

Energy of Small Fullerene Isomers

Zacharias G. Fthenakis

Institute of Electronic Structure and Laser - FORTH

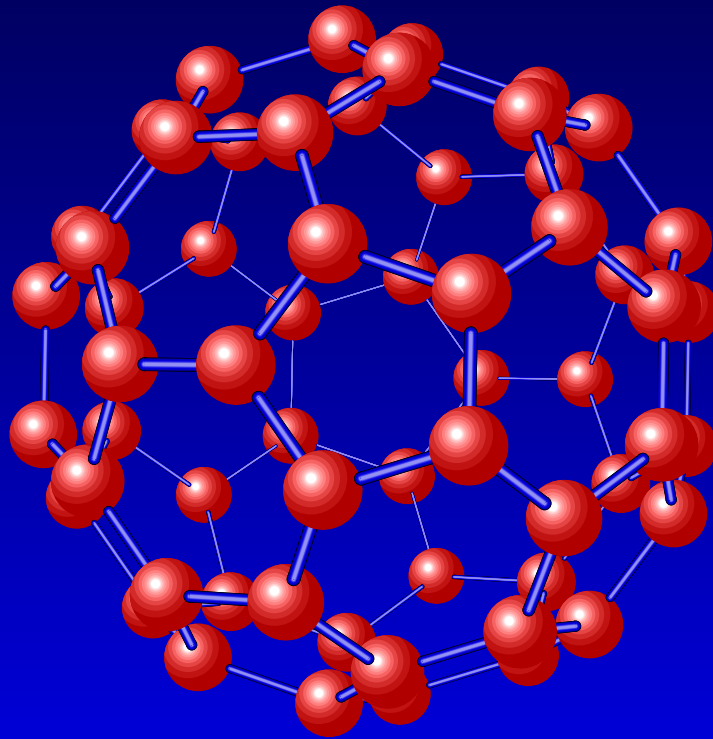
and

T.E.I. of Crete

Heraklion - Crete - Greece

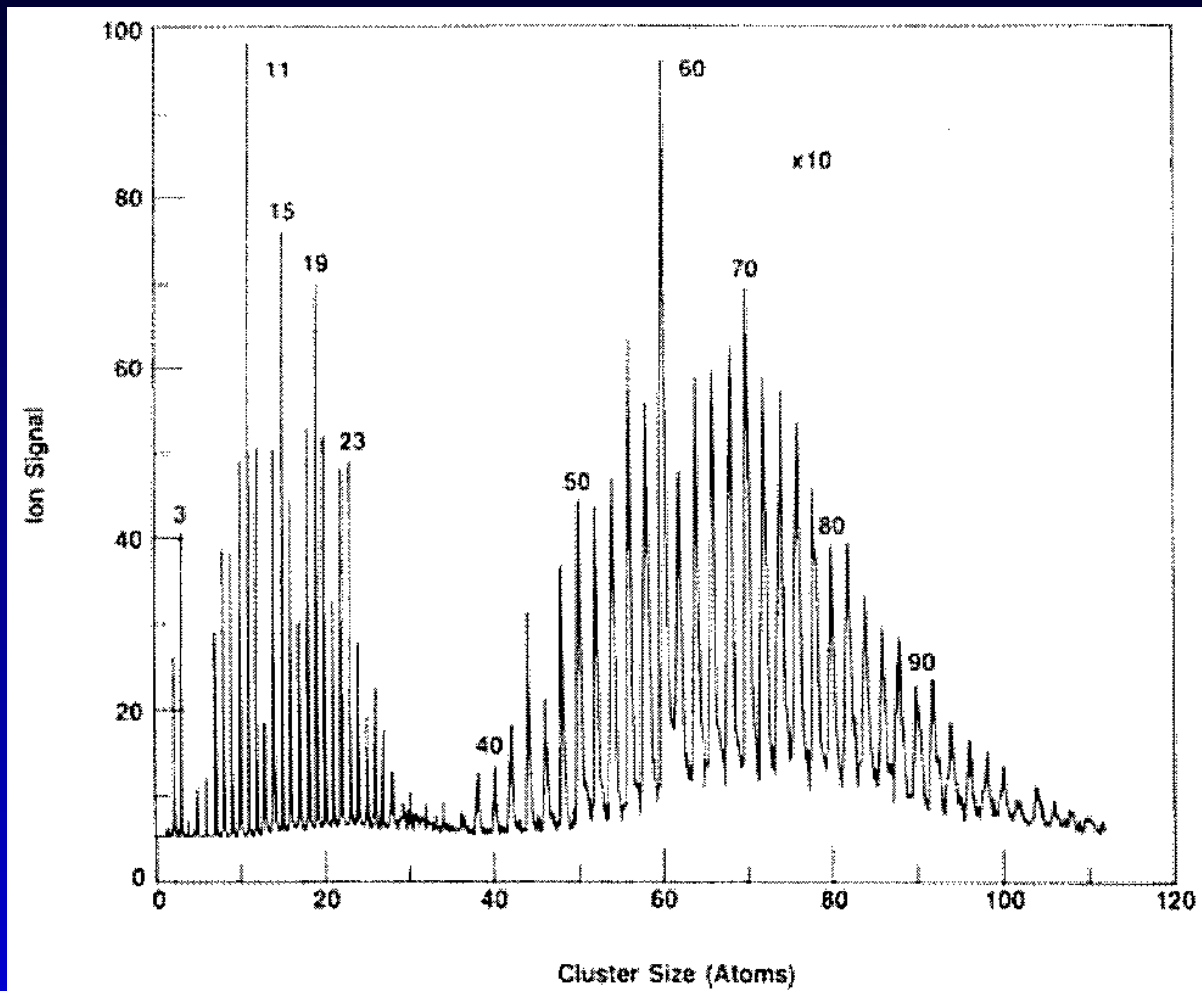
Fullerenes

C_{60} Buckminsterfullerene



H.W.Kroto, J.R.Heath,
S.C.O'Brien, R.F.Curl
and R.E.Smalley,
Nature, **318**, 162, (1985)

...but not only C_{60}



E.A.Rohlfing,
D.M.Cox and
A.Kaldor,
J.Chem.Phys. **81**,
3322, (1984)

Fullerenes construction

Definition: Closed cages with 5- and 6-member rings

Fullerenes construction

Definition: Closed cages with 5- and 6-member rings

How many pentagons and hexagons are they ?

Fullerenes construction

Definition: Closed cages with 5- and 6-member rings

How many pentagons and hexagons are they ?

Euler's theorem for the geometrical solids



- 12 pentagons

- $\frac{N}{2} - 10$ hexagons

$$N = 20, 24, 26, \dots, 2n, \quad n \in \mathbb{N}$$

Fullerenes construction

Definition: Closed cages with 5- and 6-member rings

How many pentagons and hexagons are they ?

Euler's theorem for the geometrical solids



- 12 pentagons
 - $\frac{N}{2} - 10$ hexagons
- $N = 20, 24, 26, \dots, 2n, \quad n \in \mathbb{N}$

Different arrangement of the pentagons and the hexagons gives different structures (isomers)

How many isomers are they ?

N	Isomers	N	Isomers	N	Isomers
20	1	42	45	62	2385
24	1	44	89	64	3465
26	1	46	116	66	4487
28	2	48	199	68	6332
30	3	50	271	70	8149
32	6	52	437	72	11190
34	6	54	580	74	14246
36	15	56	924	76	19151
38	17	58	1205	78	24109
40	40	60	1812	80	31924

P. W. Fowler and
D. E. Manolopoulos,
An atlas of fullerenes,
(Oxford: Clarendon Press),
1995

The question:

Can we find a prediction equation, which could predict the cohesive energy of any fullerene isomer ?

The method:

Tight Binding Molecular Dynamics

Energy Calculations for:

- All C_N isomers, $20 \leq N \leq 42$ (139 structures)
- All IPR- C_N isomers, $60 \leq N \leq 80$ (16 structures)

Totally: 155 structures

The Energy

$$U = U_{atr} + U_{rep} + U_{bond}$$

$$U_{atr} = \sum_i^{occ} \epsilon_i, \quad U_{rep} = \sum_{i < j}^N \Phi_0 e^{-4\alpha(r_{ij}-d)}$$

$$U_{bond} = N \left[A \left(\frac{n_b}{N} \right)^2 + B \left(\frac{n_b}{N} \right) + C \right]$$

$\Phi_0 = 4.0156 eV$, $\alpha = 0.7775 \text{\AA}^{-1}$ (adjustable parameters)

$d = 1.54 \text{\AA}$, $n_b/N = 1.5$

Tight Binding Hamiltonian H

$$H\Psi_i = \varepsilon_i\Psi_i$$

base: $|l, k\rangle$, $l=s, p_x, p_y, p_z$ (orbitals), $k = 1, 2, \dots, N$ (atoms)

$$H_{l',l}^{k',k} = \langle l', k' | H | l, k \rangle = \varepsilon_l \delta_{l'l} \delta_{k'k} + H_{l',l} (1 - \delta_{k',k})$$

$$H_{l'l} = \sum_{m=0}^{\min\{\mu', \mu\}} f(\bar{l}, \bar{m}, \bar{n}) V_{l'l m}(r)$$

(example: $H_{xx} = \bar{l}^2 V_{pp\sigma} + (1 - \bar{l}^2) V_{pp\pi}$)

Scaling: $V_{l'l m}(r) = V_{l'l m}(d) e^{-\alpha(r-d)}$,

Harrison's scheme: $V_{l'l m}(d) = \eta_{l'l m} \frac{\hbar^2}{m d^2}$,

$\eta_{ss\sigma} = -1.40$, $\eta_{sp\sigma} = 1.84$, $\eta_{pp\sigma} = 3.24$ and $\eta_{pp\pi} = -0.81$,

$\hbar^2/m = 7.62 eV \cdot \text{\AA}^2$

Molecular Dynamics

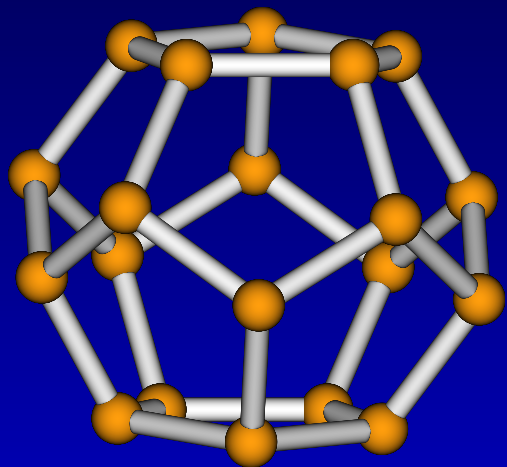
$$\mathbf{F}_q = m_q \frac{d^2 \mathbf{r}_q}{dt^2} = -\nabla_{r_q} U, \quad q = 1, 2, \dots, N$$

$$\nabla_{r_q} U_{atr} = \sum_i^{occ} \langle \Psi_i | \nabla_{r_q} H | \Psi_i \rangle$$

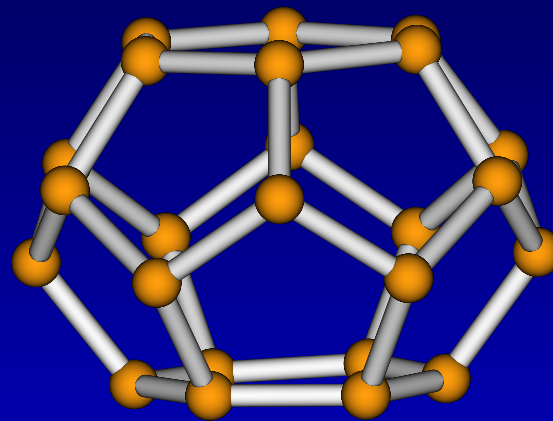
Damping molecular dynamics

$$\mathbf{v}_q(t) \longrightarrow \mathbf{v}_q(t) = (1 - a)\mathbf{v}_q(t)$$

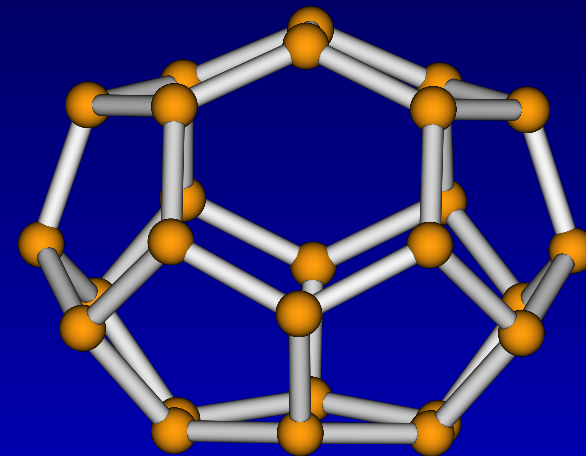
Optimum isomers



C₂₀



C₂₄



C₂₆

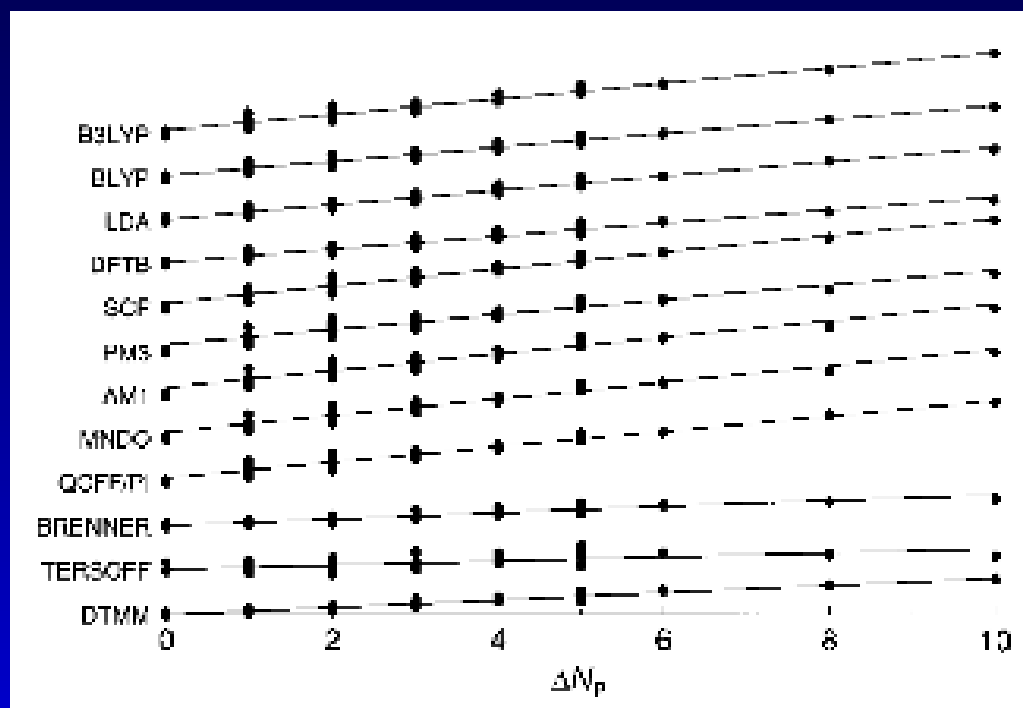
Fullerene stability (I)

