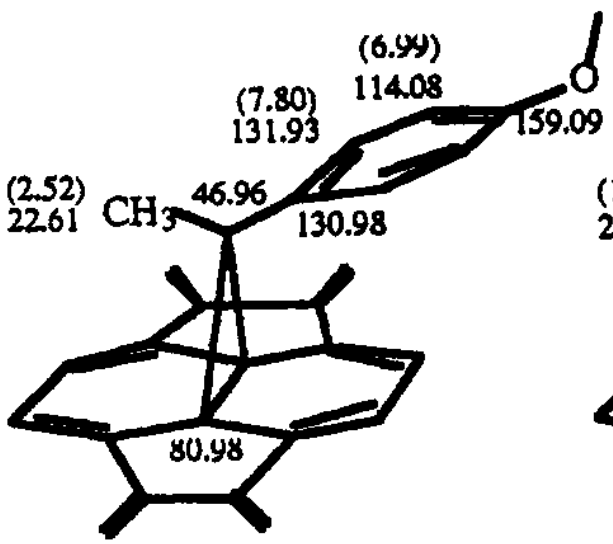
2



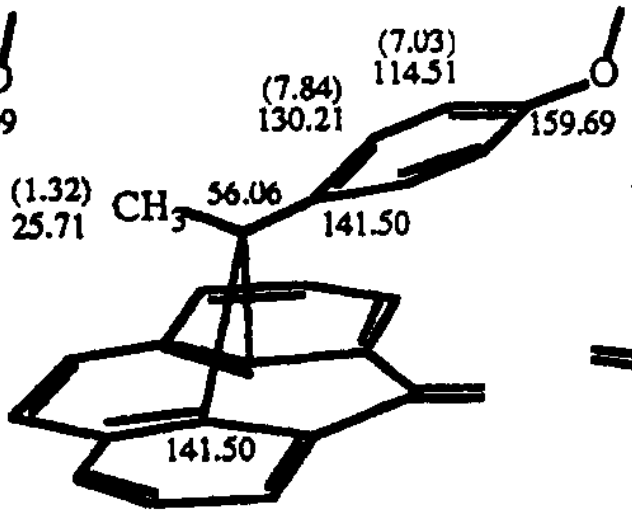
3



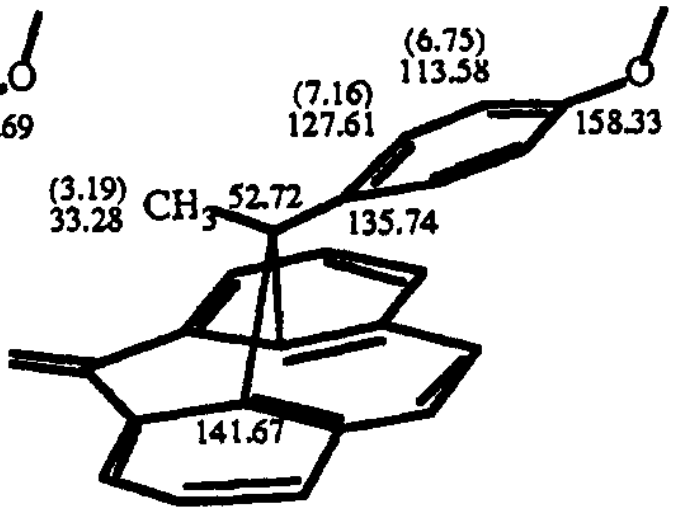
4



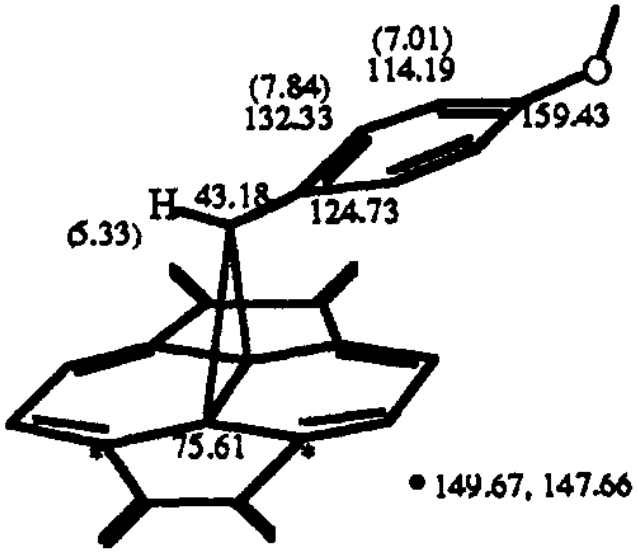
1a



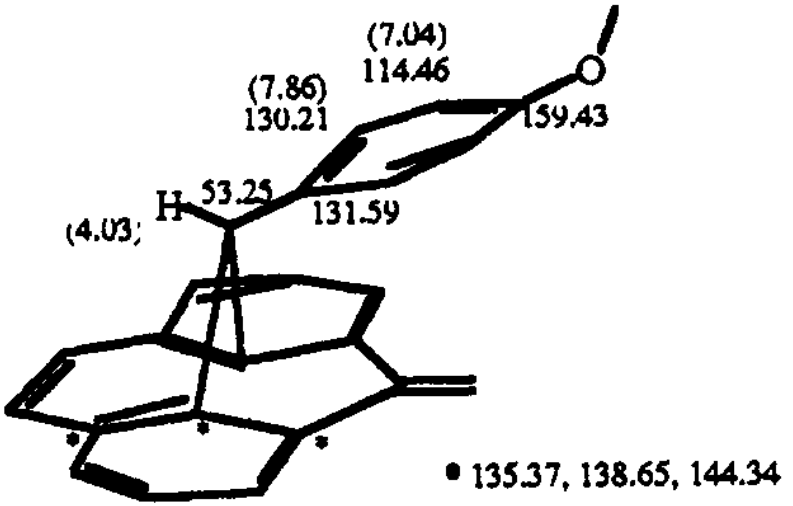
4a



4a'

