NONCOVALENT INTERACTIONS:
A USEFUL TOOL FOR CRYSTAL AND MATERIALS DESIGN

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NONCOVALENT INTERACTIONS

Noncovalent interactions (NCIs) do not involve the sharing of electrons, but rather involve electrostatics, charge transfer, vdW forces between molecules…

Dykstra and Lisy, *Journal of Molecular Structure (Theochem)* 500 (2000) 375–390

NONCOVALENT INTERACTIONS

Key role in many chemical and biological processes

· Biomolecular function and activity
· Molecular reactivity
· Bulk properties of gases
· Crystal structure
· Macroscopic properties of condensed phases
· Nonlinear optical response of solid state polymers
· Reaction dynamics in liquids
· Solvation phenomena
· Surface and electrode chemistry
· Tribology and adherence of materials

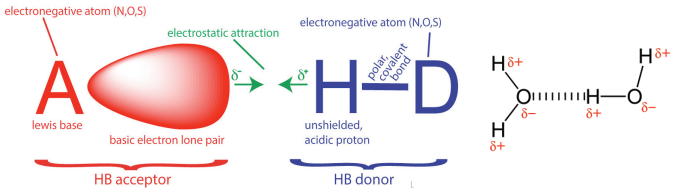
Dykstra and Lisy, *Journal of Molecular Structure (Theochem)* 500 (2000) 375–390

NONCOVALENT INTERACTIONS

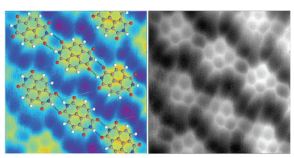
	Strength in kcal/mol
Electrostatics	
- Ionic (NaCl)	250 – 4000
- Hydrogen bonding (H_2O)	5 – 40
- Hole interactions (halogen, chalcogen, etc.)	1 – 20
Van der Waals	
- Debye forces (permanent- induced dipoles)	1 – 10
- London dispersion (alkanes)	
π-effects	
- π/π stacking (graphite)	1 – 20
- Cation and anion-π (Cl^-—C_6F_6)	

HYDROGEN BONDING

The classical hydrogen bond



F-H···F	40 kcal/mol	1 Å	Covalent
O-H···N	30 kcal/mol		
O-H···O	20 kcal/mol	2 Å	Mostly electrostatic
N-H···N	13 kcal/mol		
N-H···O	8 kcal/mol	> 2.5 A	Electrostatic

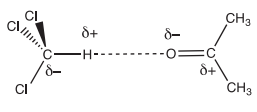


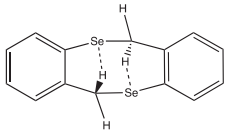
Phys. Rev. B 90 (2014), 085421

HYDROGEN BONDING

Non-classical hydrogen bonds

1. Weak donor – strong acceptor: C-H····O, C-H···N, C-H···S, P-H···O, C-H···Cl^-





2. Strong donor – weak acceptor: O-H···F-C, O-H····Se, O-H···C=C, N-H···Co

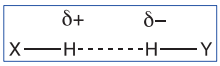
3. Weak donor – weak acceptor: C-H···Pt, C-H···F-C, C-H···Cl-C, C-H···H-Re

General features: < 4 kcal/mol, d = 2.4 – 3.0 Å, less directional, vanishing covalency