- **The Isolated Pentagon Rule (IPR)** The most stable fullerene is the one with its pentagons isolated
- The rule can be applied on C_n , $n \geq 60$
- The smallest possible IPR-fullerene: C_{60}

T. G. Schmalz, W. A. Seitz, D. J. Klein and G. E. Hite, J. Am. Chem. Soc. **110**, 1113 (1988); *ibid* Chem. Phys. Lett. **130**, 203 (1986)

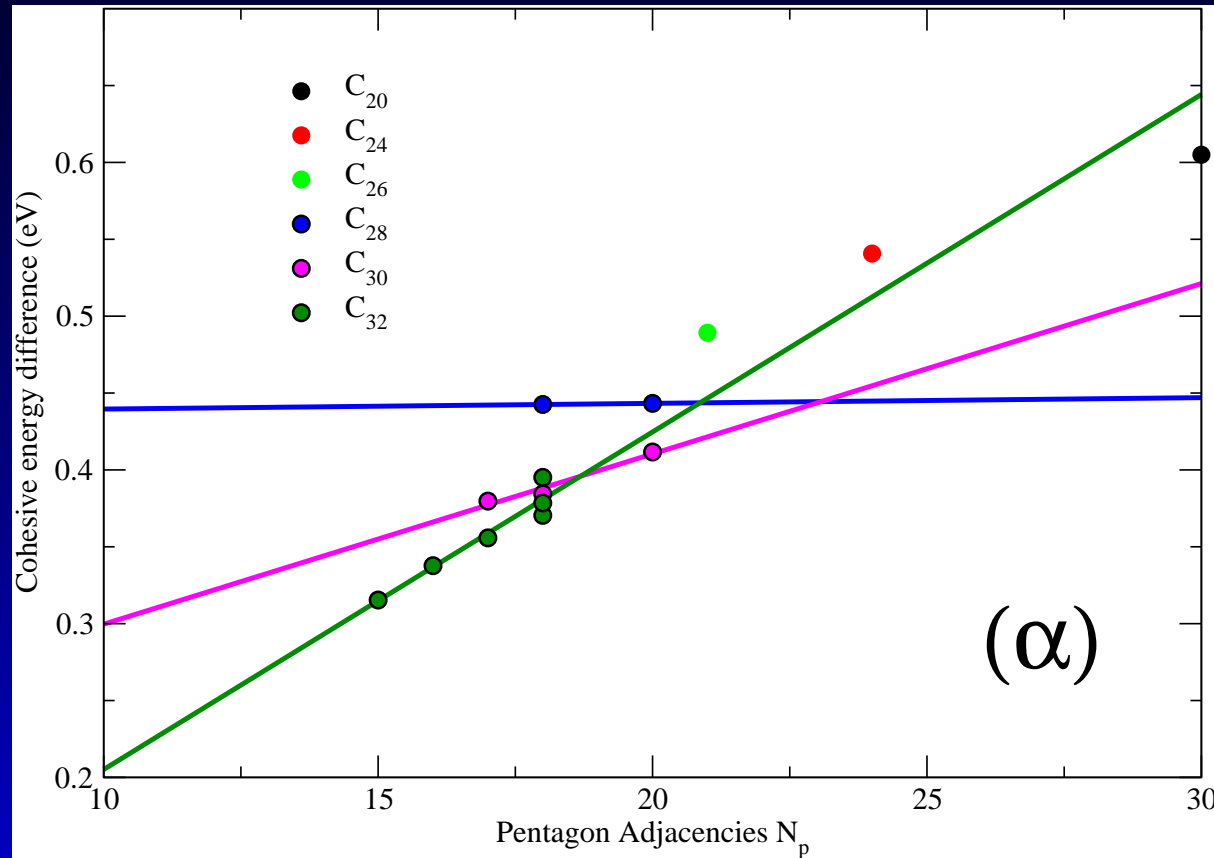
Fullerene stability (II)

The Pentagon Adjacency Penalty Rule (PAPR): The energies rise linearly with the number N_p of the pentagon adjacencies (for $n \leq 70$)

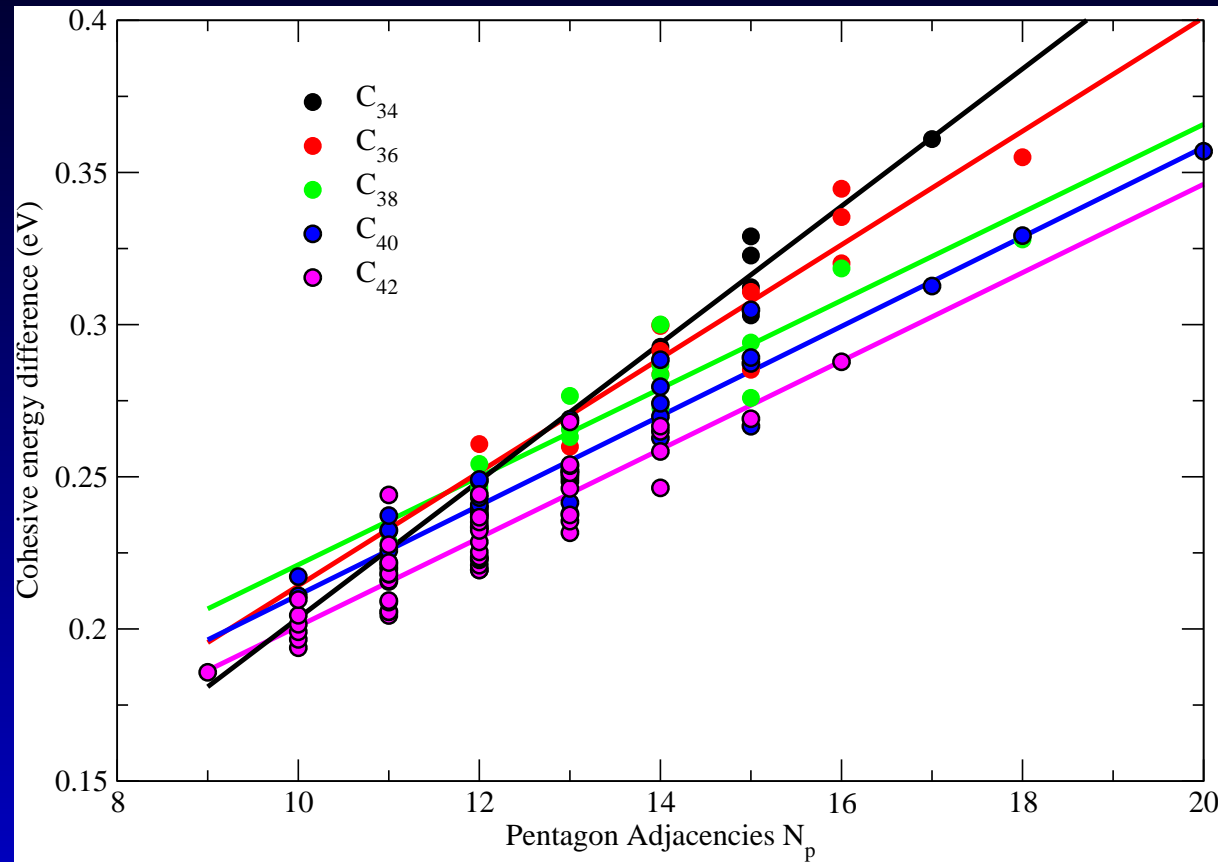


For C_{40} E. Albertazzi, C. Domene, P. W. Fowler, T. Heine, G. Seifert, C. Van Alsenoy and F. Zerbetto, Phys. Chem. Chem. Phys. **1**,2913 (1999)

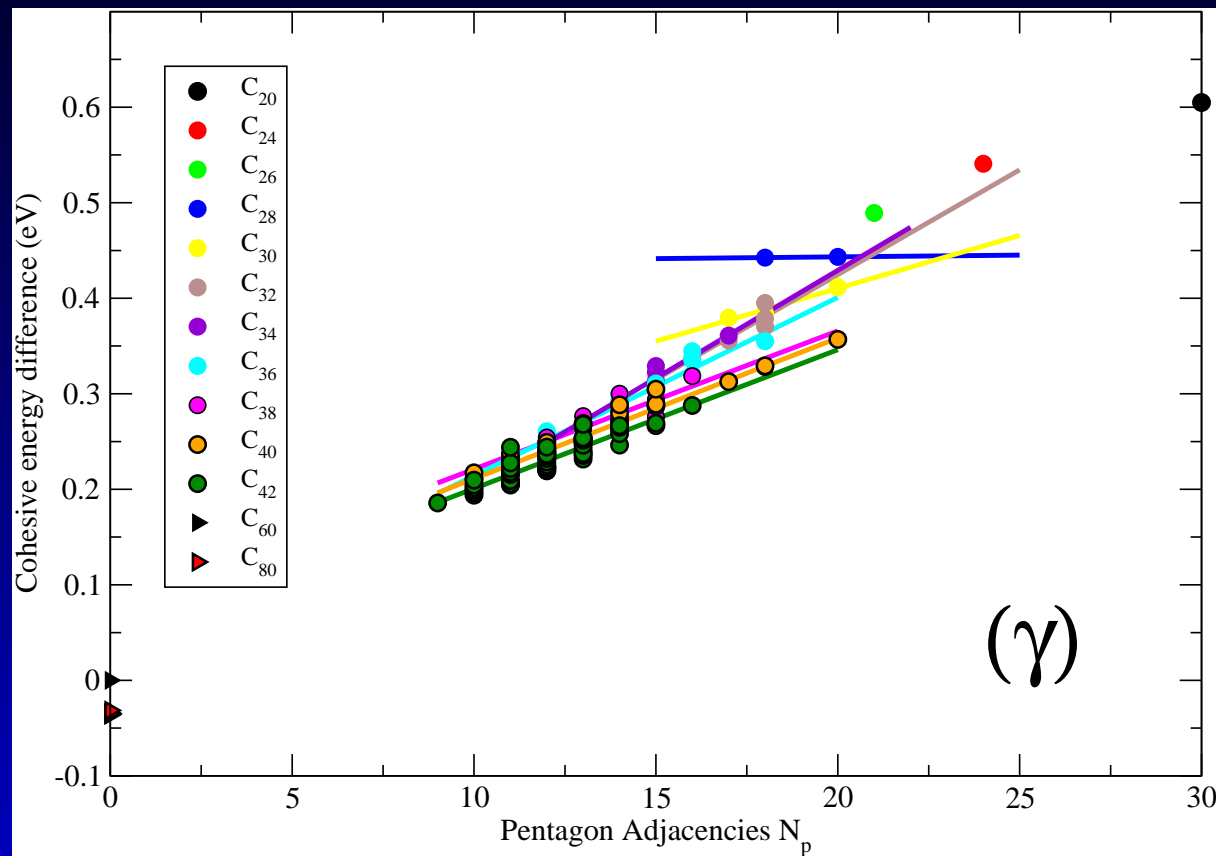
Cohesive Energy vs N_p ($20 \leq N \leq 32$)



Cohesive Energy vs N_p ($34 \leq N \leq 42$)



Cohesive Energy vs N_p (for all)



Cohesive Energy (I)

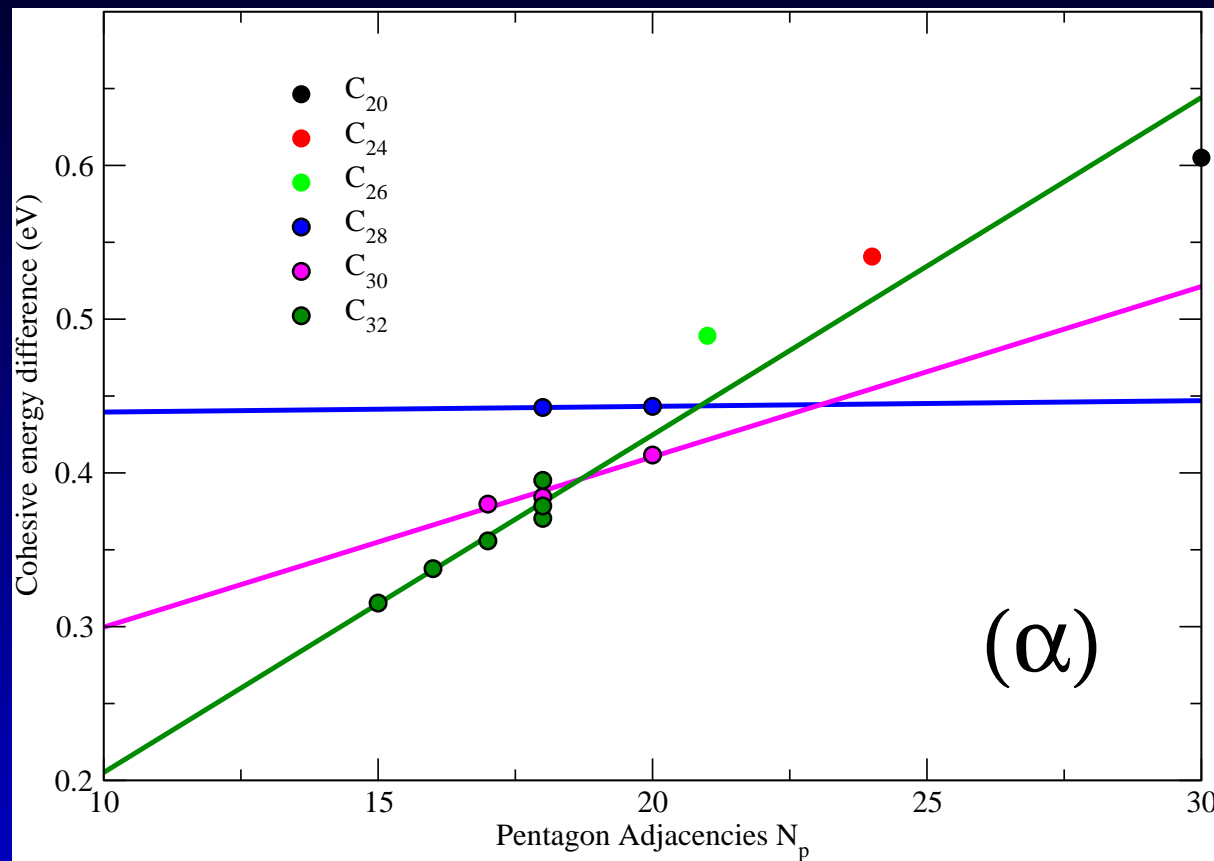
$$E_{coh} = aN_p + b$$

N	$a(eV)$	$b(eV)$	r^2	$\Delta E_{max}(eV)$
28	0.00037	0.435895	1.000	0.000
30	0.0110793	0.188846	0.980	0.004
32	0.0219506	-0.014340	0.960	0.014
34	0.0225614	-0.022061	0.928	0.013
36	0.0186716	0.027488	0.947	0.022
38	0.0144732	0.076364	0.936	0.021
40	0.0147164	0.063971	0.965	0.020
42	0.0145274	0.055595	0.918	0.029