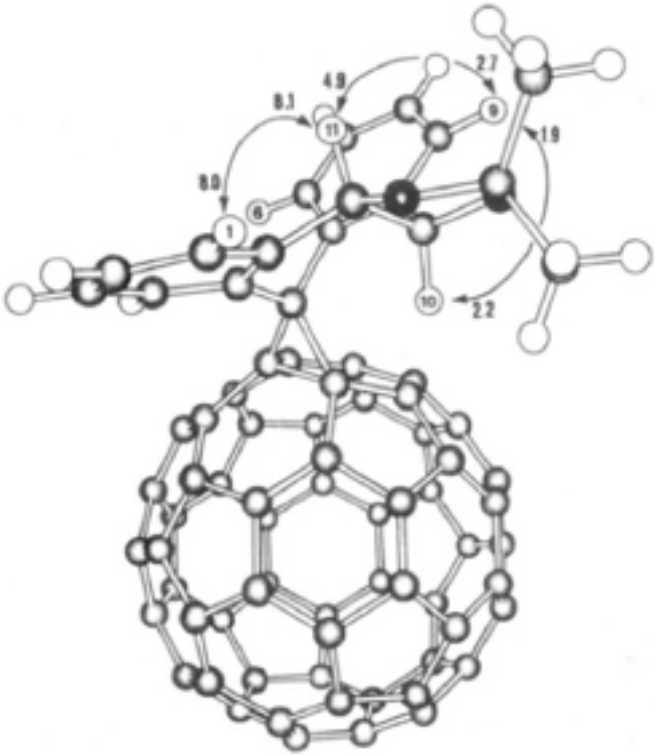


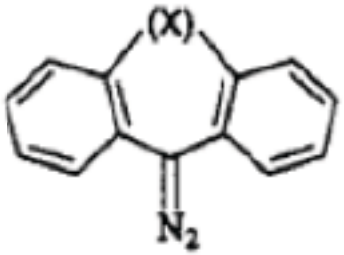
1b



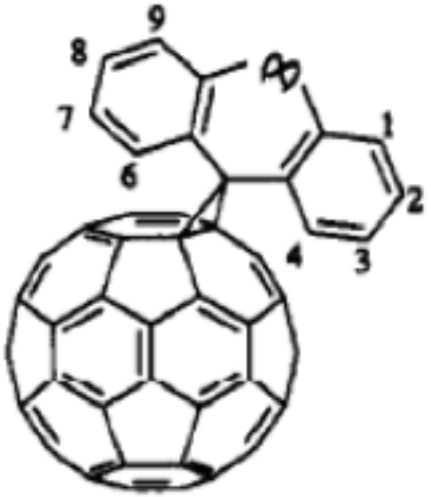
4b

J. Am. Chem. Soc. 1993, 115, 8479-8480



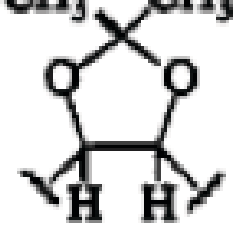


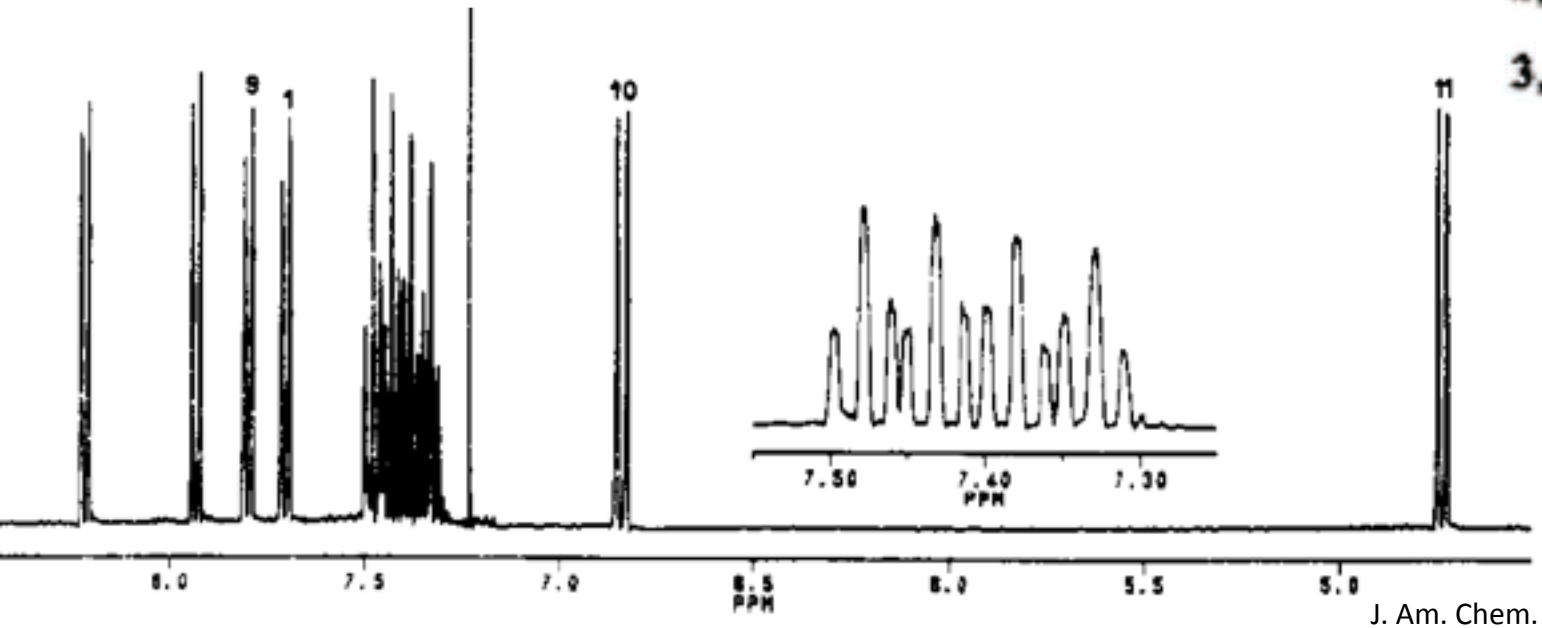
+ C_{60} ——



1, X = CH=CH

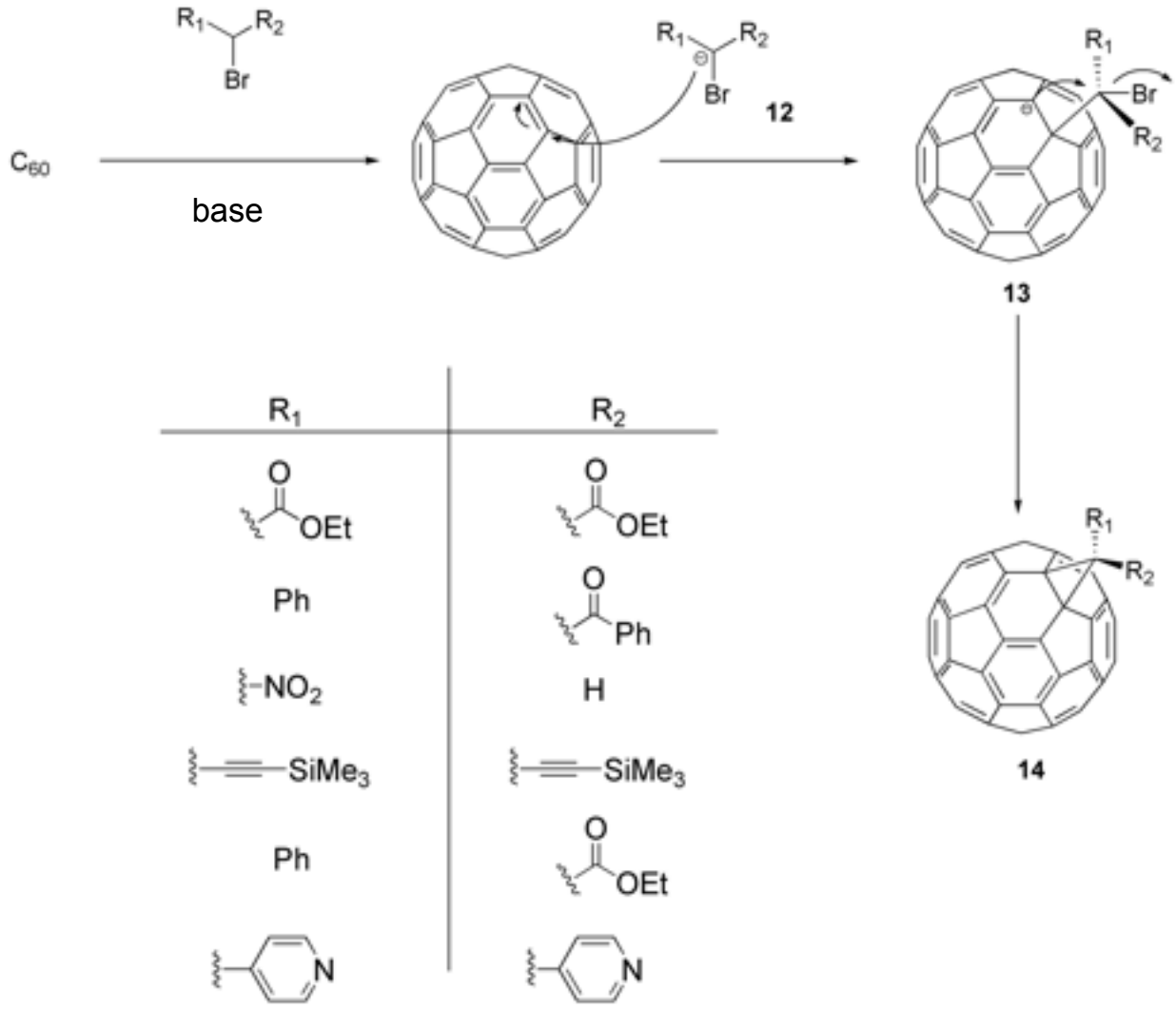
2, X = CH_2CH_2

3, X = 

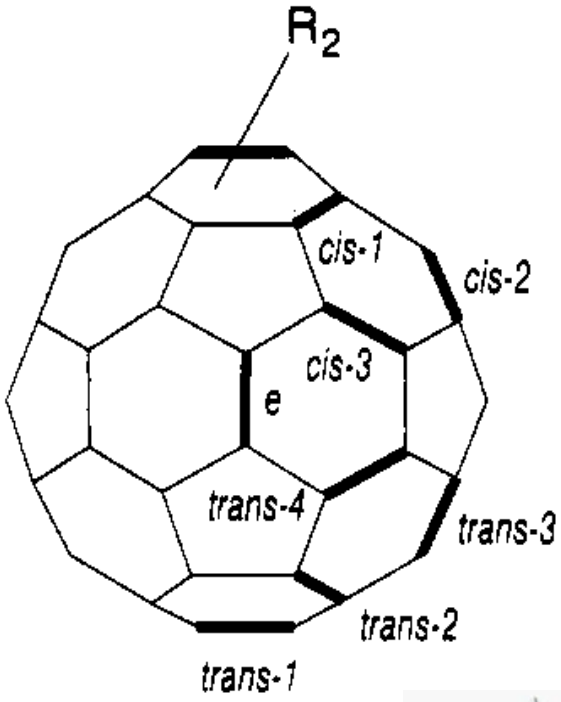


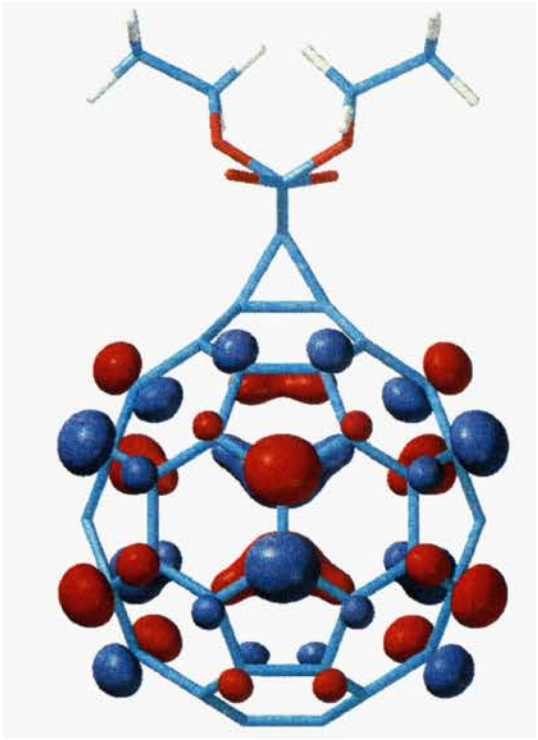
J. Am. Chem. Soc. 1993, 115, 7876-7877

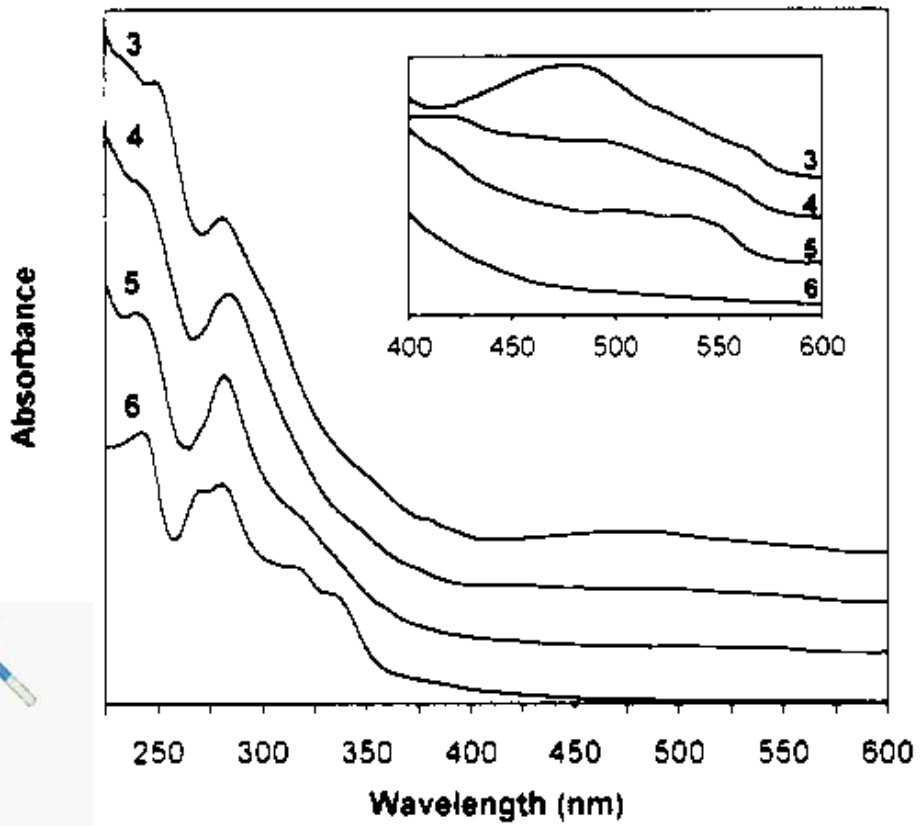
Cyclopropanation of C_{60} by nucleophilic addition of α-bromomalonate carbanions (*Bingel* reaction)