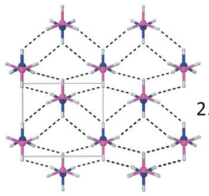
DIHYDROGEN BONDING

Dihydrogen interactions

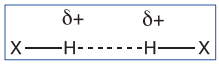
- Heteropolar dihydrogen bonds

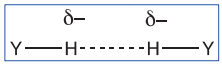


N-H···H-B in the dimer of ammonia-borane

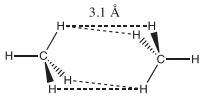


- Homopolar dihydrogen interactions

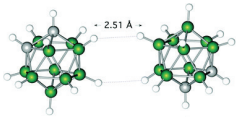




C-H···H-C in alkanes



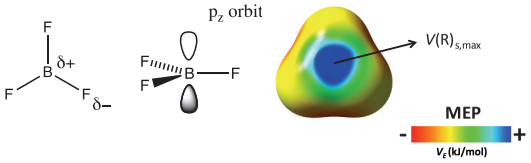
B-H···H-B in boranes



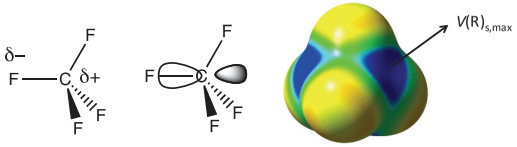
π/σ-hole interactions

The electron density hole concept

π-hole



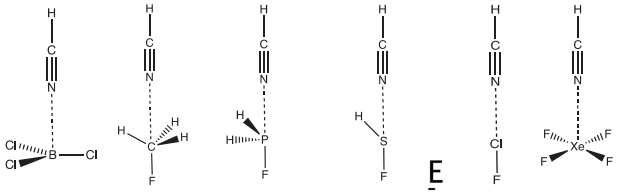
σ-hole



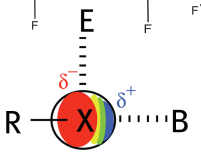
π/σ-hole interactions

A plethora of bond names…

Triel Tetrel Pnictogen Chalcogen Halogen Aerogen



- High directionality
- Electrostatically driven
- Degree of CT variable
- Present in condensed phases



B = nucleophile
E = electrophile
X = Cl, Br, I

Computational tools

Electronic structure calculations

Post-HF	CCSD(T)	"Gold Standard"
	MP2	Good but… tends to overestimate NCIs
DFT	Periodic	vdW description of surface
	Gas phase	B3LYP-D3 for dihydrogen bonds
		LC-ωPBE-D3BJ for metallophilic interactions
		M06-2X for halogen bonding
Basis sets	Triple-ξ mandatory, polarization and diffuse recommended	

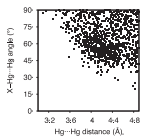
Benchmarking is usually the safest option

Computational tools

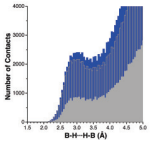
Structural database mining

Access to millions of crystal structures: CSD, PDB, ICSD, Mogadoc…

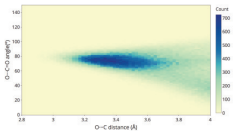
Angular dependence



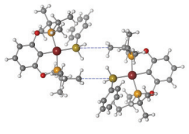
Occurrence



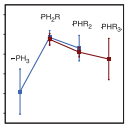
2D histrogram (Heat maps)



Specific examples

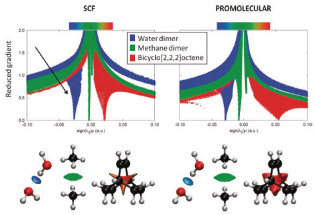


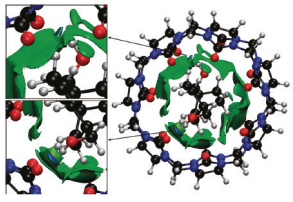
General trends



Computational tools

NCI index calculations (NCIPLOT)





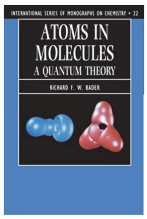
Identification of intermolecular interactions
based on the electron density and its derivatives

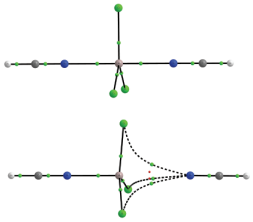
J. Am. Chem. Soc. 2010, **132**, 6498-6506; *J. Chem. Theory Comput.* 2011, **7**, 625-632

Computational tools

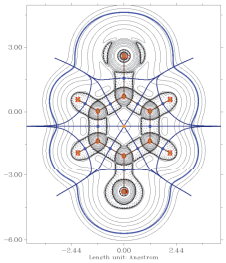
Quantum Theory of Atoms in Molecules – QTAIM (AIMAll)