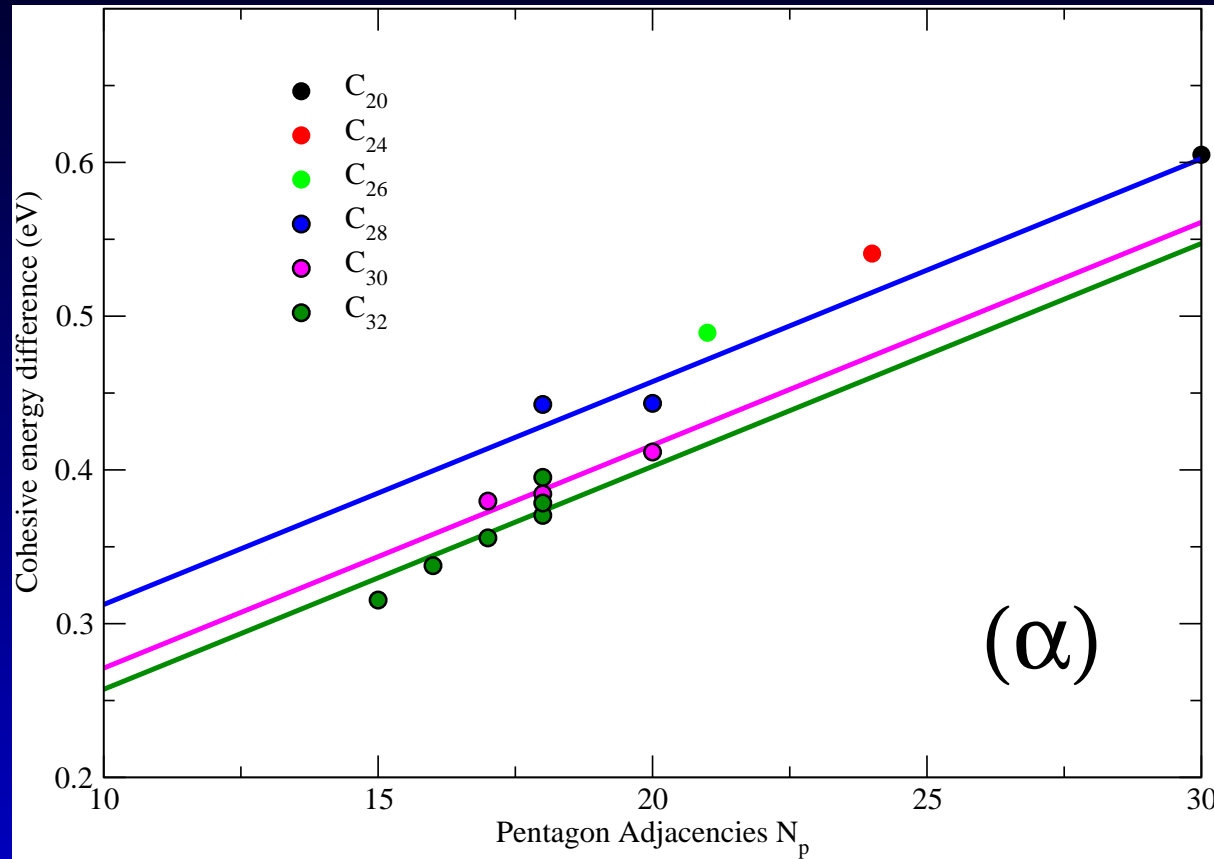
For $N = 40$, $a = 56.7 \text{ kJoule/mole}$

Albertazi et al values for a : $24.4 - 99.5 \text{ kJoule/mole}$

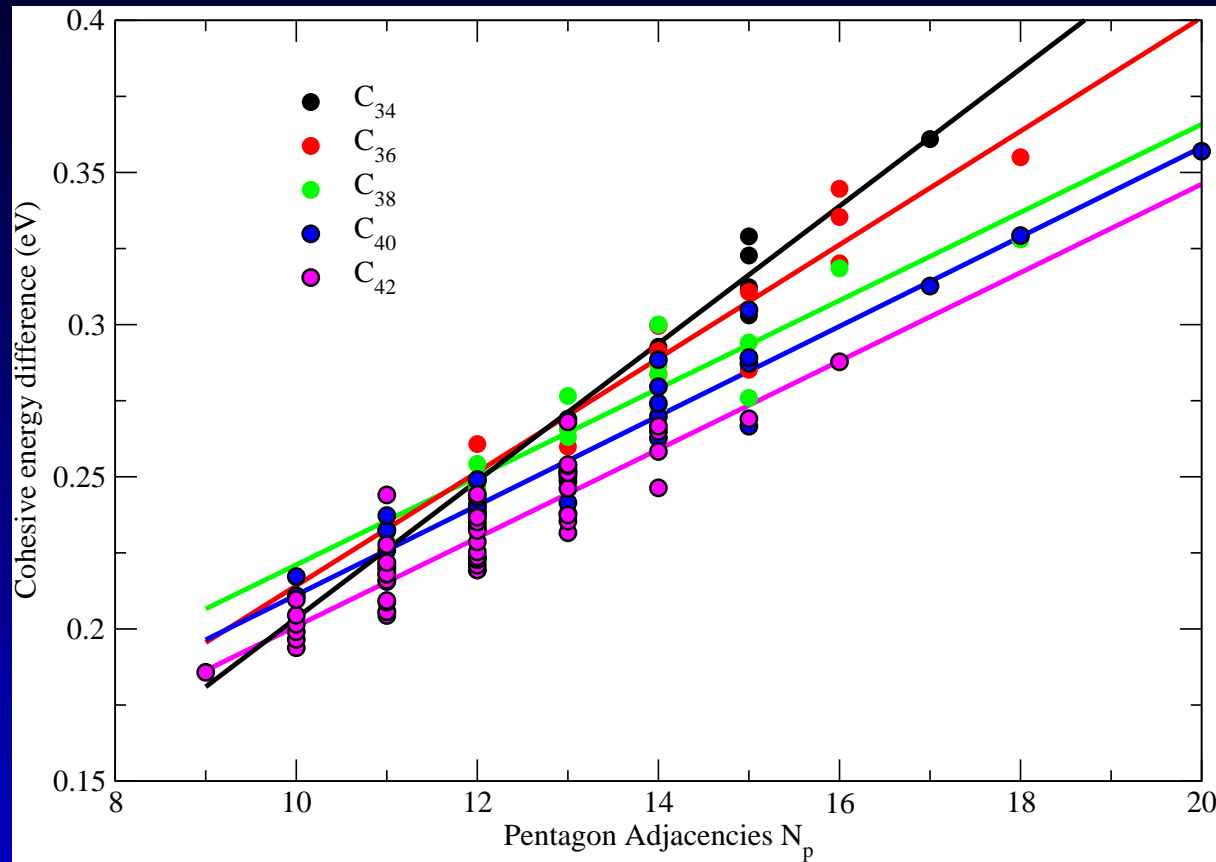
Cohesive Energy vs N_p ($20 \leq N \leq 32$)



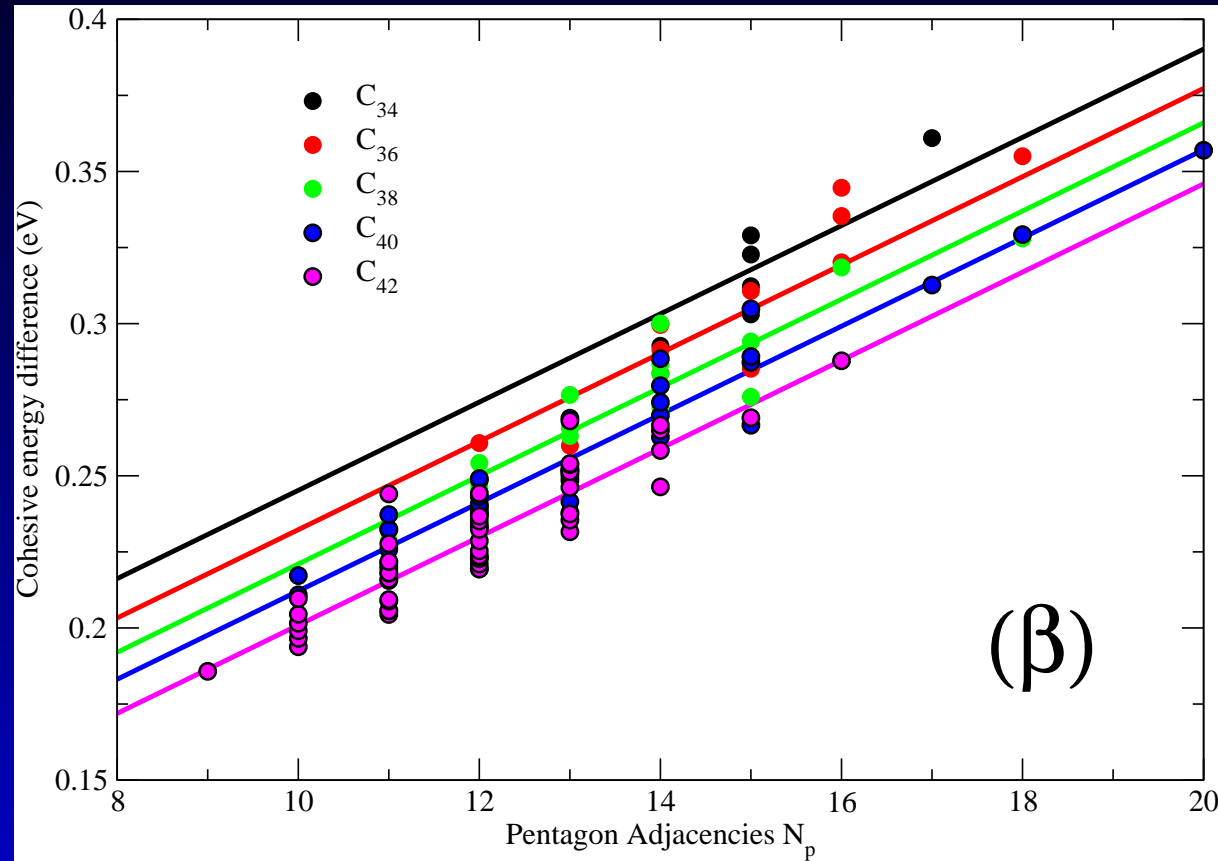
Cohesive Energy vs N_p ($20 \leq N \leq 32$)



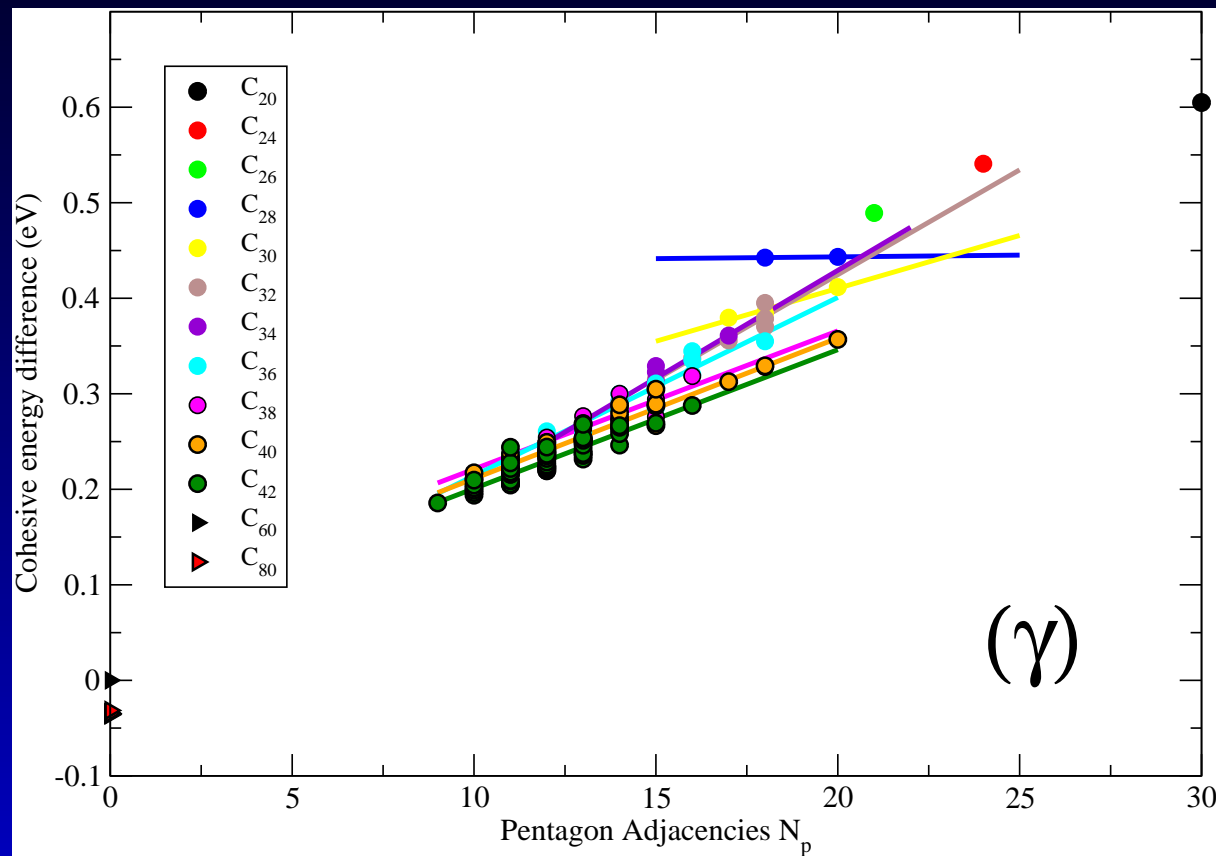
Cohesive Energy vs N_p ($34 \leq N \leq 42$)