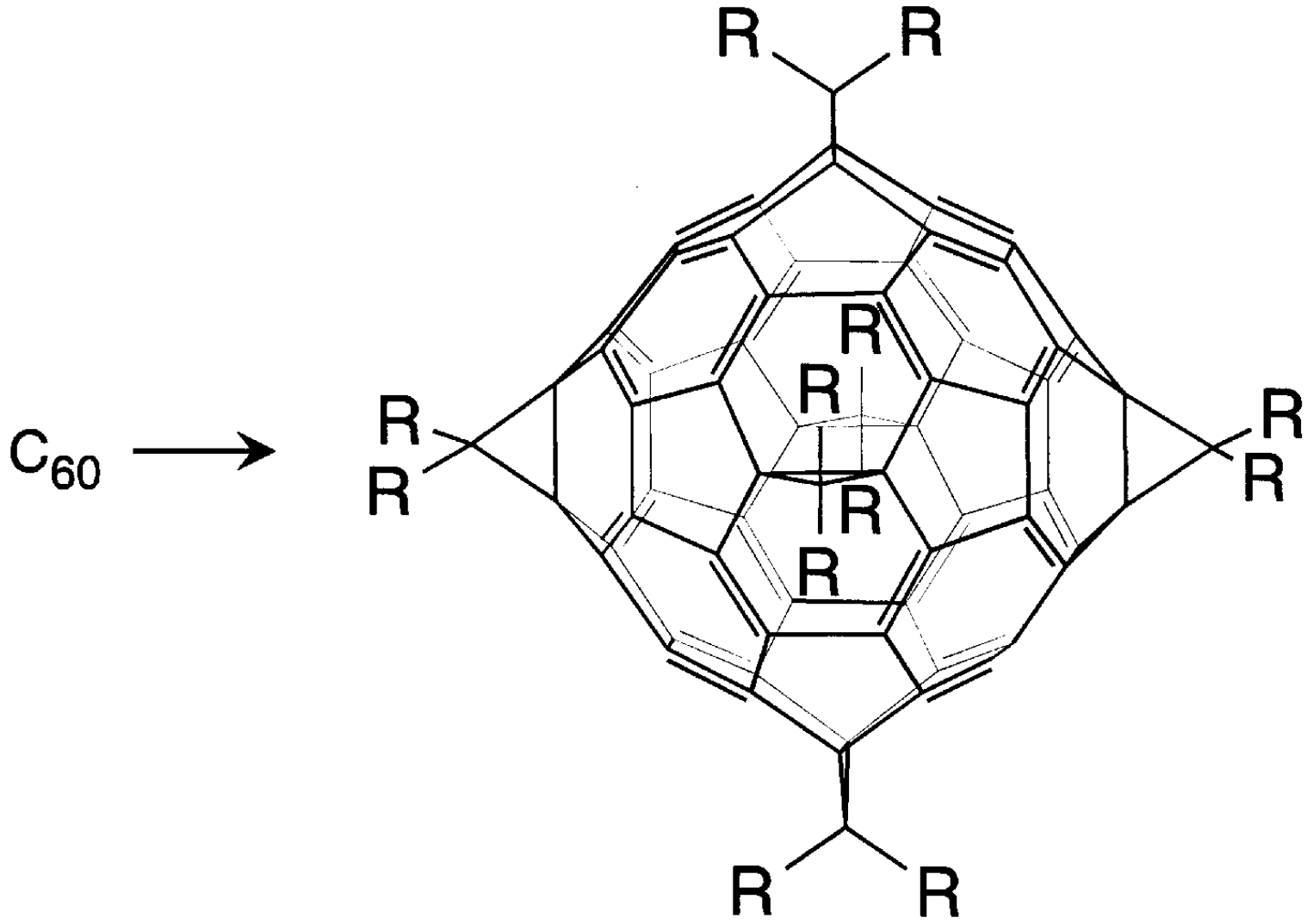
R_1	R_2
Ph	
	H
Ph	



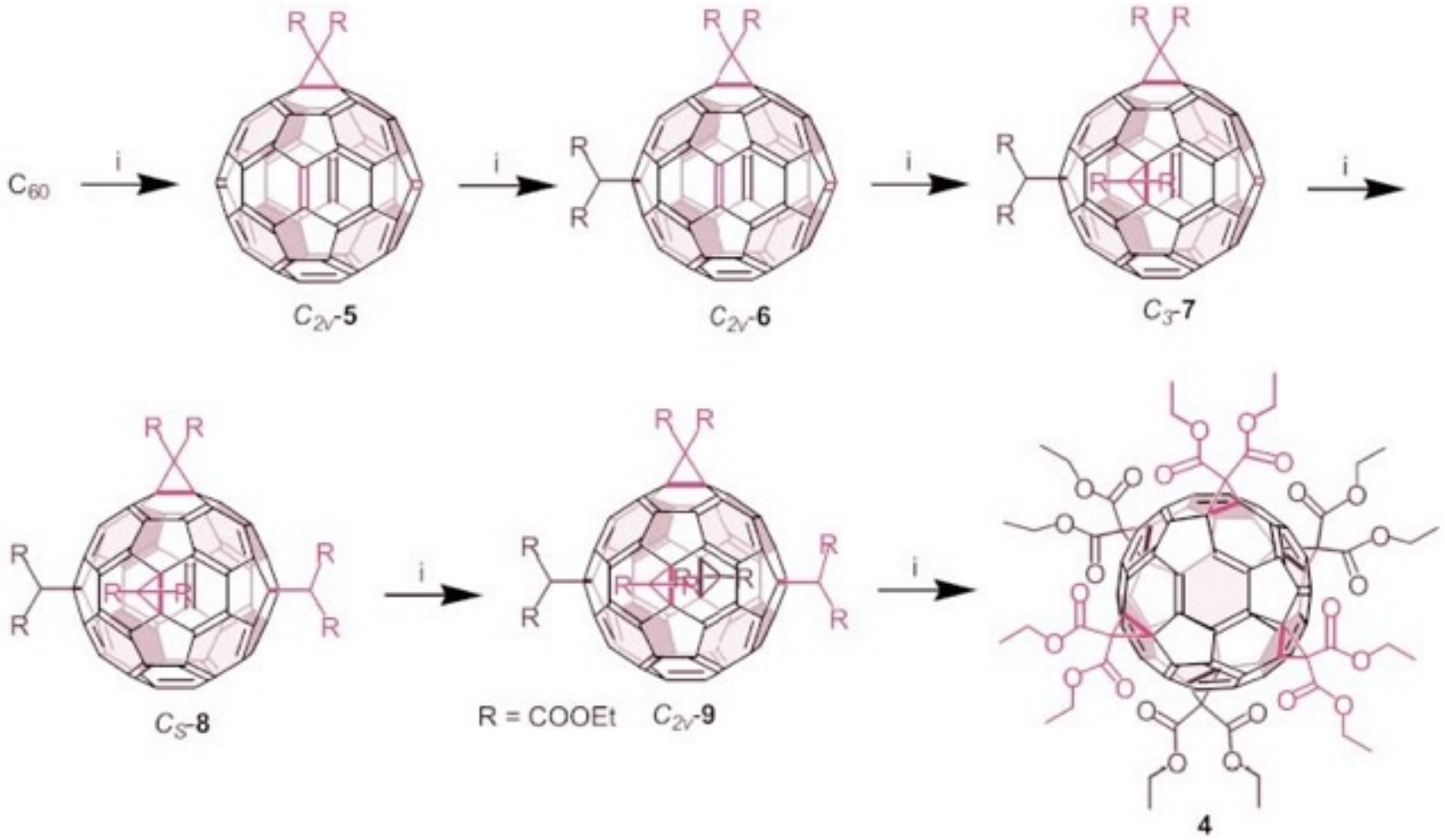




/. Am. Chem. Soc. 1994, 116, 9385-9386

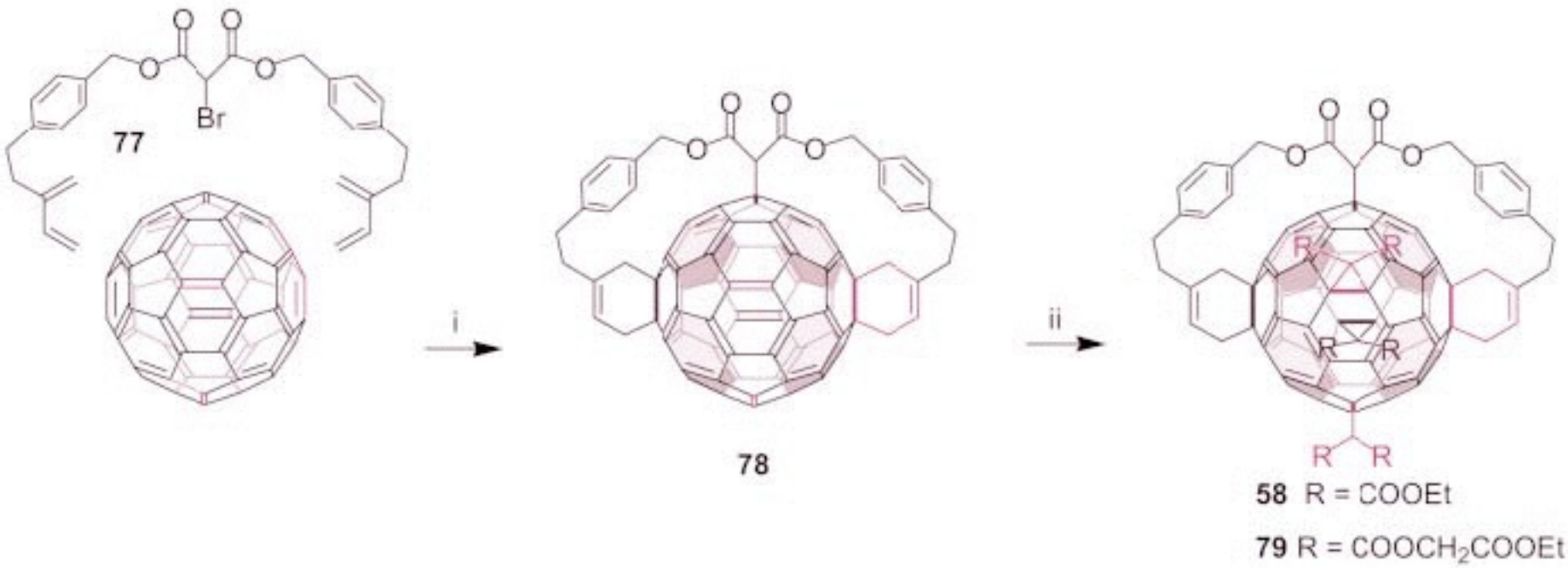

C60
R
R
R
R
R
R
R
R
R
R
R
R
R
R

Multiple cyclopropanation reactions



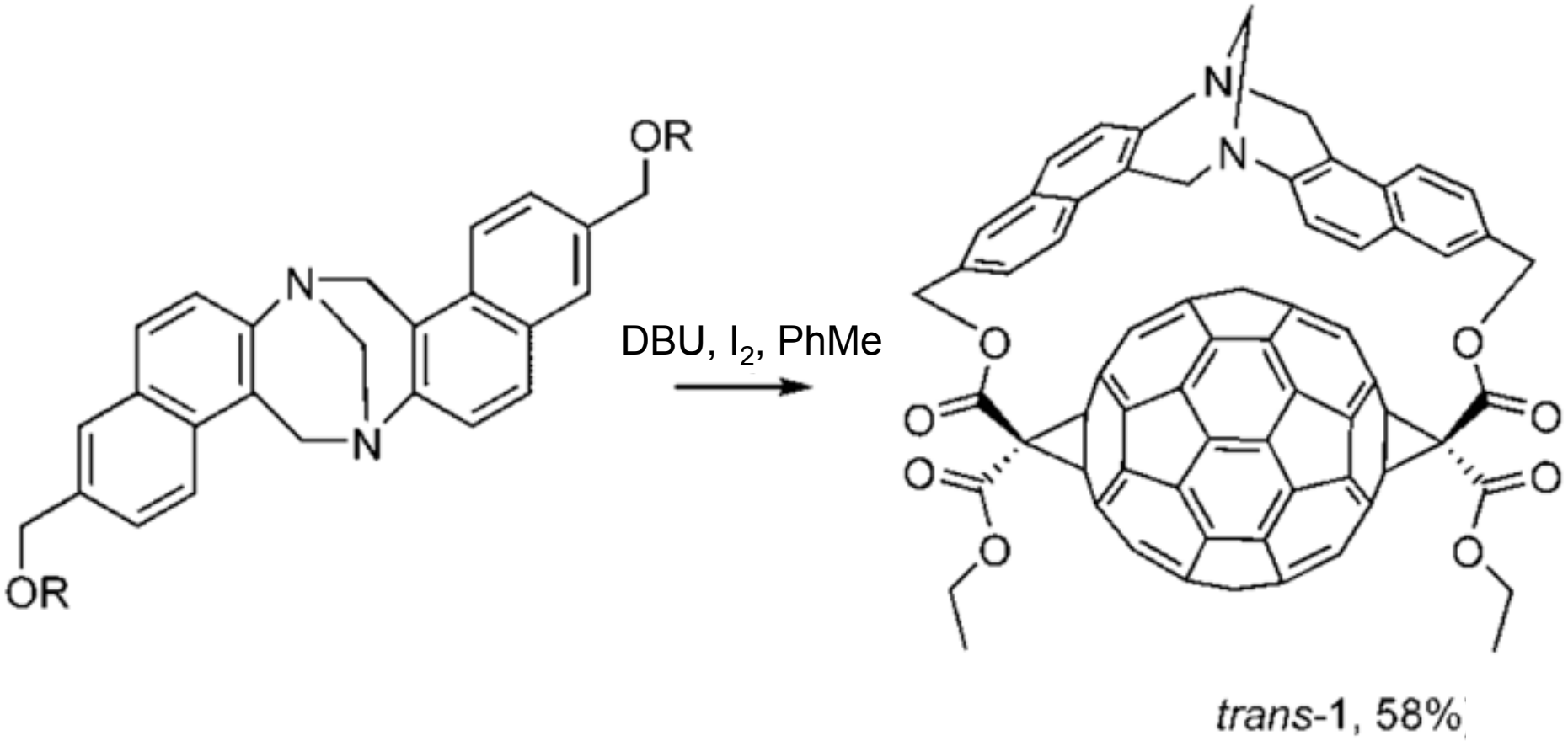
Hirsch, A. et al

