# Relative Stability of Highly Charged Fullerenes Produced in Energetic Collisions

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- Nat. Chem. \_
- Nat. Commun. -
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- JACS -
- Angew. Chem. -

#### **Charged Fullerenes**



### Outline

#### • Motivation

Why charged fullerenes are special: structure-stability problem

• Stability Models

-Previous models -Our CSI model

- Applications Exp. & theo. Cations & anions
- Conclusions & Outlook

### Complexity in Fullerene Science

#### There are a huge number of isomers, but nature chooses only a very few ones.

44 (D<sub>2d</sub>)

 $220 (D_2)$ 

 $356 (C_1)$ 

Fullerene C <sub>2n</sub>	All possible isomers	Synthesizable isomers
C <sub>60</sub>	1, 812	1
C <sub>70</sub>	8, 149	1
C <sub>76</sub>	19, 151	1
C <sub>78</sub>	24, 109	3
C <sub>80</sub>	31, 924	1
C <sub>82</sub>	39, 718	3
C <sub>84</sub>	51, 592	4
C <sub>90</sub>	99, 918	1

 $1123 (D_2)$  $1124 (C_2)$  $1286 (D_2)$  $1547 (C_2)$ 1548 (C. B  $1757 (C_s)$  $1756 (C_1)$  $1761 (C_{3v})$  $1793 (D_2)$ J. Chem. Soc., Perkin Trans. 2, 18 (2001) 1803 (D<sub>3</sub>)  $1804 (C_s)$ 1805 (D<sub>2d</sub> 1808 (D<sub>2d</sub>)  $1809 (C_{2v})$ 1812 (I<sub>h</sub>) 1810 (D<sub>2b</sub>)  $1811 (D_3)$ 

 $993 (C_1)$ 

1079 (C<sub>2h</sub>)

A needle in a haystack job !!

C<sub>60</sub> has ~2,000 possible isomers, only one produced in experiments.

#### Known Rules for Neutral Fullerenes

The 12 pentagons prefer to stay as far as possible from one another.

**1. Isolated Pentagon Rule (IPR)** Nature, **329**, 529 (1987) Pentagons in stable isomers should be isolated by hexagons.



JACS 125, 5572 (2003)

#### Neutral Fullerenes Follow the Rules

Fullerene C <sub>2n</sub>	All possible isomers	<b>IPR</b> isomers	Synthesized isomers
C <sub>60</sub>	1, 812	1	1 (IPR)
$C_{70}$	8, 149	1	1 (IPR)
C <sub>76</sub>	19, 151	2	1 (IPR)
C <sub>78</sub>	24, 109	5	3 (IPR)
C <sub>80</sub>	31, 924	7	1 (IPR)
C <sub>82</sub>	39, 718	9	3 (IPR)
C <sub>84</sub>	51, 592	24	4 (IPR)
C <sub>90</sub>	99, 918	46	1 (IPR)

An Atlas of Fullerenes. Clarendon Press: Oxford, U. K. (1995)

# Three Neutral Isomers of $C_{70}$



Nat. Chem. 7, 927 (2015)

#### Charged Fullerenes Break the Rules



### Plenty of Rulebreakers Found in Experiments

#### Experimentally synthesized endohedral metallofullerenes (EMFs):



# Plenty of Rulebreakers Found by DFT calculations

#### Positively and negatively charged fullerenes:

Isomer stability order differs, depending on charge state q and cage size 2n.



#### Previous Theories & Models

- Previous models are only for **negatively** charged and are **controversial**:
  - Maximum aromaticity (M. Solà 2013)  $ALA = \sum_{r=1}^{N_{ring}} A_r$  (A<sub>r</sub> is local aromaticity of ring r)
  - Minimum electrostatic repulsion
     (H. Zettergren 2008, J.M. Poblet 2010)
  - Minimum strain
     (A. Popov 2008)

IPSI =  $\sum_{i=1}^{12} \sum_{j>i}^{12} 1 / R_{ij}$  (R<sub>ij</sub> are interpentagon distances)