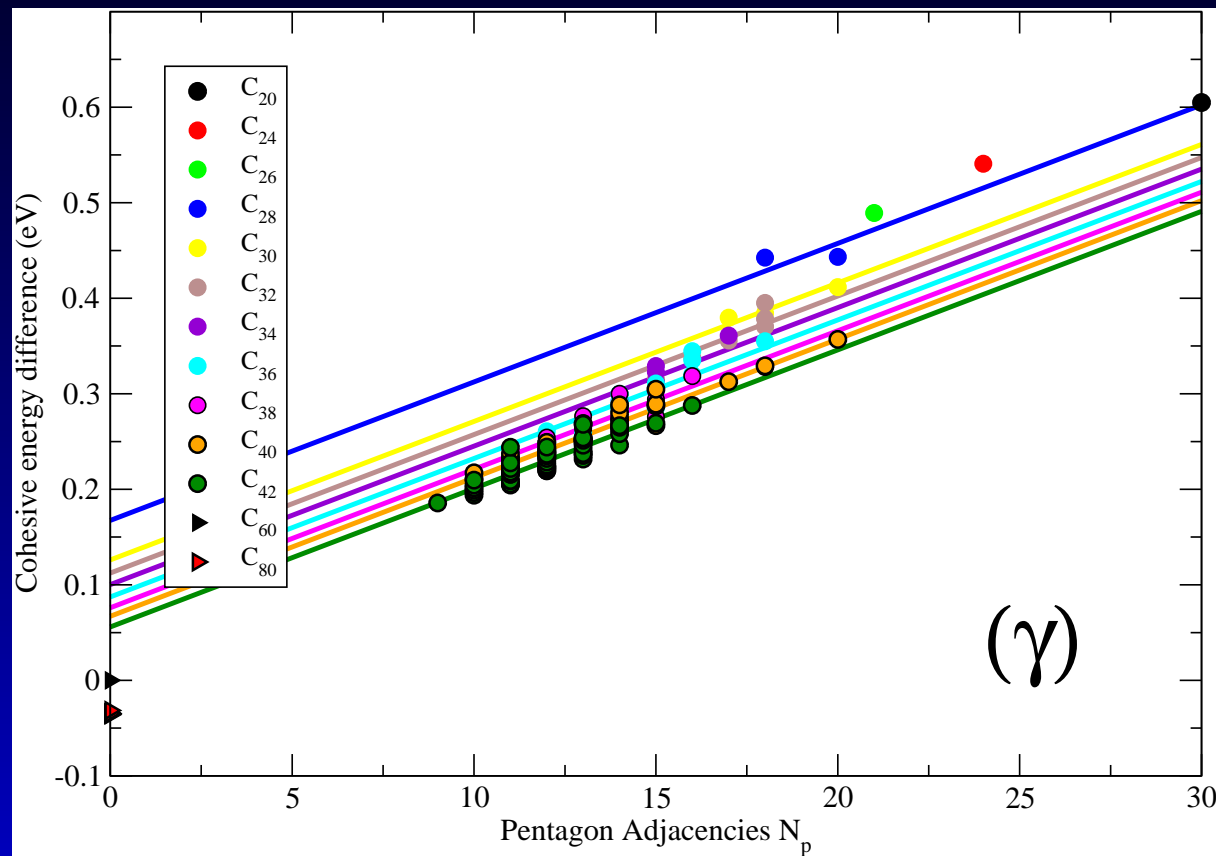
Cohesive Energy vs N_p ($34 \leq N \leq 42$)



Cohesive Energy vs N_p (for all)



Cohesive Energy vs N_p (for all)

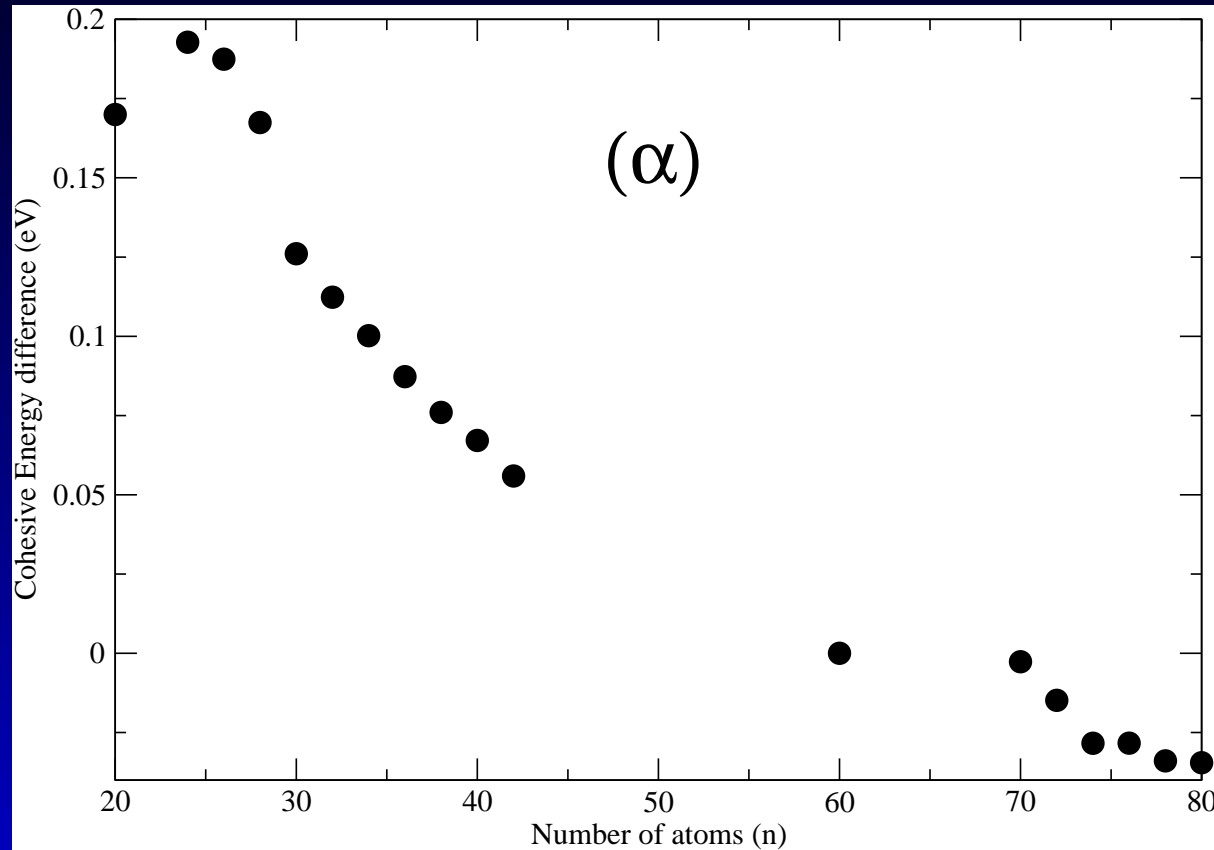


Cohesive Energy (II)

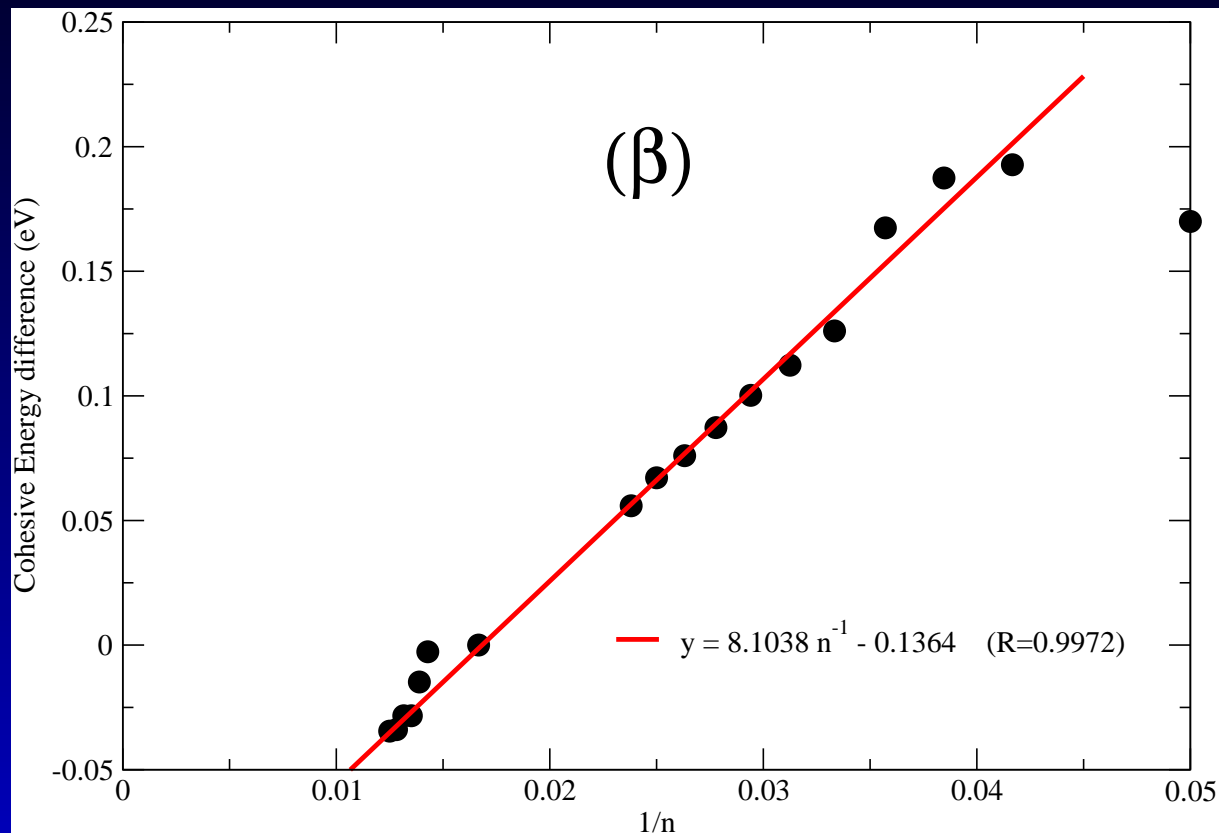
Value of intercept b , if the slope is fixed to the value $a = 0.0145$ for all N

N	b (eV)	N	b (eV)	N	b (eV)
20	0.16997	34	0.10020	70	-0.00267
24	0.19275	36	0.08728	72	-0.01482
26	0.18743	38	0.07600	74	-0.02837
28	0.16743	40	0.06714	76	-0.02835
30	0.12605	42	0.05592	78	-0.03394
32	0.11232	60	0.00000	80	-0.03453

Intercept b vs N

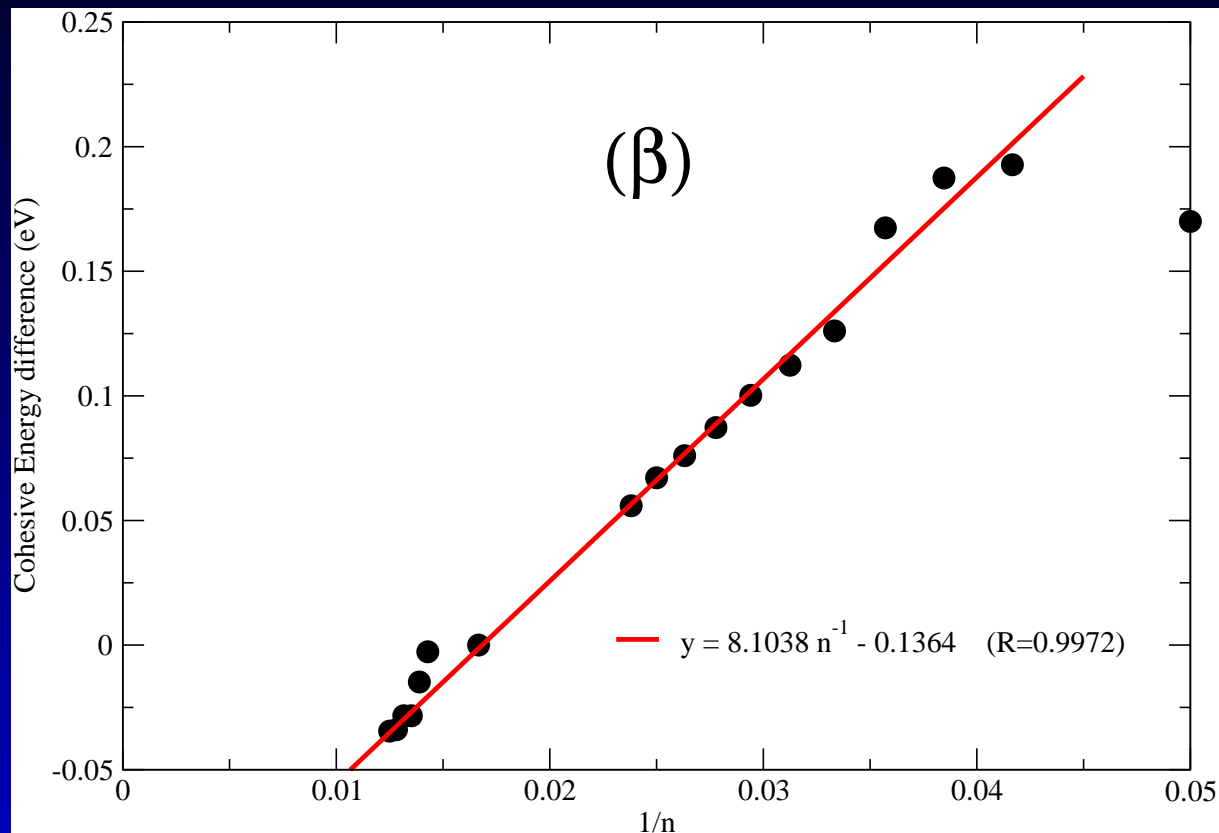


Intercept b vs N^{-1}



Without $N = 20$ case:
$$b = \frac{8.1038}{N} - 0.1364, \quad (R = 0.9972)$$

Intercept b vs N^{-1}



Without $N = 20$ case: $b = \frac{8.1038}{N} - 0.1364, \quad (R = 0.9972)$

Conclusion: b is a function of N

Cohesive Energy vs N

For large IPR-fullerenes:

- G. B. Adams, O. F. Sankey, M. O’Keffe, J. B. Page and D. A. Drabold, Science **256**, 1792 (1992)

$$E_{coh} = \frac{a}{N} + \frac{b}{N^2}$$

- J. Tersoff, Phys. Rev. B **46**, 15546 (1992)

$$E_{coh} = \frac{a}{N} + b \frac{\ln N}{N}$$

- A. Maiti, C. J. Brabec and J. Bernholc, Phys. Rev. Lett. **70**, 3023 (1993)

$$E_{Coh} = E_{graphene} + 4.6164N^{-(0.561+0.0022 \ln N)}$$

Cohesive Energy vs N

- T. A. Witten and H. Li, Europhys. Lett **23**, 51 (1993)

$$E_{coh} = AN^{-5/6}$$

- J. L. Morán-López, K. H. Bennemann, M. Cabrera-Trujillo and J. Dorantes-Dávila, Solid State Commun. **89**, 977 (1994)

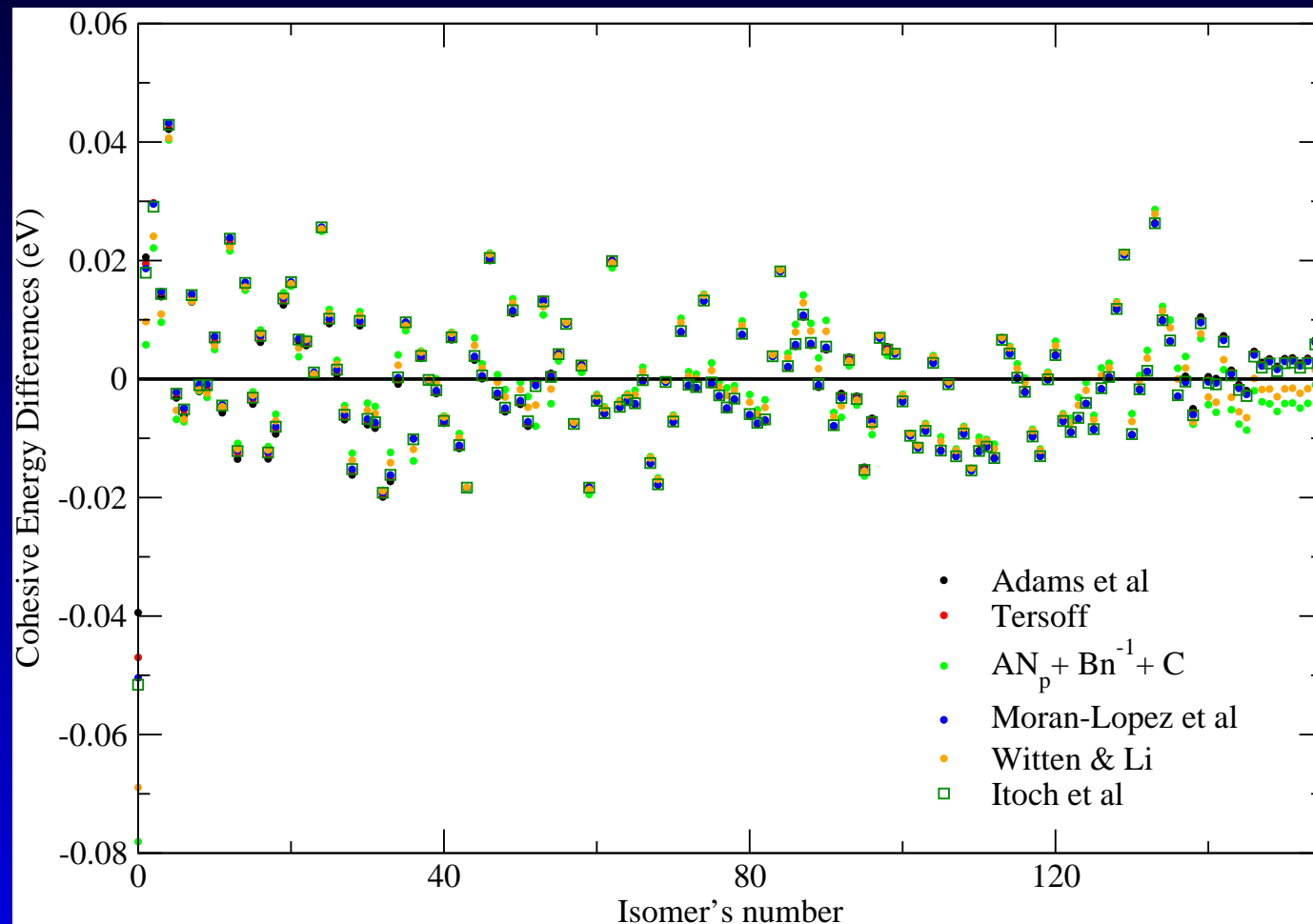
$$\Delta E_{coh} = \frac{A}{N} + \frac{B}{\sqrt{N}} + C$$

- S. Itoh, P. Ordejón, D. A. Drabold and R. M. Martin, Phys. Rev. B **53**, 2132 (1996)

$$E_{coh} = AN^{-B}$$

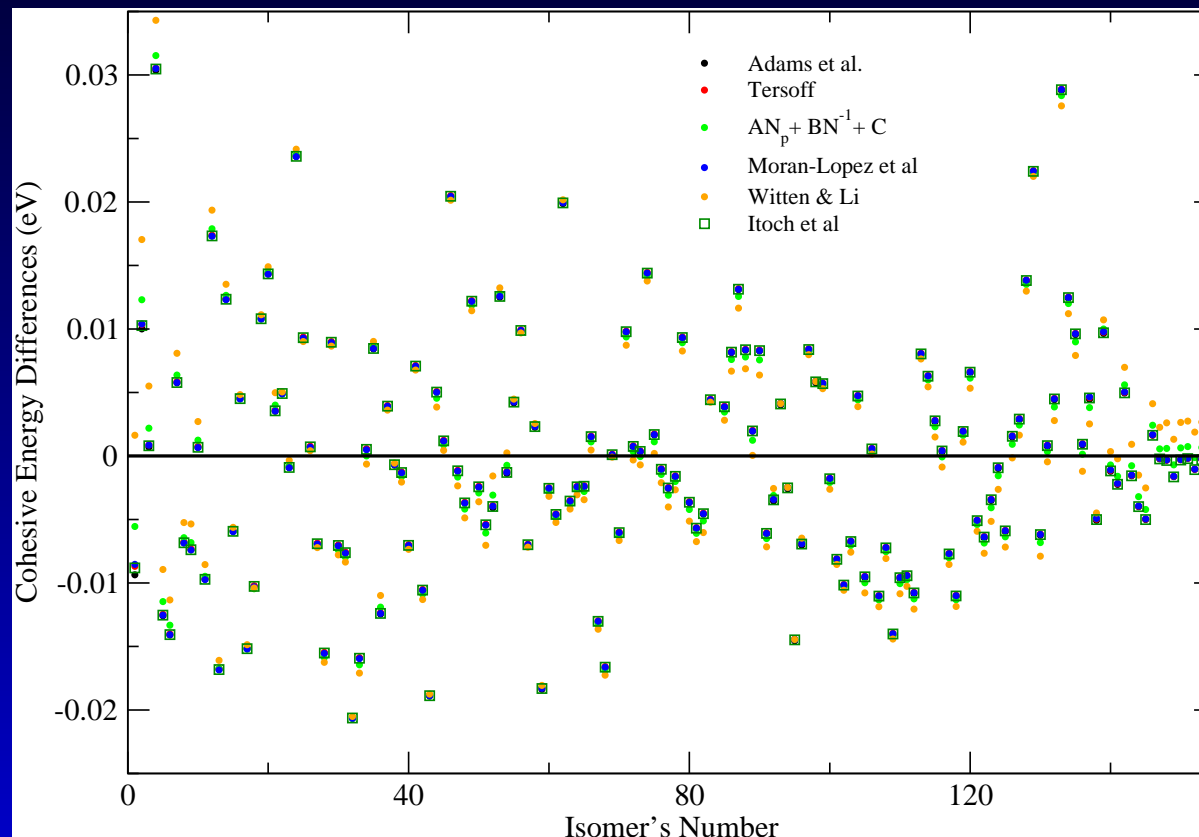
Testing the models (I)

Error for all (155) isomers:



Testing the models (II)

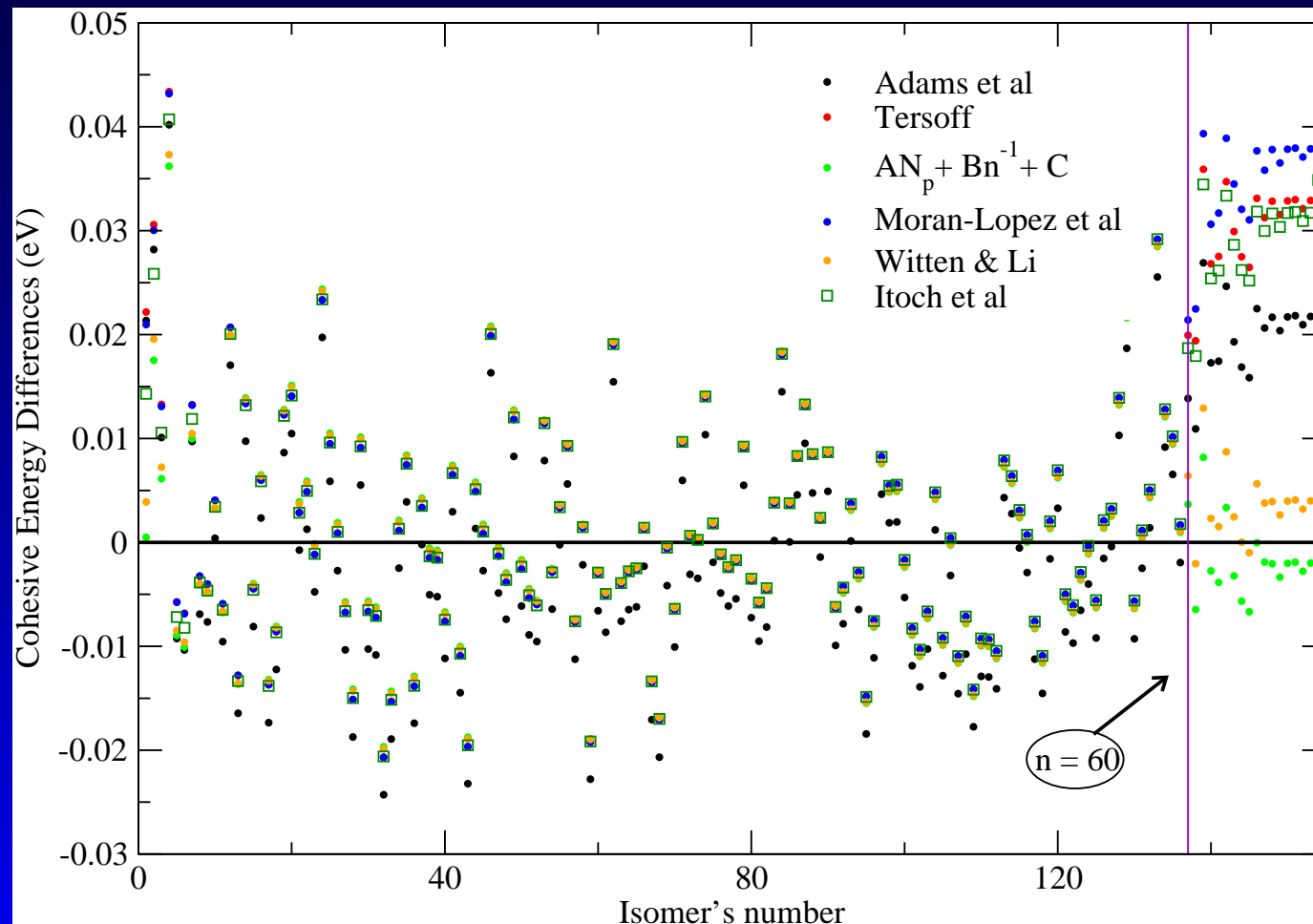
Error for all isomers without $N = 20$ case (154):



Testing the models (III)