Tether-directed selective functionalization



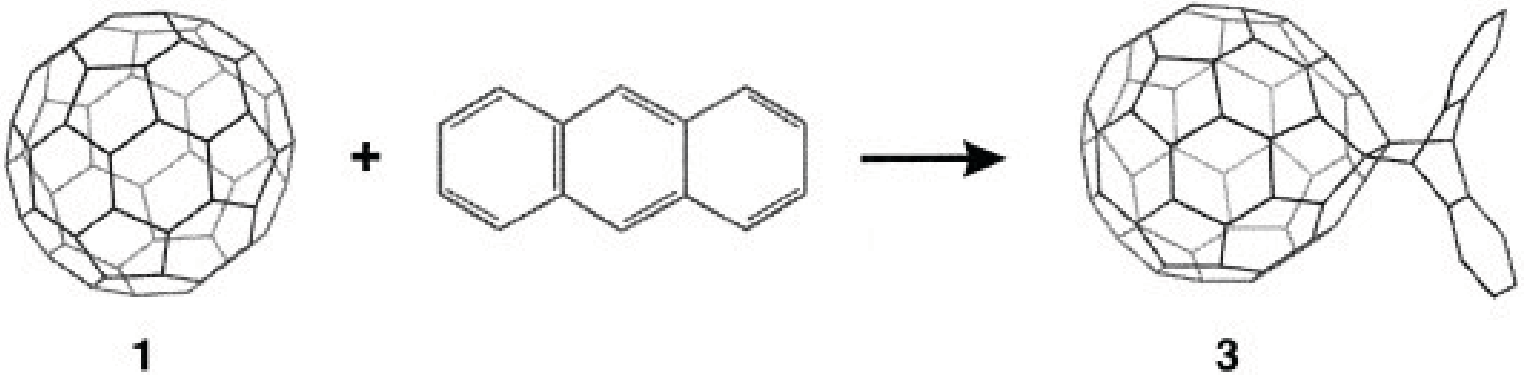
Diederich, F., et al.

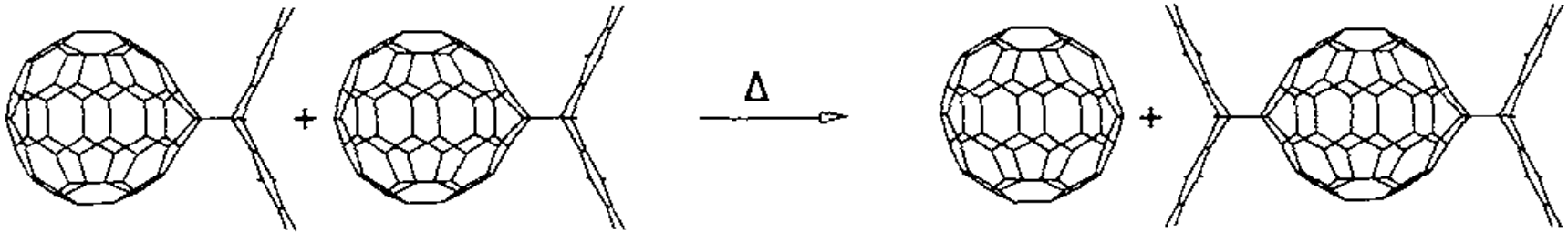
Regio and stereoselective tether-directed remote functionalization of C_{60} by Tröger spacers (trans-1)



trans-**1**, 58%

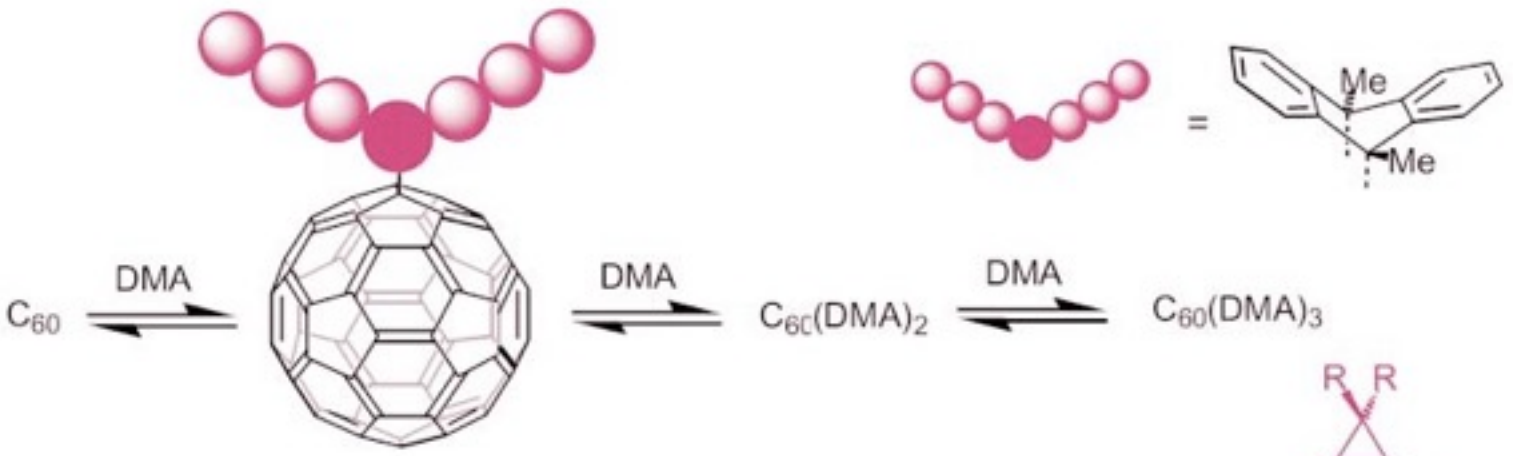
Diederich, F., et al.