- Angew. Chem. Int. Ed. **52**, 9275 (2013) Nat. Chem. **2**, 955 (2010) JACS **129**, 11835 (2007)
- They are **not convenient** for practical use:
  - Sophisticated quantum chemistry methods (at least semiempirical)
  - Geometry optimization
  - Iterative electronic structure calculation
  - Failure and exceptions in some cases

### Previous Theories & Models





Handbook of Nanophysics. CRC Press: London, Vol. 2, Chpt. 25 (2010)

#### Simple Models for $\pi$ Systems

#### Particle-on-a-sphere model 1.

 $\pi$  electron: a particle confined to the 2D surface of a fullerene cage

Wave functions: Energy levels:

 $Y_{l}^{m}(\theta, \varphi)(l = 0, 1, 2, ...;$  $E_{l,m}=\frac{\hbar^2}{2m_{\rm e}R_{\rm s}^2}l(l+1)=$ 



$(l = 0, 1, 2,; m = 0, \pm 1,, \pm l)$ $\frac{\hbar^2}{m_e R^2} l(l+1) = \frac{e^2 a_0}{(4\pi\epsilon_0) 2R^2} l(l+1)$	
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Atomically esolved phase transition of in cations solvated in helium droplets

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### 2. Hückel Model (Tight-Binding)

A simple LCAO treatment with some simplifying approximations:



des Benzols und verwandter Verbindungen<sup>1</sup>).

Von Erich Hückel in Stuttgart.

Mit 10 Abbildungen. (Eingegangen am 28. April 1931.)

Z. Phys. **70**, 204 (1931); **72**, 310 (1931); **76**, 628 (1932)

### Advantages of Hückel Model

1. Almost computationally costless

Require only:Connectivity information (molecular graph theory)No need for: - Iterative electronic structure calculation<br/>- Geometry optimization

2. Describes exclusively the  $\pi$  effect

 $\pi$  effect is clearly separated from other effects (e.g. strain, steric etc.)

3. Conceptual & Parameter-free / Analytic

No parameters ( $\alpha$  or  $\beta$ ) at all: wave function, atomic charges, bond orders, ...

Or, in units of  $-\beta$ : relative energies, band gaps, ...

#### π-Conjugated Organic Molecules





#### Band Structure of Graphene

$$E(k_x, k_y) = \alpha \pm \beta \sqrt{1 + 4\cos\left(\frac{\sqrt{3}k_y a}{2}\right)\cos\left(\frac{k_x a}{2}\right) + 4\cos^2\left(\frac{k_x a}{2}\right)}$$



#### Band Structure of Nanotubes



### **Application to Charged Fullerenes**



- $\alpha$ : Coulomb integral (negative value)
  - $\beta$ : resonance integral (negative value)
- $R_{\pi}^{*}$ : effective cage radius

q: charge

Phys. Rev. A 80, 033201 (2009)

Nat. Chem. 7, 927 (2015)

- The only **variables**: eigenvalues  $\{\chi_k^i\}$ 

## Combining $\sigma$ and $\pi$ effects



### Relative isomer energy (Hückel + PAPR)

Total  $\pi$  energy of isomer *i* with charge *q*:

$$E_{\pi}^{i,q} = (2n-q) \left( \alpha - \frac{q}{2R_{\pi}^*} \right) + 2\beta \sum_{k=1}^{n-q/2} \chi_k^i$$

Energy change due to charging ( $\pi$  *stabilization energy*):

$$\Delta E_{\pi}^{i,q} = E_{\pi}^{i,q} - E_{\pi}^{i,0} = -2\beta X_i^q - q\alpha + \frac{(2n-q)q}{2R_{\pi}^*}$$

Relative energy of **neutral** isomer *i*:

$$E_{
m rel}^{i,0} = 0.2\,{
m NAPP}_i(-2eta)$$
 Eq. of PAPR ( energy penalty: 0.2 (-2 $eta$ )

Relative energy of **ionic** isomer *i* with charge *q*:



We define Charge Stabilization Index (CSI):

$$\mathrm{CSI}_i^q \equiv X_i^q + 0.2 \,\mathrm{NAPP}_i$$

$$X_{i}^{q} \equiv \begin{cases} \sum_{k=n-q/2+1}^{n} \chi_{k,i} & \text{if } q > 0 \\ \\ \sum_{k=n+1}^{n-q/2} \chi_{k,i} & \text{if } q < 0 \end{cases} \xleftarrow{\text{HOMOs}} \\ \text{Only over frontier} \\ \text{orbitals involved in} \\ \text{the charge transfer} \\ \xleftarrow{\text{LUMOs}} \end{cases}$$

### Charge Stabilization Index (CSI)



- More negative CSI  $\rightarrow$  more stability
- A clear physical interpretation
- Almost parameter-free: no  $\alpha$ ,  $\beta$ ,  $R_{\pi}^{*}$
- Depends only on cage connectivity

(in units of  $-2\beta$ )



#### One rule for the electron-rich...

A vast number of possible isomers exist for each fullerene, yet few are observed experimentally. Neutral fullerenes typically minimize adjacent pentagons, but charged ones often tolerate them. Now, a simple model taking into account structural strain and  $\pi$  electronic aspects predicts the asymmetric relative stabilities of charged isomers.

Patrick Fowler

nature ARTICLES chemistry PUBLISHED ONLINE: 19 OCTOBER 2015 | DOI: 10.1038/NCHEM.236

#### Cage connectivity and frontier $\pi$ orbitals govern the relative stability of charged fullerene isomers

Yang Wang<sup>1,2</sup>, Sergio Díaz-Tendero<sup>1</sup>, Manuel Alcamí<sup>1,2</sup> and Fernando Martín<sup>1,2,3\*</sup>

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A Test Case:  $C_{42}^{4-}$ 



### Efficiency of CSI

Time cost for calculating all 99,918 isomers of  $C_{90}^{6+}$  on a single processor computer:

Method	Time cost	
CSI	15 min	
AM1	~20 days	
SCC-DFTB	~80 days	
DFT (B3LYP/6-31G*)	~600 years	

# $\Delta$ CSI as a Prescreening Tool

 $\Delta \mathrm{CSI}_i = \mathrm{CSI}_i - \mathrm{CSI}_{i0}$ 

*i*: a given isomer

 $i_0$ : the lowest-energy isomer in neutral state

 $\Delta CSI_i > 0$ : Unstable isomers of charged fullerenes  $\Delta CSI_i \le 0$ : Eligible candidate of stable charged isomers

Applications: Anions  $C_{80}^{q-}$ 



Applications: Cations  $C_{80}^{q+}$ 



- Impressive prediction power

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Our model predicts ALL experimentally synthesized and computationally determined isomers!!

The IPR & PAPR are stilled obeyed by fullerene cations, but frequently broken by fullerene anions, in which  $\pi$ effect plays over  $\sigma$  strain.



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#### Also works for small cages: $C_{2n}^{q-}(2n = 28-50; q = 2,4,6)$





### Conclusions

- 1. The stability of charged fullerenes is govened by the **interplay** between charge delocalization over frontier  $\pi$  orbitals and  $\sigma$  strain. The former can be quantified by simple HMO theory and the latter by counts of APPs, which gives rise to the CSI model.
- 2. The CSI model provides a unified view of both positively and negatively charged fullerenes, and offers a common theoretical frame for previous models (LUMO gaps, electronstatic repulsion, aromaticity, etc).
- 3. CSI can be easily calculated requiring only the connectivity between atoms, allowing a rapid prediction of the most stable isomers of charged fullerenes and endohedral metallofullerenes.

The FULLFUN software package, avaible at:



http://fullfun.sourceforge.io

#### Outlook

1. Improvement of the CSI model, by combining our generalized motif model for fullerenes.

$$CSI_{IPR,i}^{q} = X_{i}^{q} + \sum_{m=1}^{30} E_{m}N_{m}^{i} + J\ln\frac{2n+L}{60}$$

PCCP, DOI: 10.1039/c7cp01598d JCTC, to be submitted

- 2. Extension to exohedral fullerenes: the XSI model JACS, 139, 1609 (2017)
- 3. Applications to study reactions of fullerenes. (paper submitted)
- 4. Possible extensions to related systems: PAHs, graphene, ...

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### Thank you for your attention!!