Fitting for $30 \leq N \leq 42$

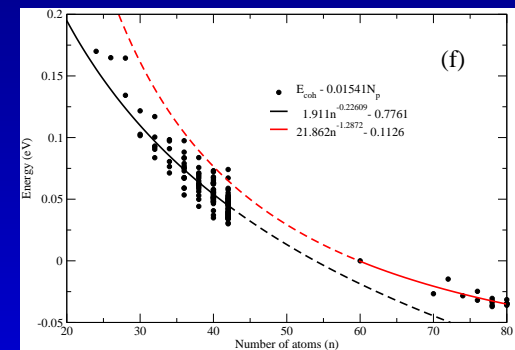
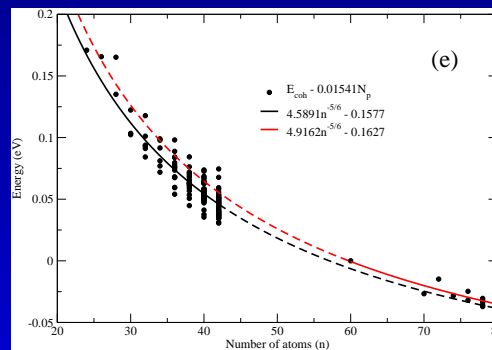
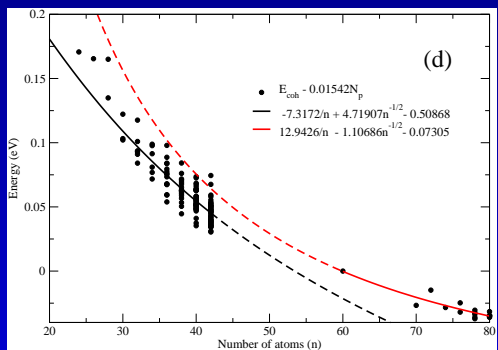
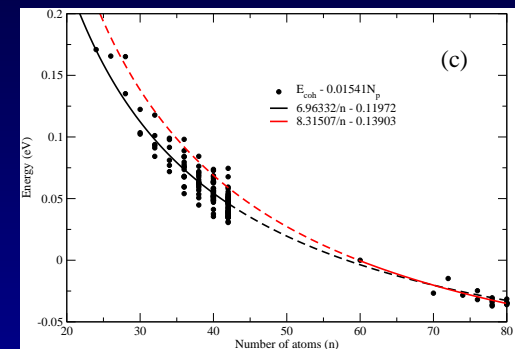
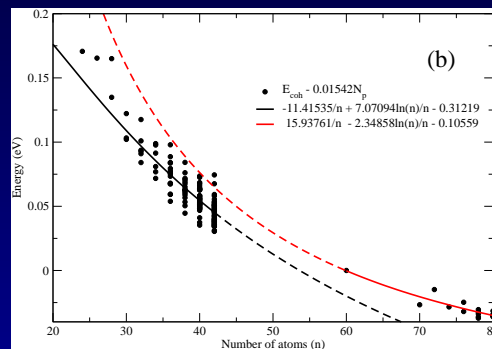
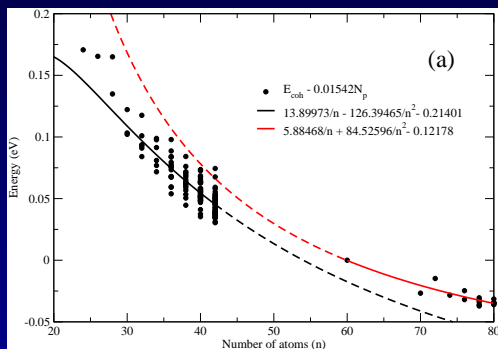
Error from extrapolation for IPR $60 \leq N \leq 80$



Testing the models (IV)

Fitting for $60 \leq N \leq 80$

Error from extrapolation for $30 \leq N \leq 42$



(a) Adams et al, (b) Tersoff, (c) n^{-1} , (d) Morán-López et al, (e) Witten and Li and (f) Itoh et al

Results

- Whitten and Lee

$$E_{coh} = 0.01477N_p + 4.9528N^{-5/6} - 0.16585, \quad R^2 = 0.9927.$$

- N^{-1}

$$E_{coh} = 0.01504N_p + \frac{7.5657}{N} - 0.1299, \quad R^2 = 0.9929$$

Results

- Whitten and Lee

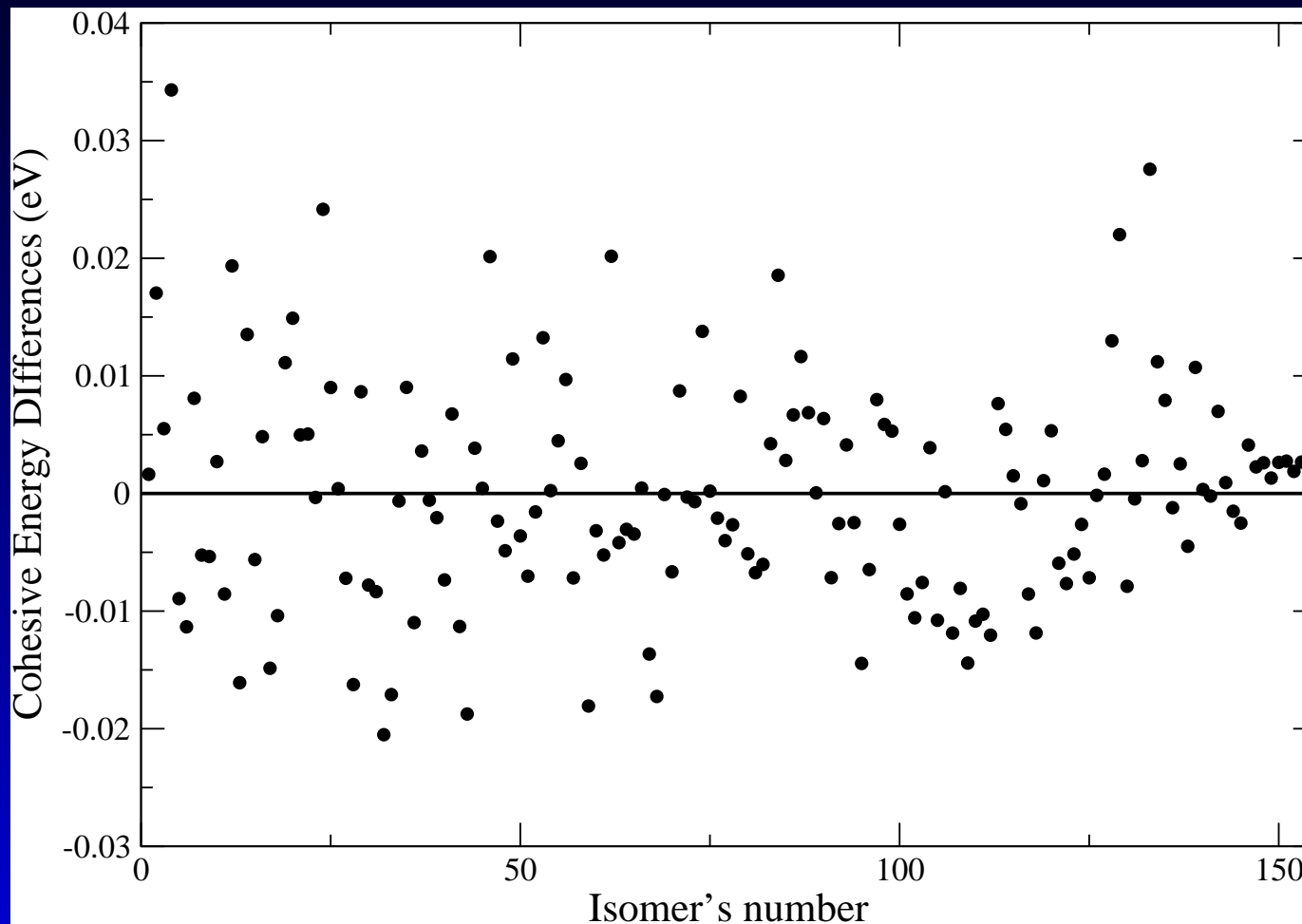
$$E_{coh} = 0.01477N_p + 4.9528N^{-5/6} - 0.16585, \quad R^2 = 0.9927.$$

- N^{-1}

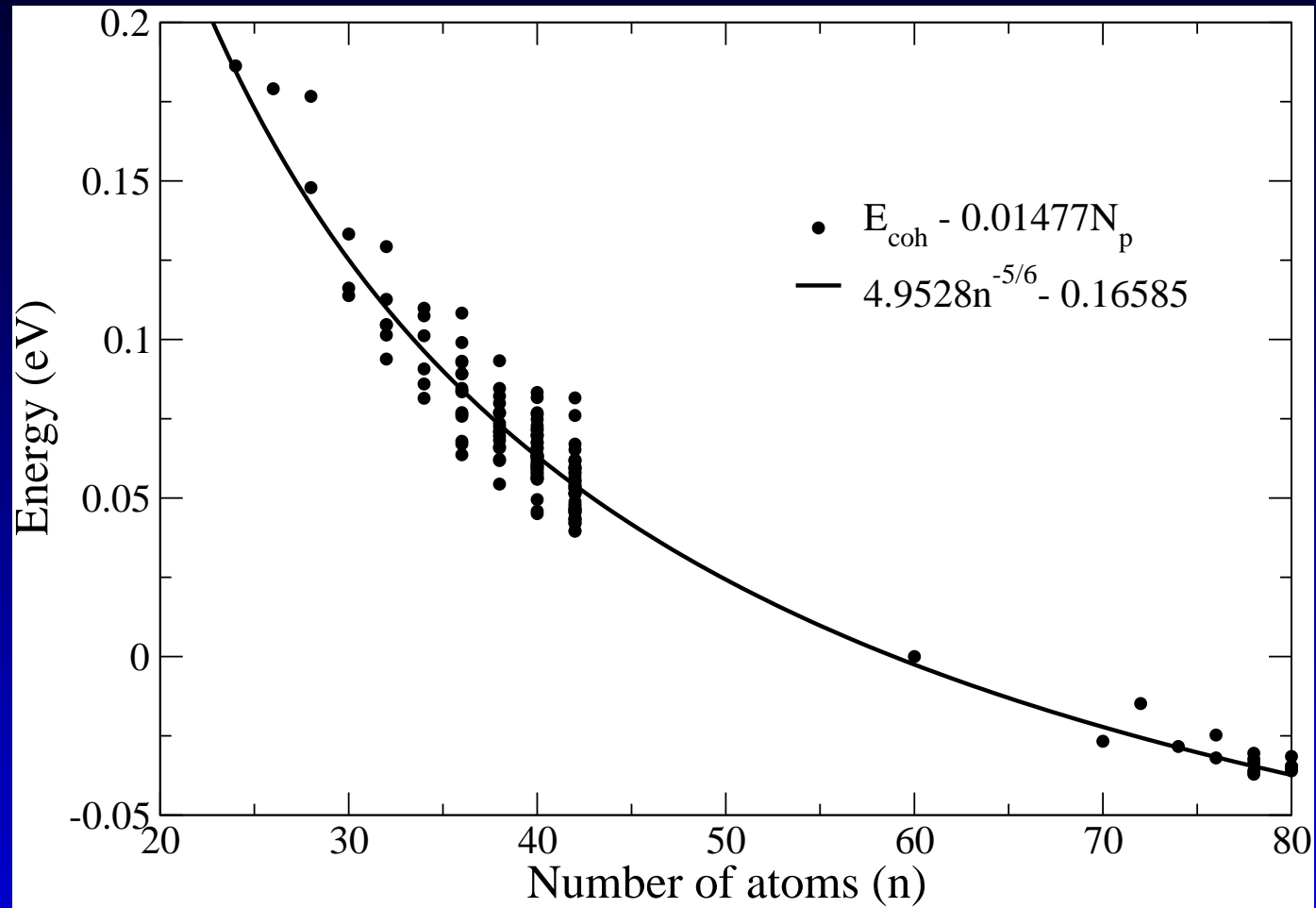
$$E_{coh} = 0.01504N_p + \frac{7.5657}{N} - 0.1299, \quad R^2 = 0.9929$$

- If $N \rightarrow \infty$ then: $E_{coh} = AN_p + B$
If $\Delta N_p = 1$ then $\Delta E_{coh} \approx 0.015eV$
just for a single defect !!!

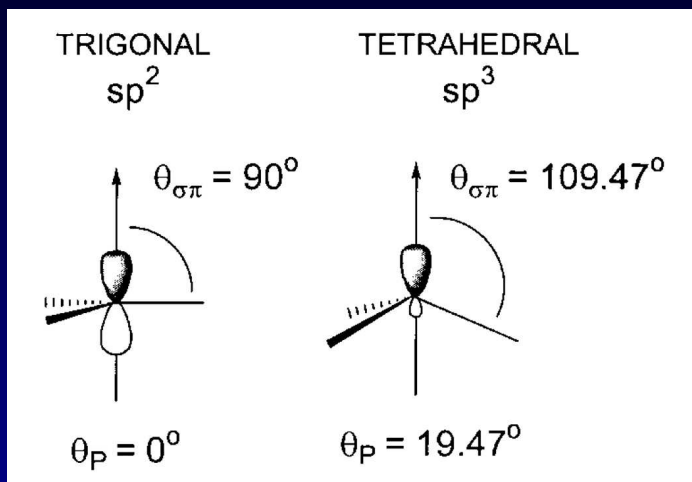
Error for the Whitten and Lee Model



E_{coh} vs N for the Whitten and Lee Model



Pyramidalization angle



Pyramidalization
angle

$$\theta_{p_i} = \theta_{\sigma\pi_i} - 90^\circ$$

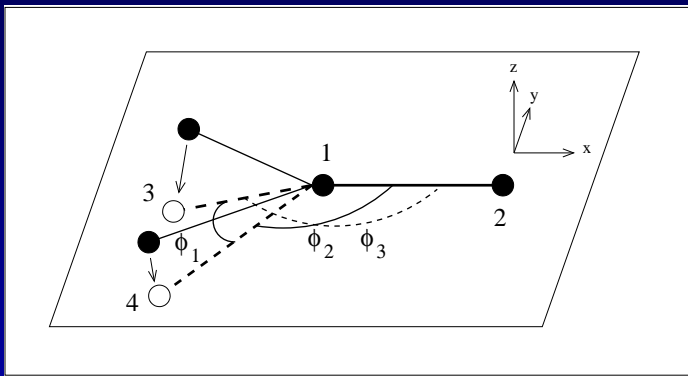
$$\Delta H_f^c = a \left(\frac{1}{N} \sum_{i=1}^N \theta_{p_i}^2 \right) + b.$$

ΔH_f^c = heat of formation per atom

D. Bakowies and W. Thiel, J. Am. Chem. Soc **113**, 3704 (1991)

Alternatively...