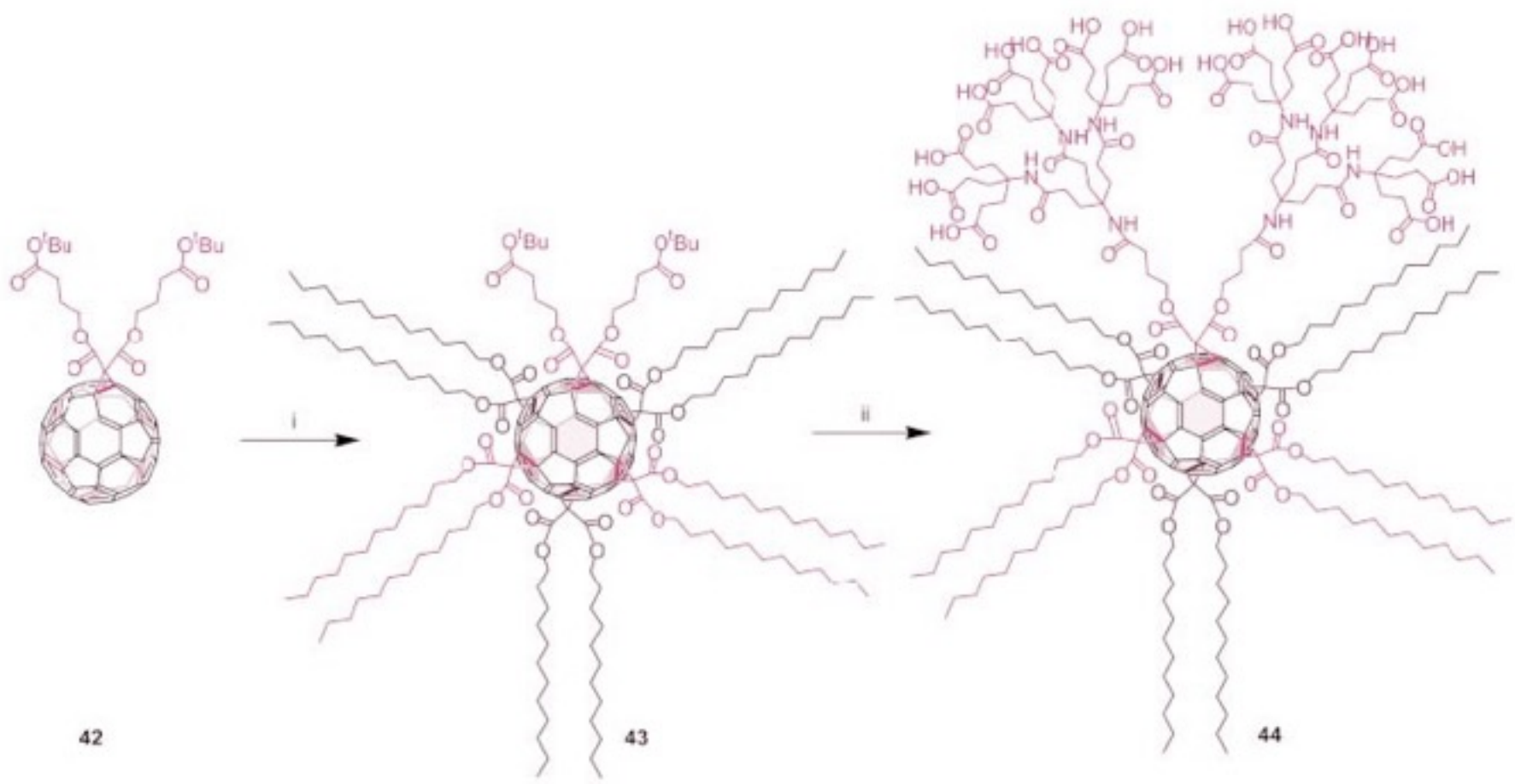
Angex.. Chem. In!. Ed. Engl. 1996, 35, No. 11, 1204

Selected synthesis of hexakis-adducts assisted by the presence of dimethylanthracene (DMA)