Analyzes the topology of the electron density





HCN···$AlCl_3$···NCH



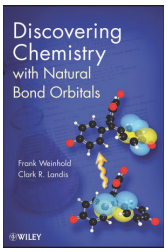
CH_4BrCl

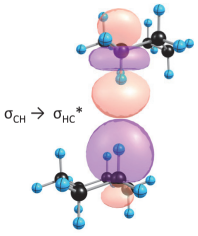
R. Bader, *Atoms in Molecules: A Quantum Theory*. USA: Oxford University Press. (1994)

Computational tools

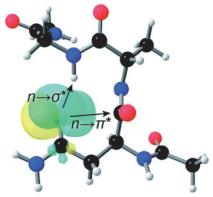
Natural Bond Orbitals – NBO Analysis (NBO6, Gaussian)

Atomic Orbital → NAO → NHO → **NBO** → NLMO → Molecular orbital





Intermolecular



Intramolecular

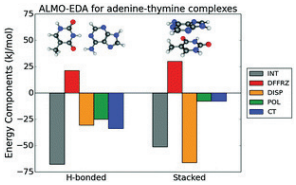
Computational tools

Energy Decomposition Analysis – EDA (Q-Chem, GAMESS, ADF, etc.)

· There are in fact many EDAs… ALMO-EDA, EDA-NOCV, SAPT(DFT)…

· Decomposes total interaction energy in a supermolecule into several energetic terms that are chemically meaningful

$$\Delta E_{int} = \Delta E_{Pauli} + \Delta E_{elect} + \Delta E_{disp} + \Delta E_{pol} + \Delta E_{CT}$$

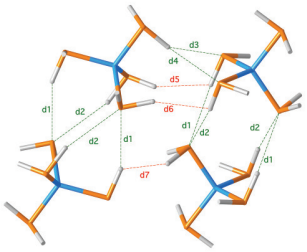


Head-Gordon et al. *Phys. Chem. Chem. Phys.* 2016, **18**, 23067

DIHYDROGEN BONDING

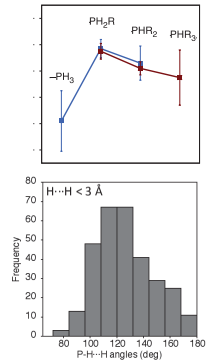
Theoretical study of P-H···H-P interactions

40 structures with H···H < 2.65 Å (CSD)



Tetraphosphanylsilane (ICSD Refcode 408432)

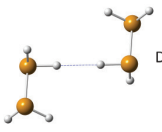
H···H → d5 = 2.52, d6 = 2.55, d7 = 2.12 Å



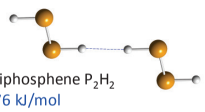
Echeverría et al. *Phys. Chem. Chem. Phys.* 2017, **19**, 28044-28055

DIHYDROGEN BONDING

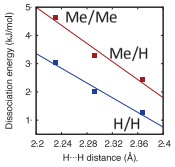
Contact	H···H (Å)	ΔE^{BSSE} (kJ/mol)
CH_4···H_4C^*	2.642	0.539
SiH_4···H_4Si	2.687	0.794
BH_3···H_3B	2.790	0.334
B_2H_6···H_6B_2 [terminal H]	2.631	0.669
$(CH_3)_3CH$···$HC(CH_3)_3$	2.138	3.050
PH_3···H_3P	2.367	1.254
$(CH_3)PH_2$···$H_2P(CH_3)$	2.296	2.174
$(CH_3)_2PH$···$HP(CH_3)_2$	2.230	3.051
P_2H_2···H_2P_2	2.164	2.759
P_2H_4···H_4P_2	2.161	2.550
P_5H_5···H_5P_5 [central H]	2.046	4.473
P_5H_5···H_5P_5 [terminal H]	2.174	2.758
$(CH_3)_2OPH$···$HPO(CH_3)_3$	2.258	4.096