- $\phi_a = \phi_1 + \phi_2 + \phi_3$ ($\phi_a^{(ideal)} = 360^\circ - 12^\circ n_{p_i}$)
- Defect angle: $\phi_d = 360^\circ - \phi_a$ ($\phi_d^{(ideal)} = 12^\circ n_{p_i}$)



$$\theta_p^2 \propto \phi_{di}$$

- Descartes theorem:

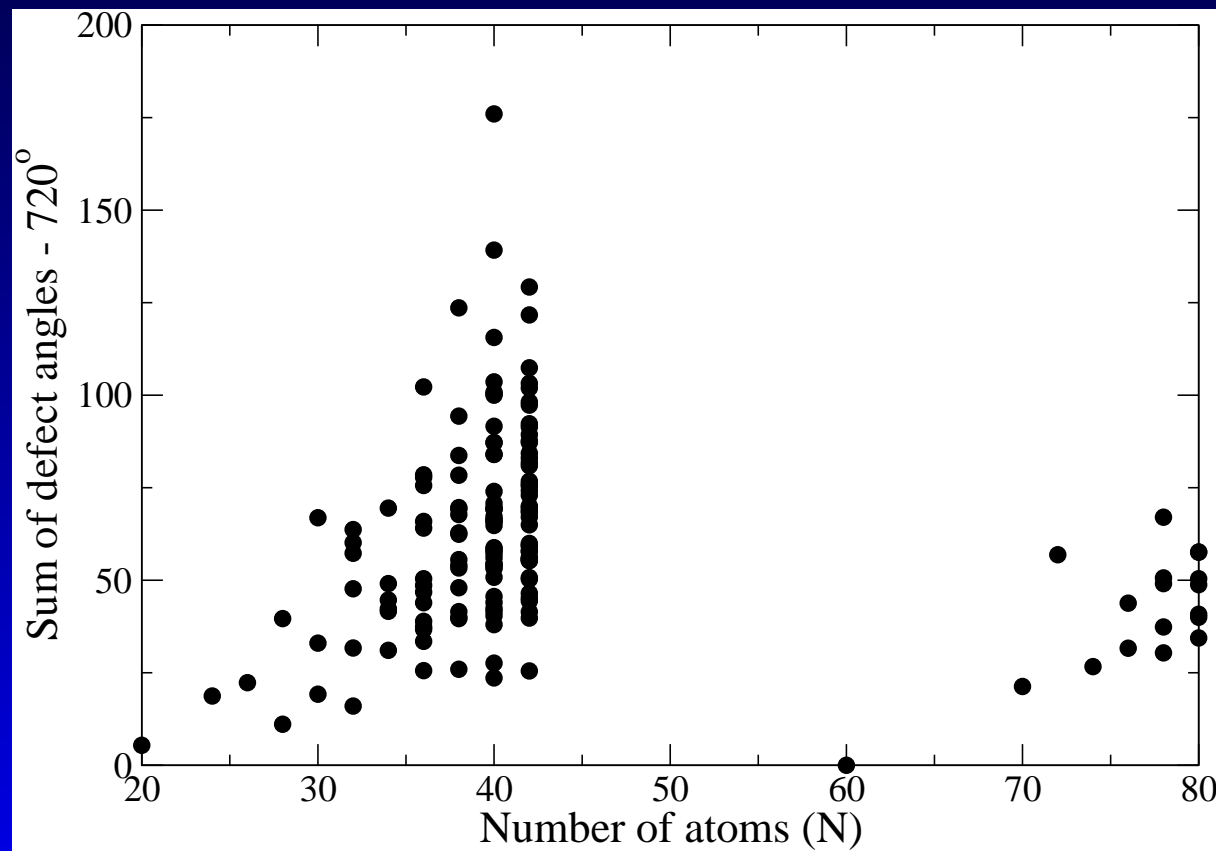
$$\sum_{i=1}^N \phi_{di} = 4\pi$$

(T. G. Schmalz, W. A. Seitz, D. J. Klein and G. E. Hite, J. Am. Chem. Soc. **110**, 1113 (1988));

P. J. Federico *Descartes on Polyhedra*, Springer Verlag, Berlin (1982)

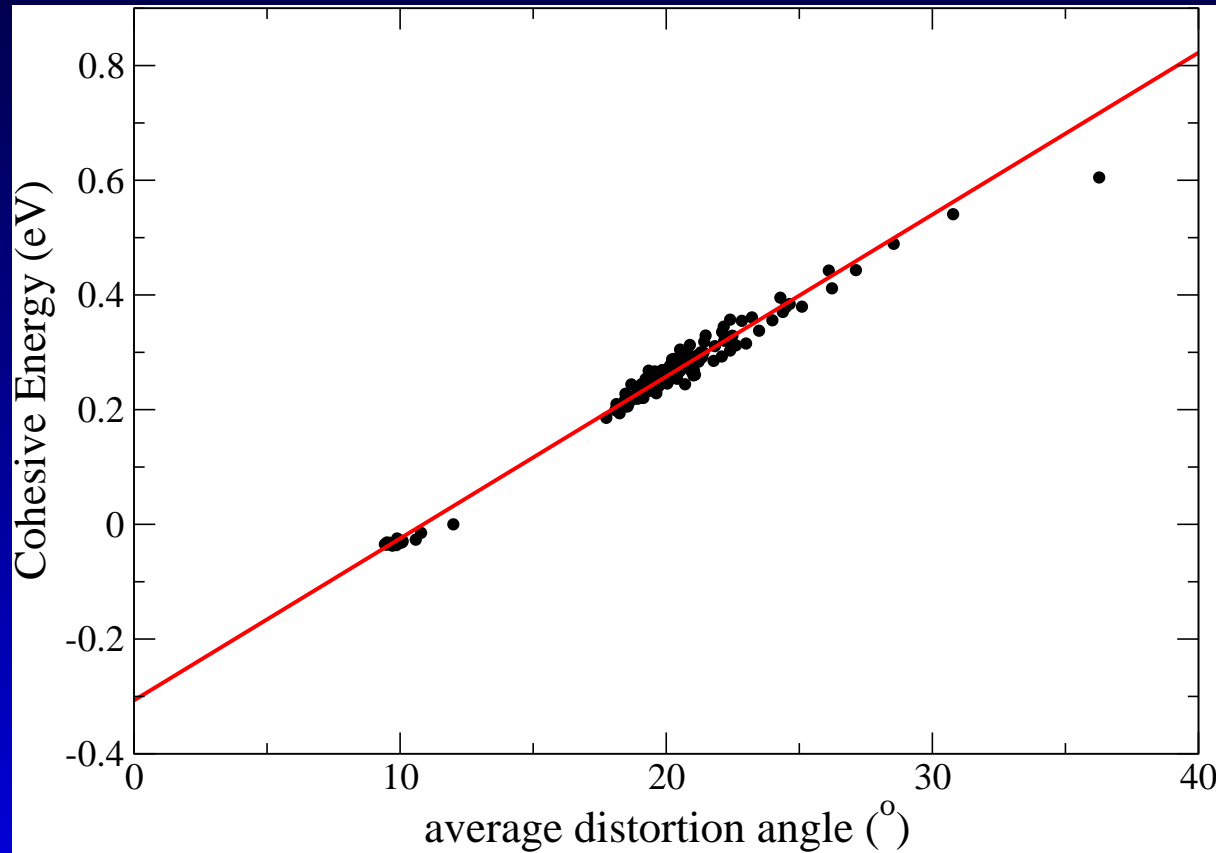
Descartes theorem "violation"

The difference $\sum_{i=1}^n \phi_{di} - 4\pi$ vs n

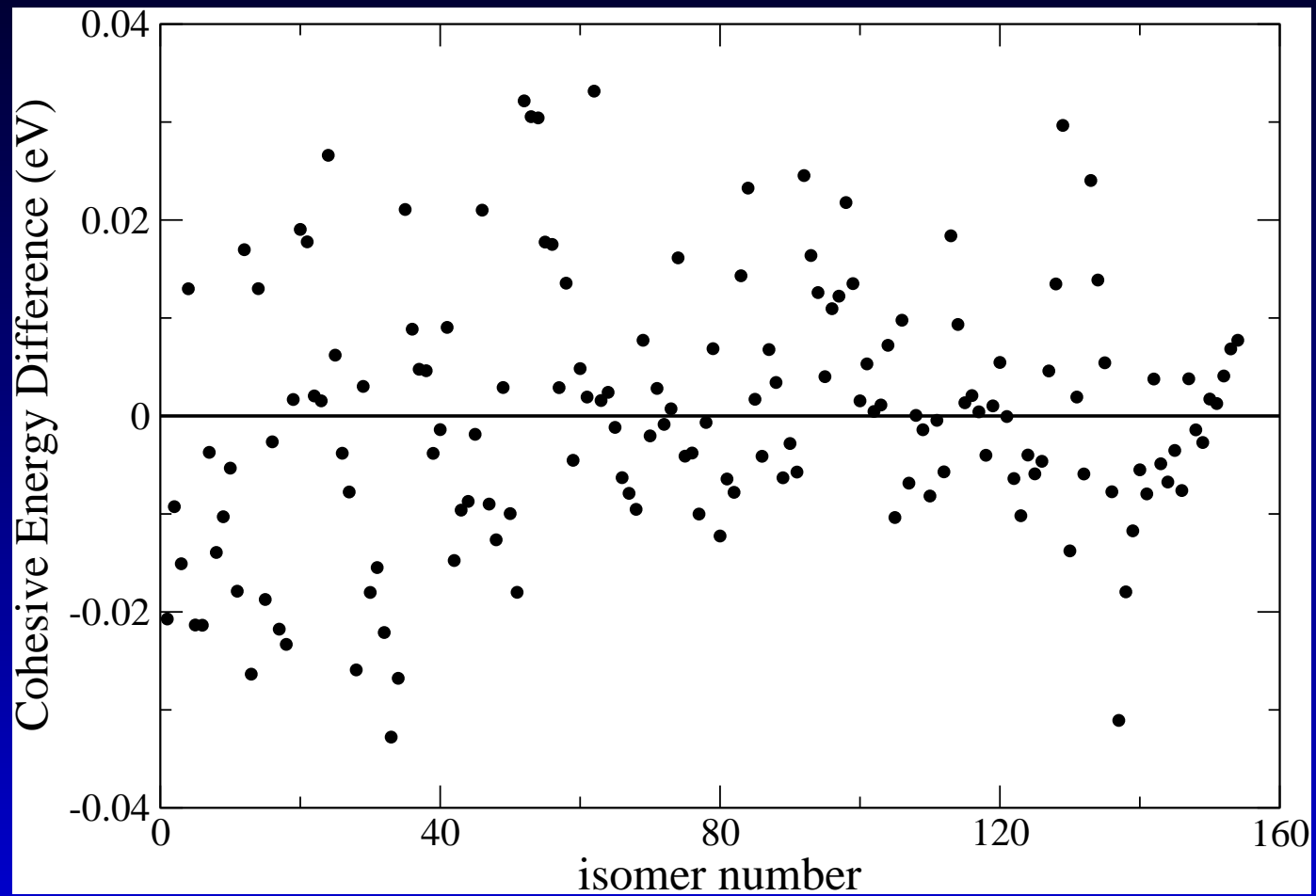


Cohesive Energy vs $\langle \phi_d \rangle$

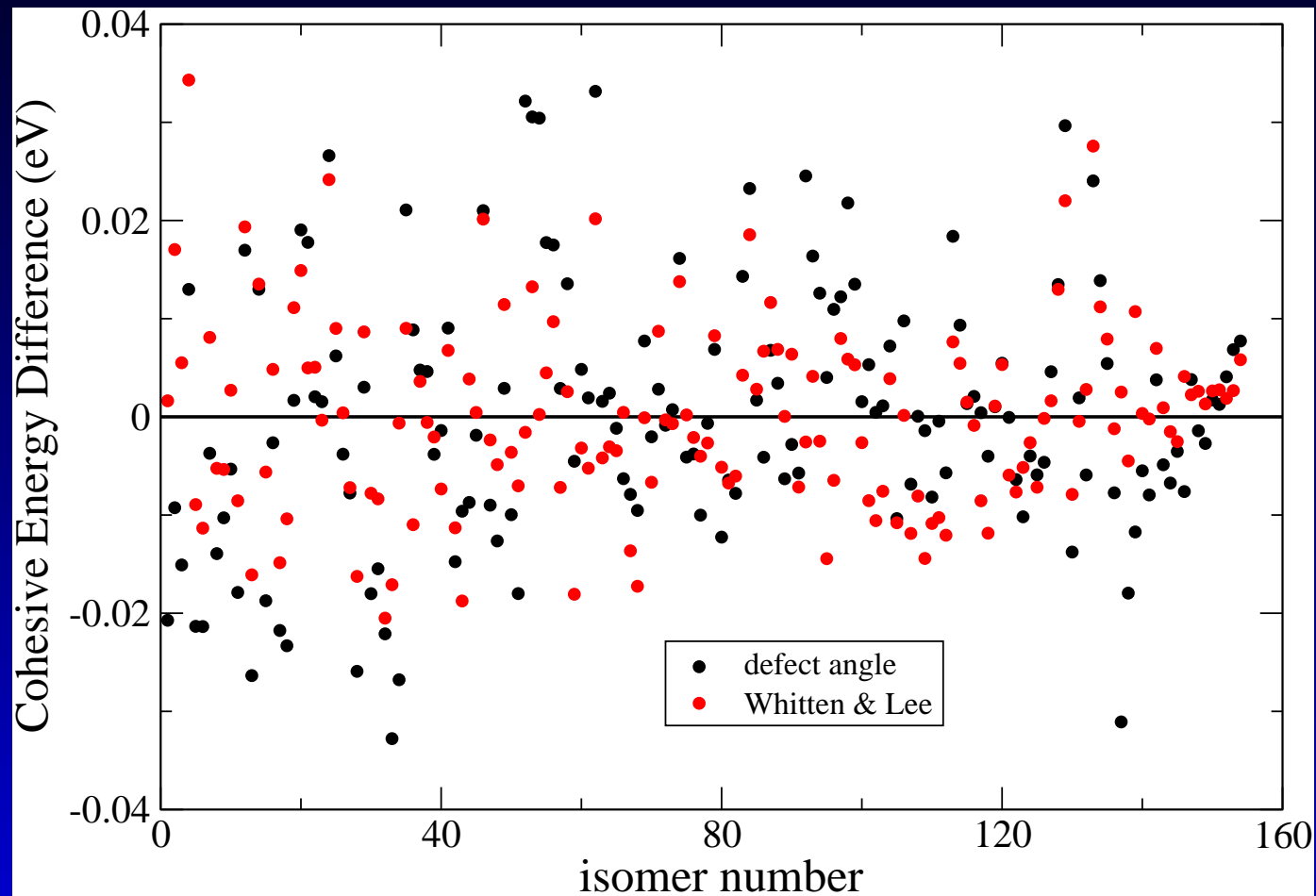
$$E_{coh} = 0.02824\langle \phi_d \rangle - 0.30783(eV)$$