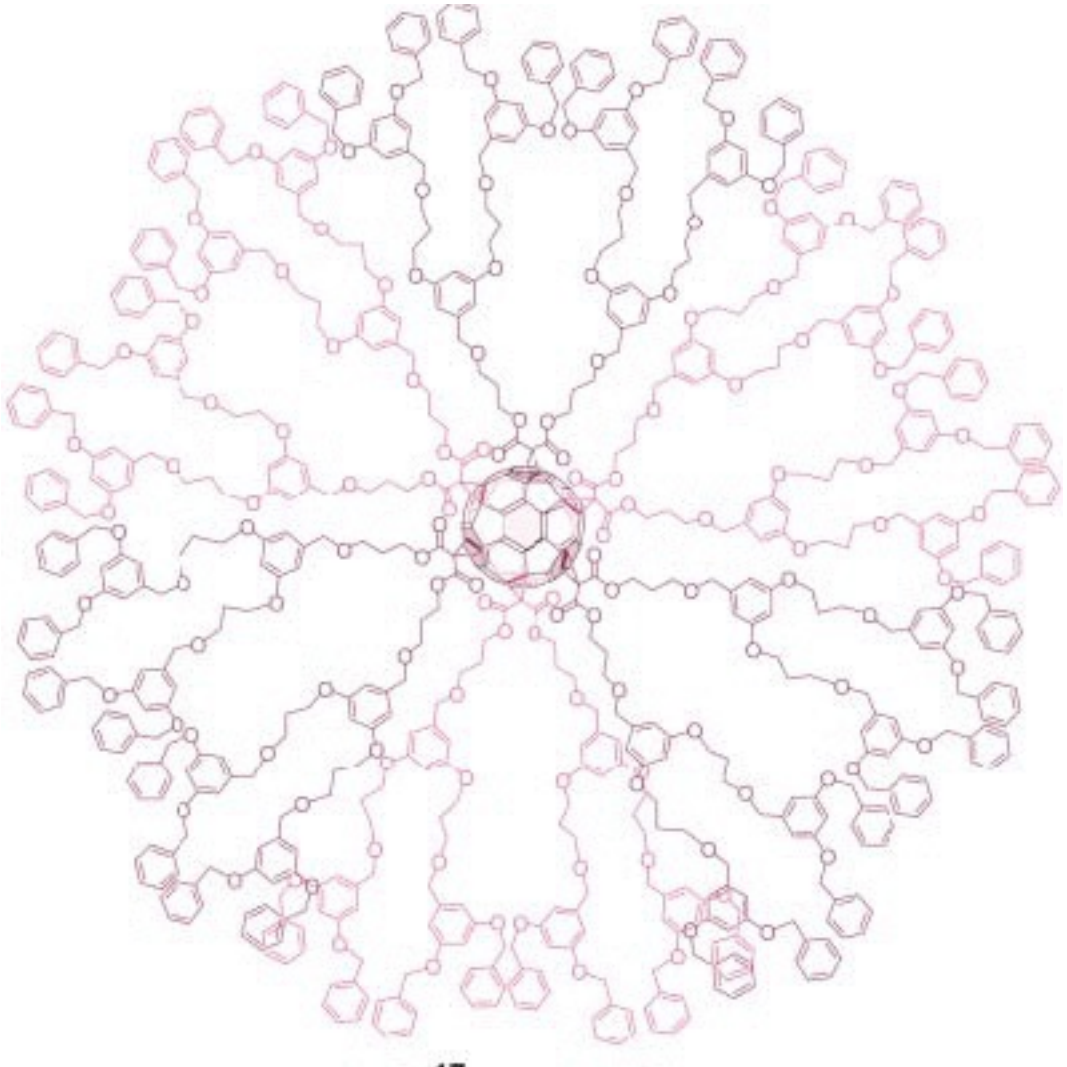


4 R = COOEt

Hirsch, A. et al

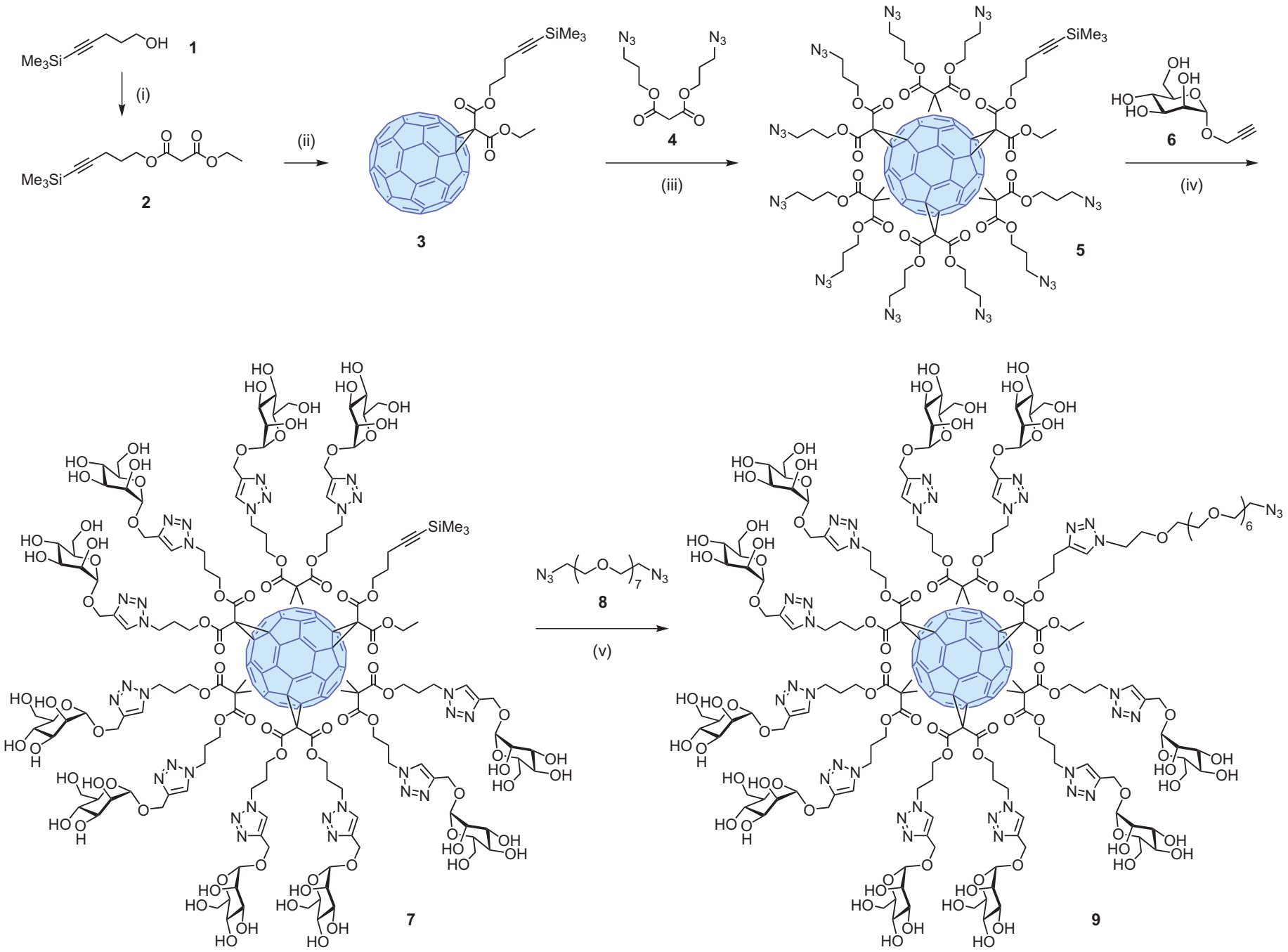


A. Hirsch, O. Vostrowsky. Eur. J. Org. Chem. **2001**, 829



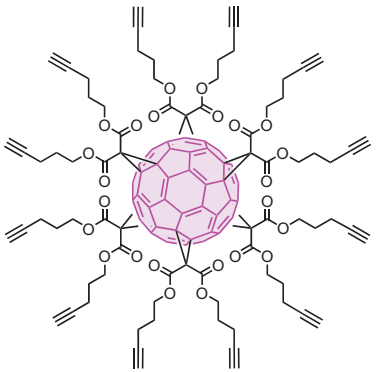
17

Hirsch, A. et al


1
(i)
2
(ii)
3
4
(iii)
5
6
(iv)
7
8
(v)
9

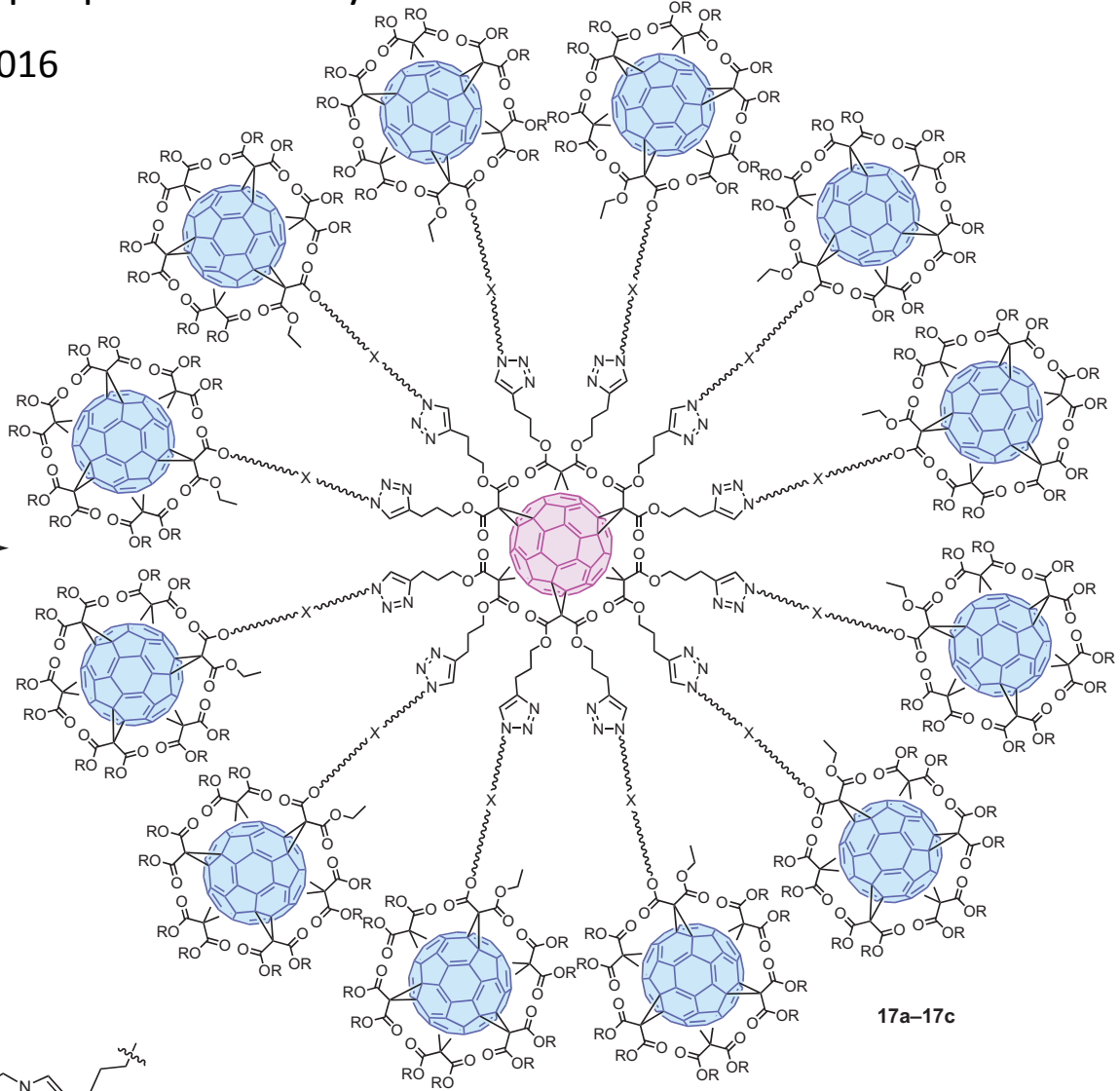
Tridecafullerenes decorated with 120 peripheral carbohydrate subunits

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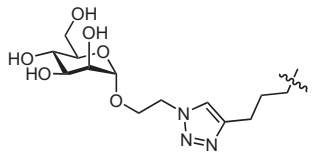
16

(i)

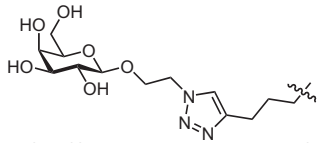


17a–17c

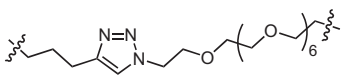
17a X = —$(CH_2)_6$— R =



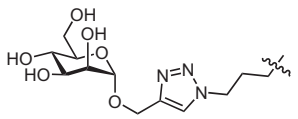
17b X = —$(CH_2)_6$— R =



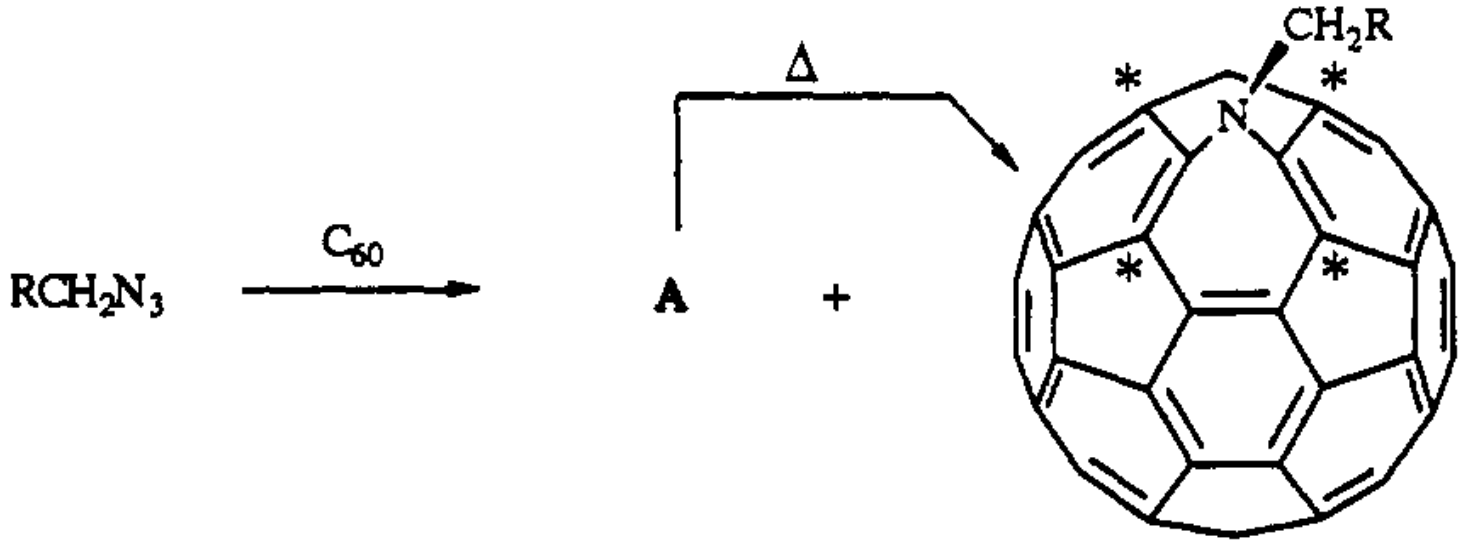
17c X =



R =



Infection assays show that these superballs are potent inhibitors of cell infection by an artificial Ebola virus with half-maximum inhibitory concentrations in the subnanomolar range