Error



Error



Relation between $\langle \phi_d \rangle$ and N_p

-

$$U_{coh} = AN_p + \frac{B}{N} + C$$

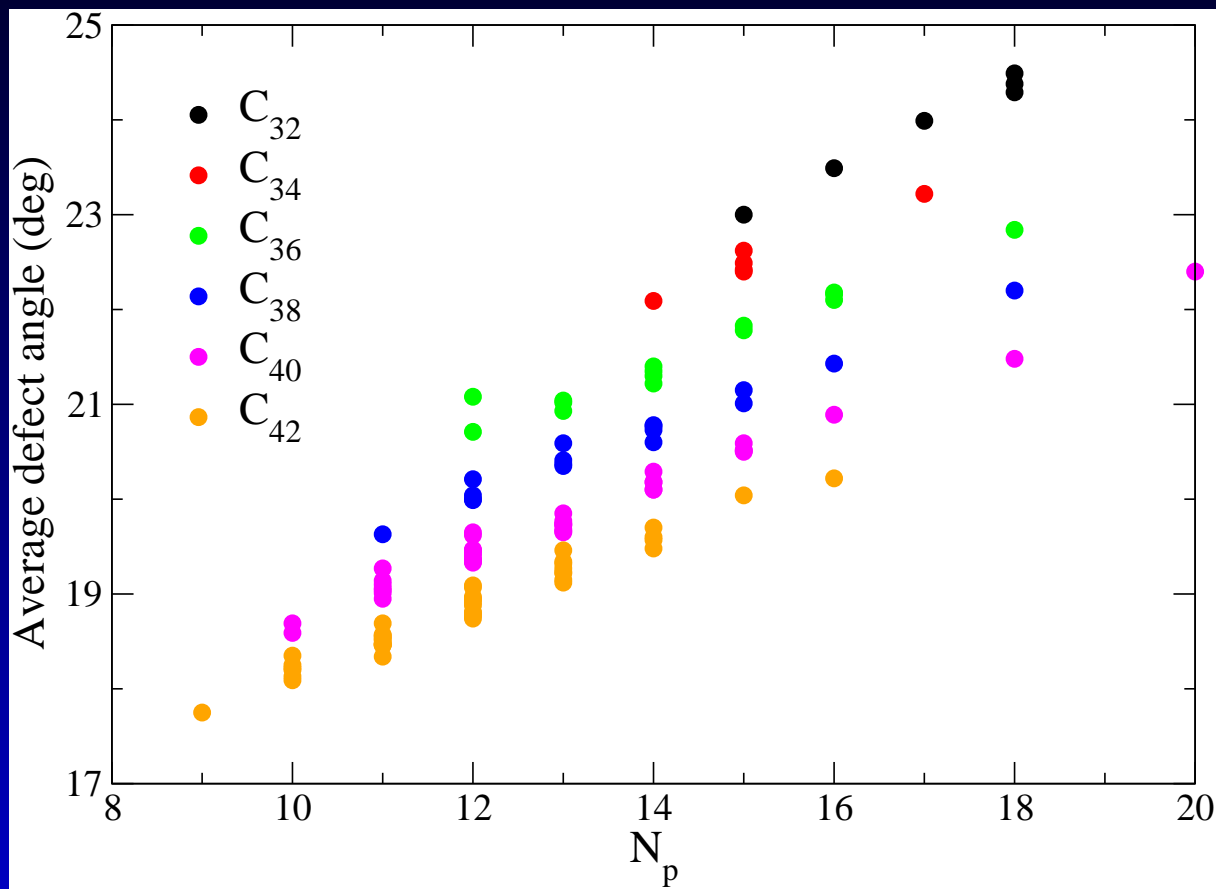
-

$$U_{coh} = a\langle \phi_d \rangle + b$$

CONSEQUENTLY:

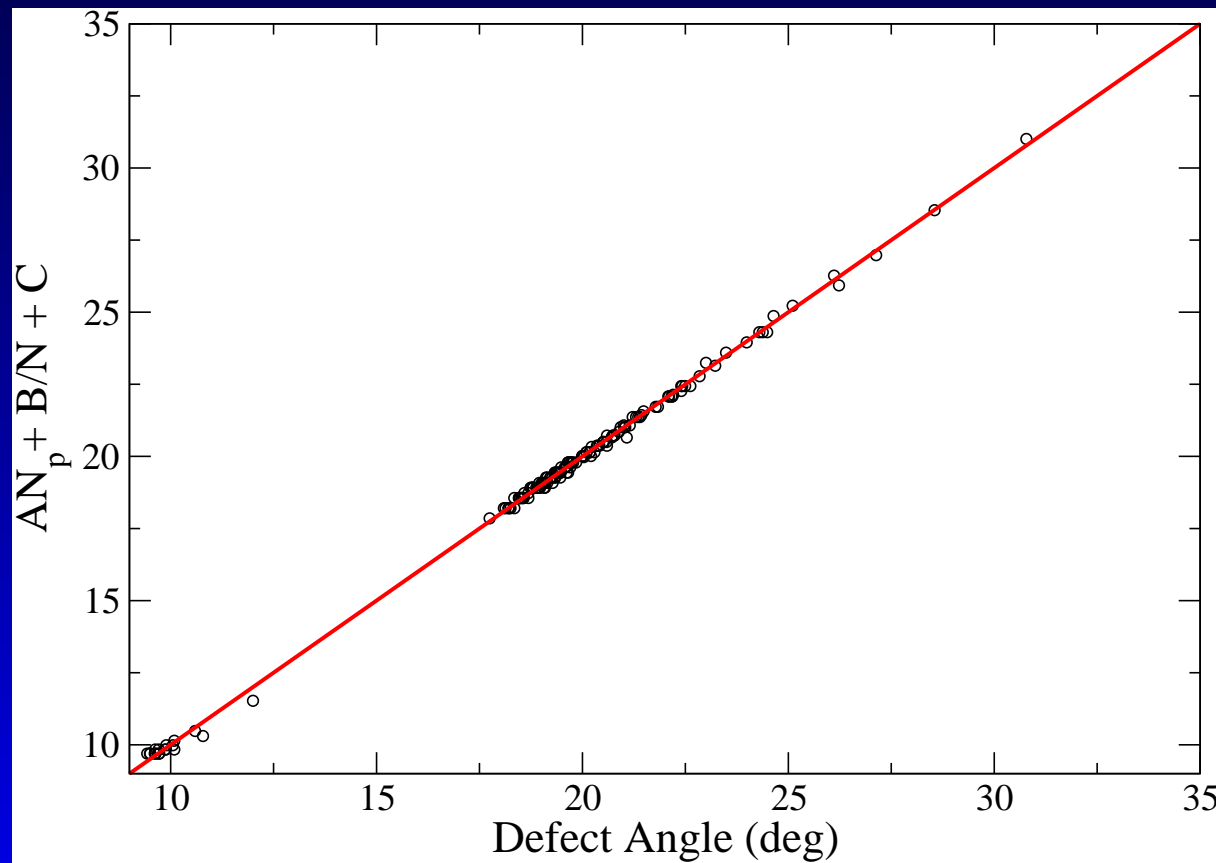
$$\langle \phi_d \rangle = A'N_p + \frac{B'}{N} + C'$$

$\langle \phi_d \rangle$ vs N_p



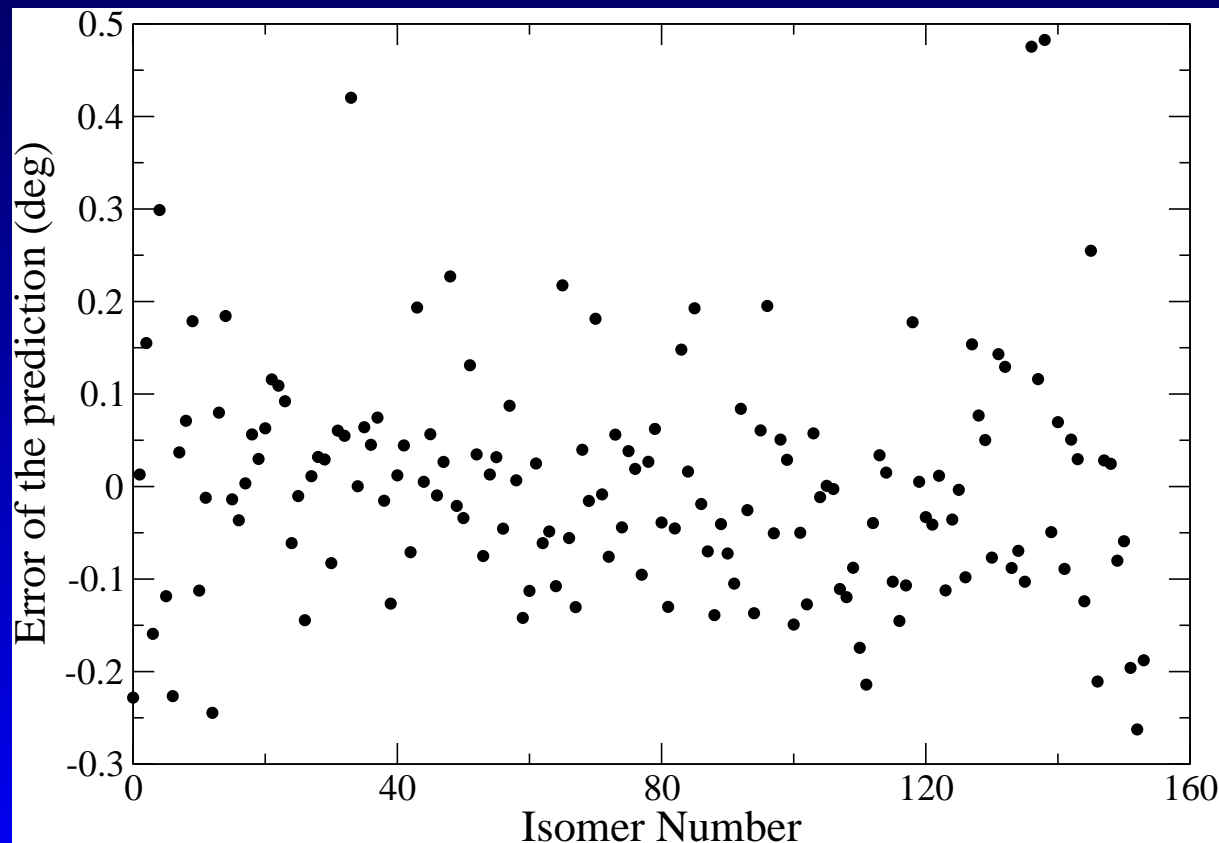
$\langle \phi_d \rangle$ prediction

$$\langle \phi_d \rangle = 0.3541 N_p + \frac{439.44}{N} + 4.2005$$



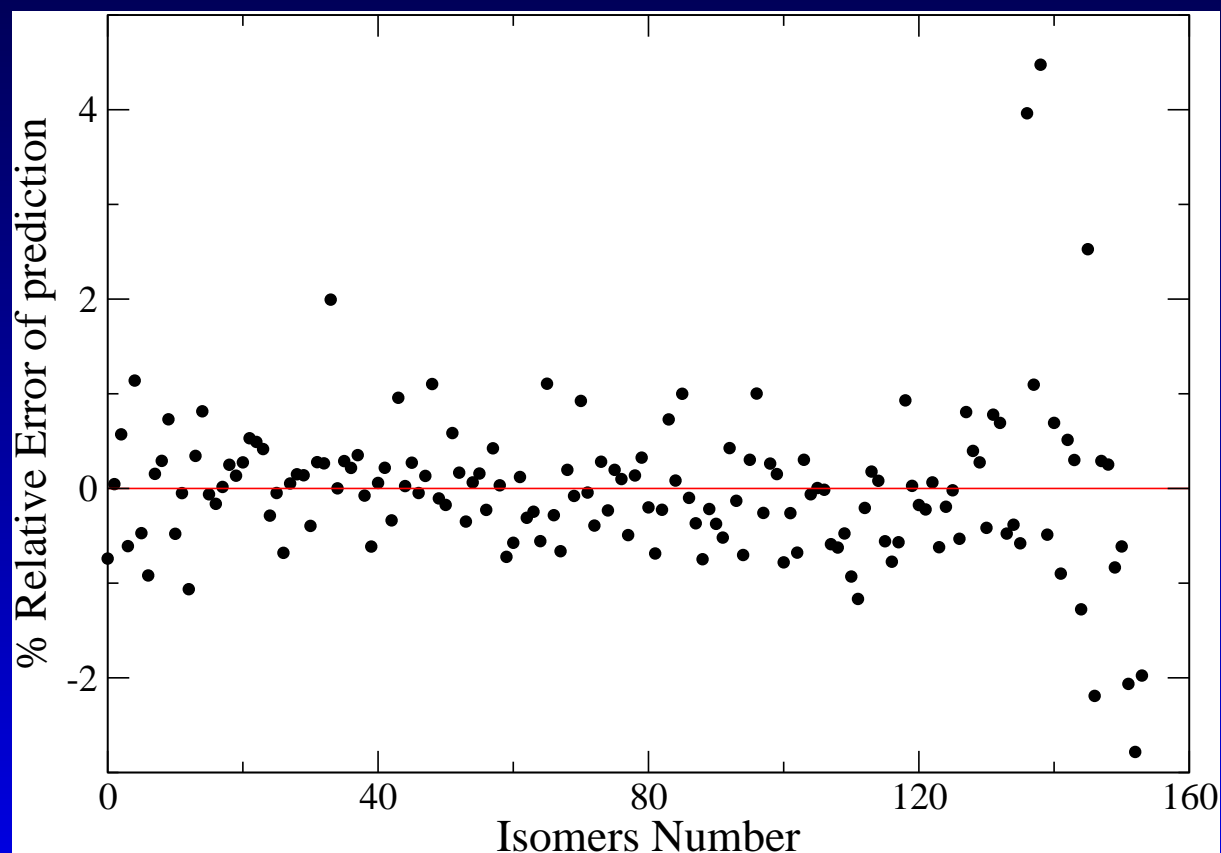
Error of the prediction

$$\text{Error} = \langle \phi_d \rangle - \left(0.3541 N_p + \frac{439.44}{N} + 4.2005 \right)$$



Relative error of the prediction

$$\% \text{ Relative Error} = 100 \times \frac{\langle \phi_d \rangle - \left(0.3541 N_p + \frac{439.44}{N} + 4.2005 \right)}{\langle \phi_d \rangle}$$



Conclusion

- U_{coh} can be predicted vs N_p and N
- $\langle \phi_d \rangle$ can be predicted vs N_p and N
- Distortions on planar surfaces of pentagons and hexagons are related with N_p and N
- The cohesive energy dependence on N_p comes from the surface distortions of the pentagons and hexagons