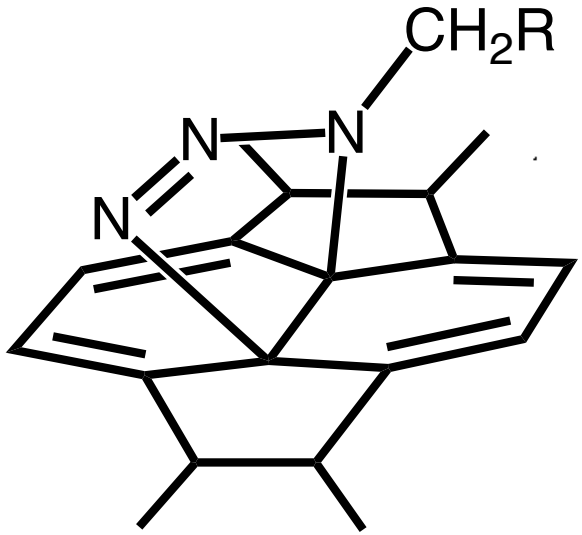
1

a, R = $OCH_2CH_2SiMe_3$

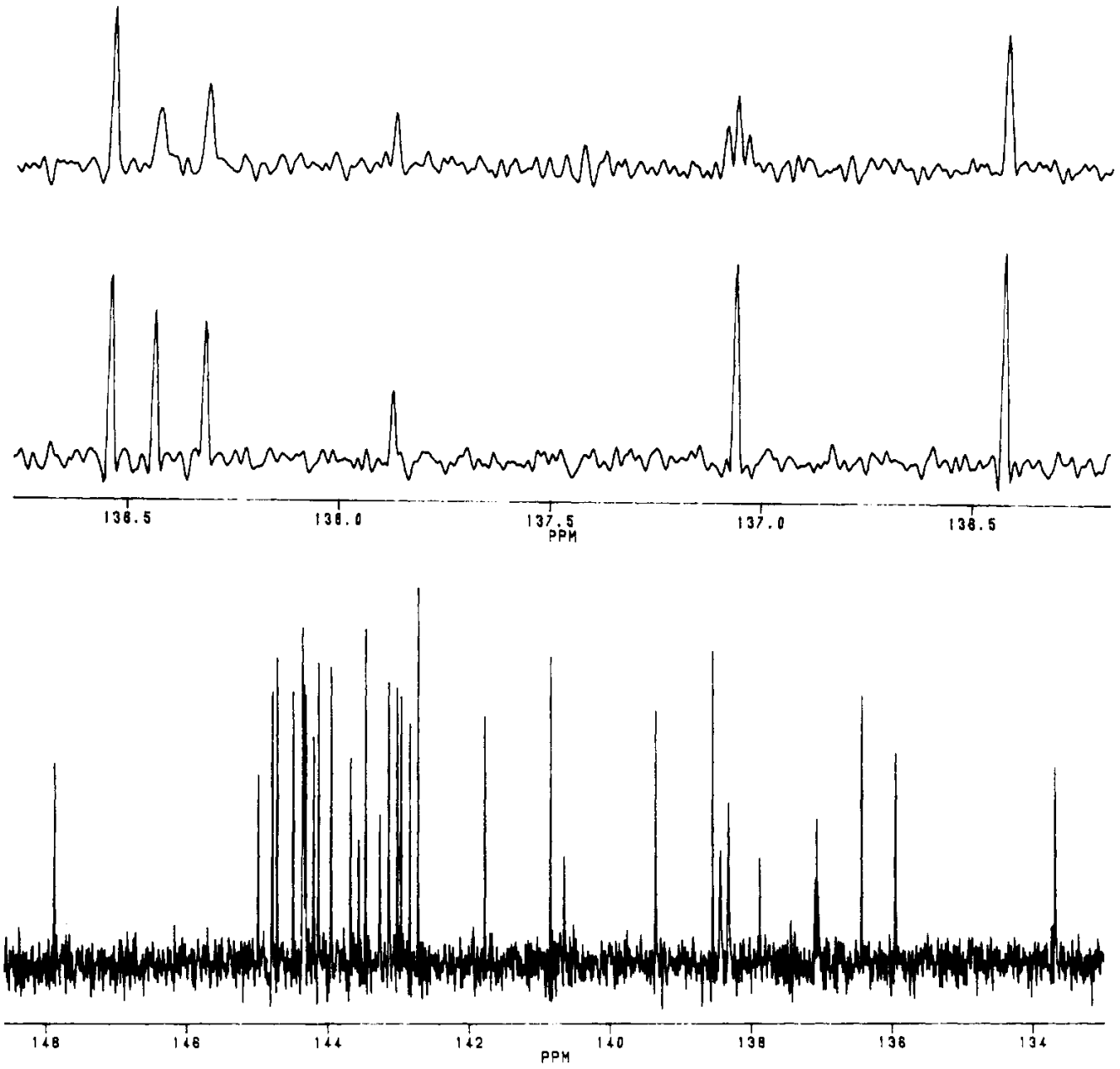
b, R = C_6H_5

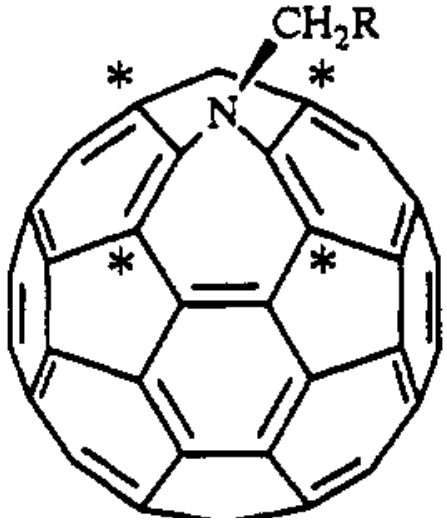
c, R = 4-C_6H_4-OMe

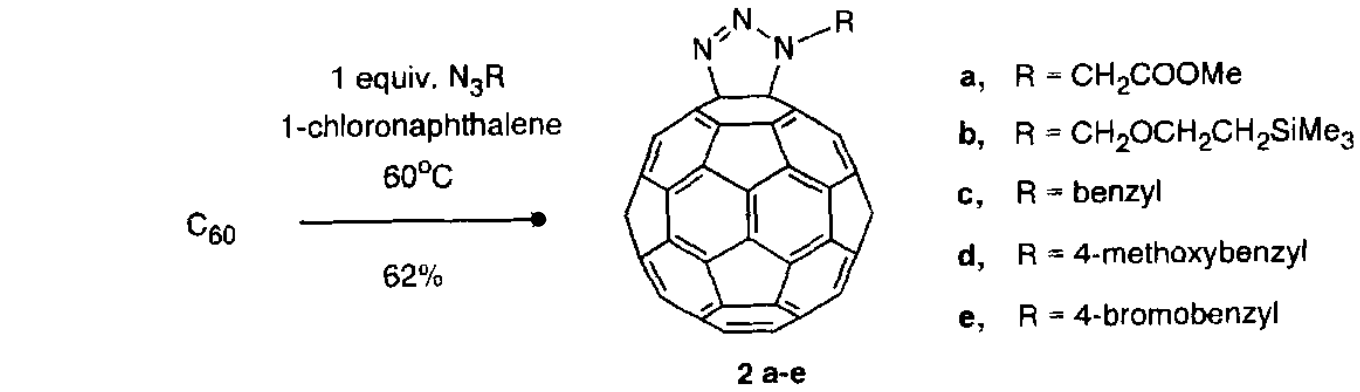
d, R = 4-C_6H_4-Br



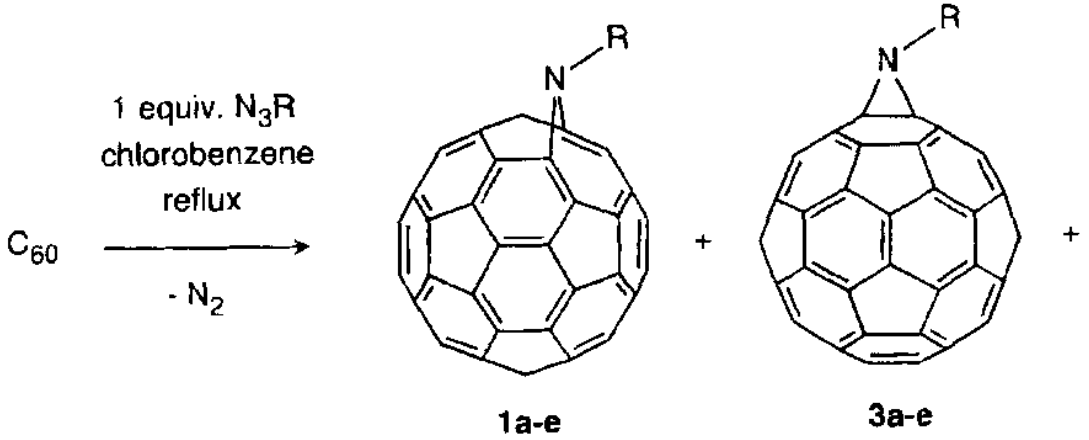
total of 32 signals, of which 28 have a relative intensity of 2 and 4 of 1



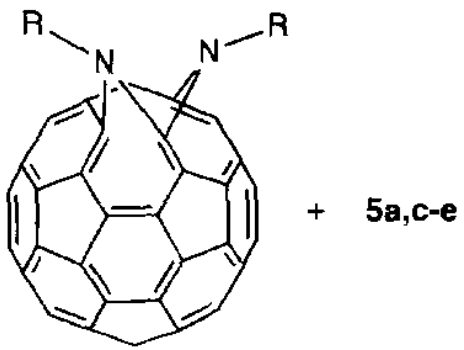




2 a-e



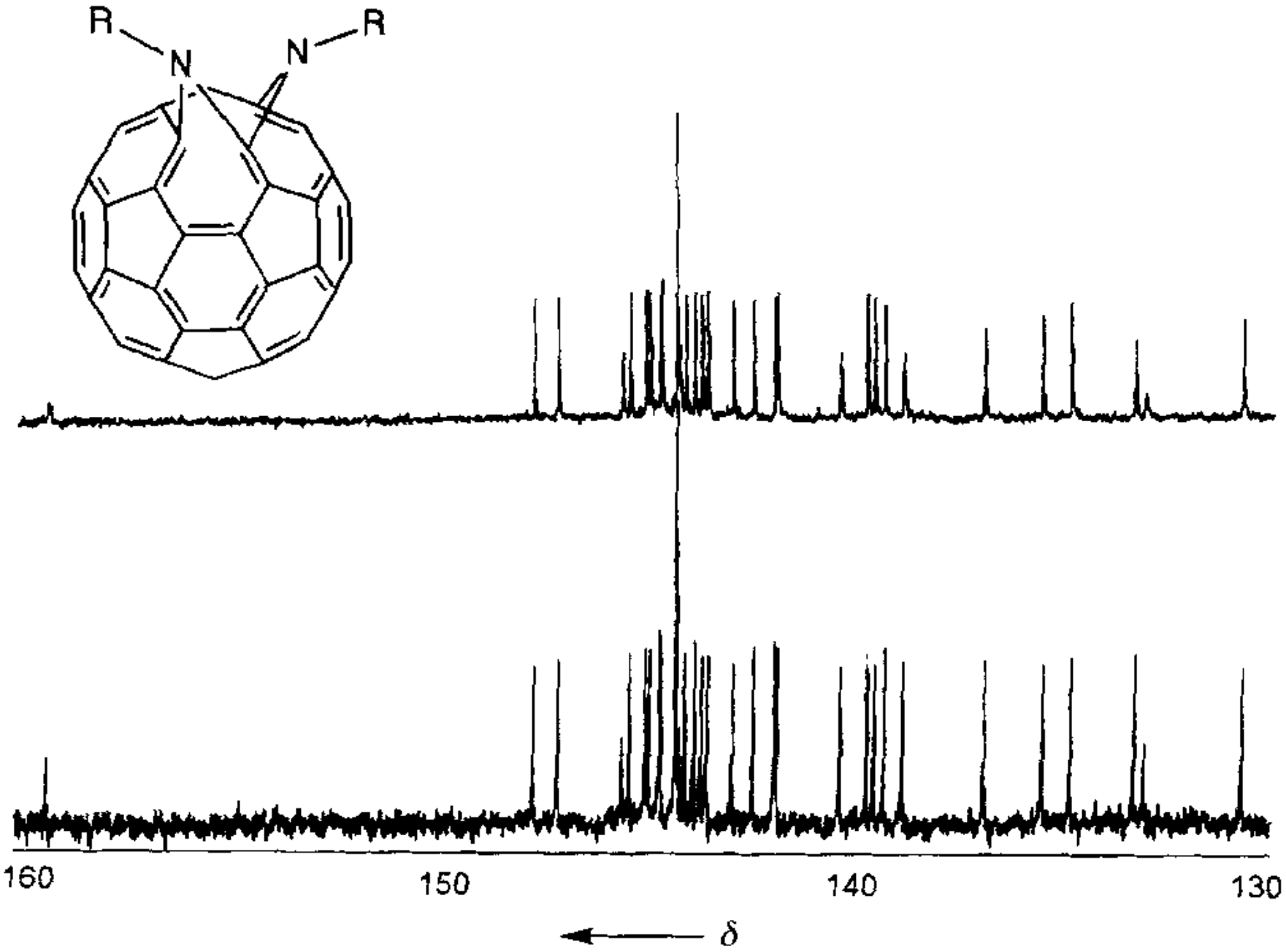
1a-e + **3a-e** +

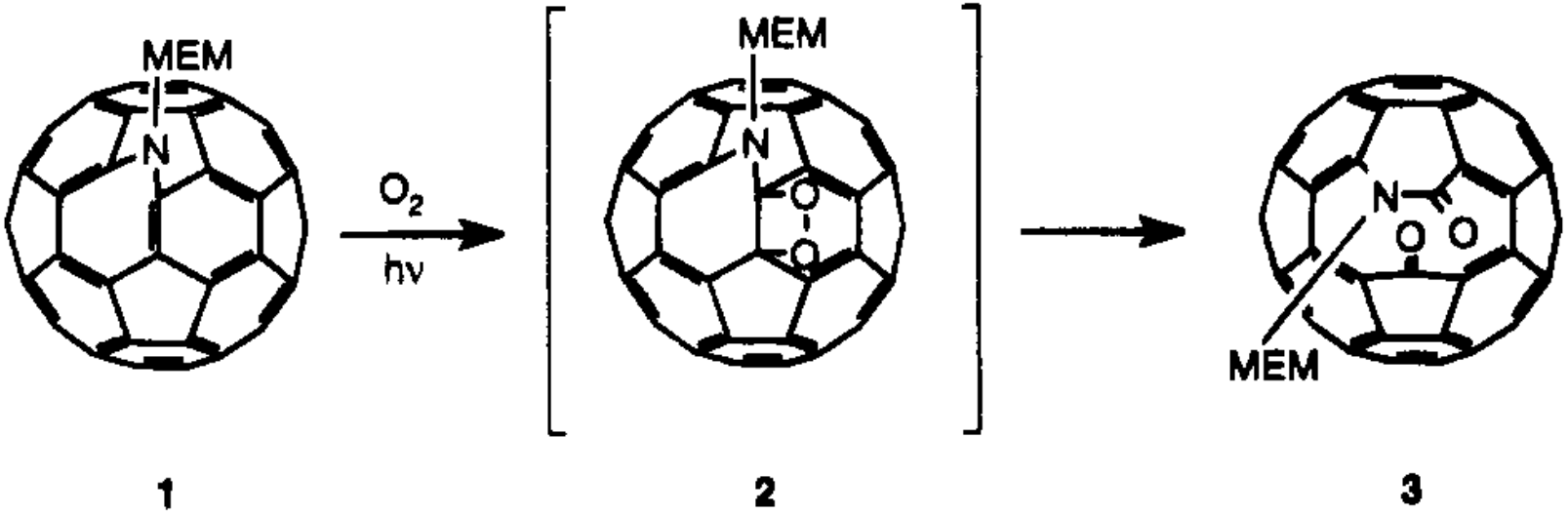


+ **5a,c-e**

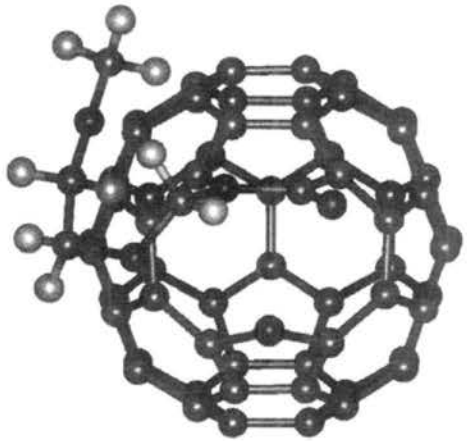
4a-e

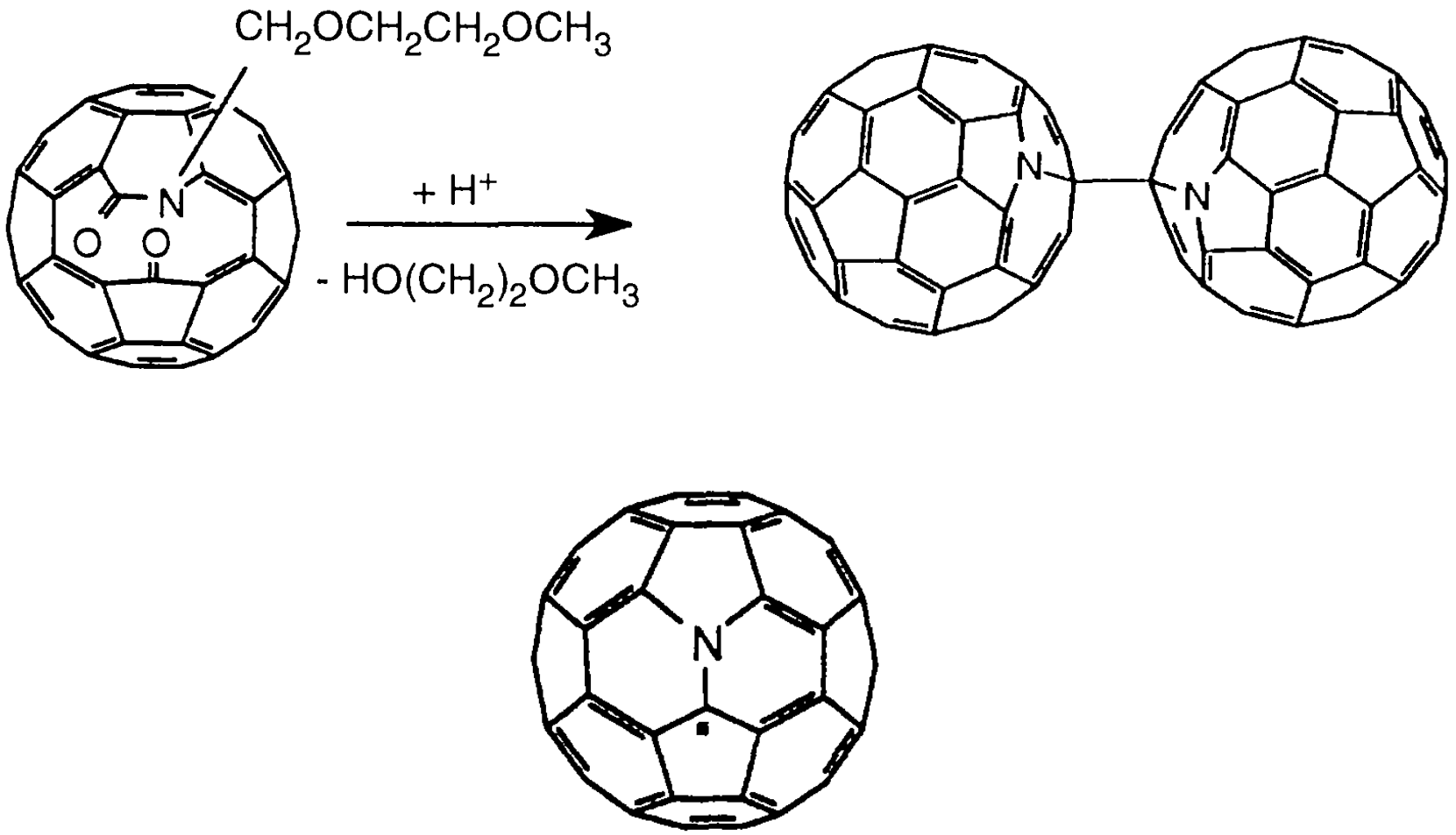
Angex.. Chem. In!. Ed. Engl. 1995, 34, No. 12, 1393


R
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160
150
140
130
δ



1 2 3




$CH_2OCH_2CH_2OCH_3$
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O
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+ H^+
- $HO(CH_2)_2OCH_3$
N
N
N