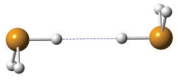
Diphosphane P_2H_4
2.55 kJ/mol

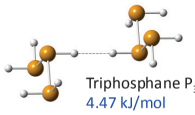


Diphosphene P_2H_2
2.76 kJ/mol



Computational analysis
MP2 / aug-cc-pVTZ



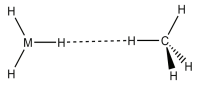


Triphosphane P_3H_5
4.47 kJ/mol

Echeverría et al. *Phys. Chem. Chem. Phys.* 2017, **19**, 28044-28055

DIHYDROGEN BONDING

Abundance and strength of M-H···H-C (M = Al, Ga, In) contacts



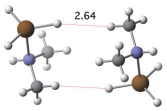
CH_4···H_3Al dimers with topology 1:1

Method	H···H (Å)	ΔE (kJ/mol)	ΔE^{BSSE}
CCSD(T)/CBS	2.594	1.492	-
CCSD(T)/aug-cc-pVQZ	2.588	1.547	1.379
CCSD(T)/aug-cc-pVTZ	2.531	2.006	1.338
MP2	2.553	1.881	1.129
M06-2X	3.062	0.961	0.711
M06-2X-D3	3.053	1.174	0.920
B3LYP-D3	2.519	1.630	1.254
PBE0-D3	2.500	2.215	1.881
ωB97xD	2.509	1.588	1.212
LC-ωPBE-D3BJ	2.660	1.379	1.045

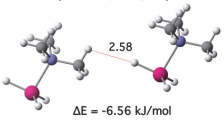
Echeverría, *Cryst. Growth Des.* 2017, **17**, 2097-2103

DIHYDROGEN BONDING

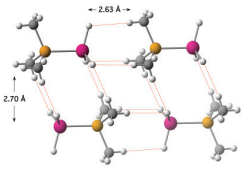
Abundance and strength of M-H···H-C (M = Al, Ga, In) contacts



ΔE = -22.03 kJ/mol

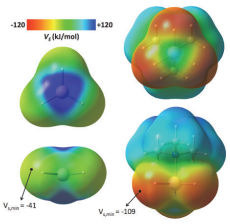


ΔE = -6.56 kJ/mol



ULEYIT: Only **Ga-H···H-C** contacts
Head-to-tail = 25.6 kJ/mol
Side-to-side = 41.2 kJ/mol

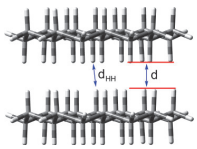
Molecular electrostatic potential (MEP)



Echeverría, *Cryst. Growth Des.* 2017, **17**, 2097-2103

DIHYDROGEN BONDING

Self-association of graphane



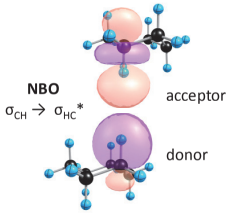
BLW-EDA method

$\Delta E_{binding} = \Delta E_{def} + \Delta E_{int}$

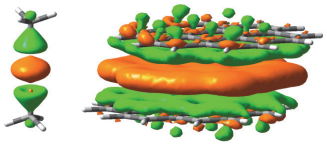
$\Delta E_{int} = \Delta E_{froz} + \Delta E_{pol} + \Delta E_{CT} + \Delta E_{disp}$

-216 187 -4 -33 -368

(kJ/mol) 73C model



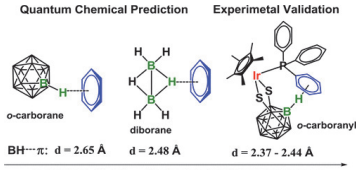
Electron density difference (**EDD**) maps



Schreiner, Shaik et al. *J. Chem. Theory Comput.* 2015, **11**, 1621-1630

HYDROGEN BONDING

The controversy of B-H···π hydrogen bonding



· ΔE_{int} = 21 kJ/mol (ωB97xD)
· Stretching force constant ≈ water
· Electrostatic in nature

Zhang et al. *J. Am. Chem. Soc.* 2016, **138**, 4334 – 4337

… but force constants were not properly calculated…

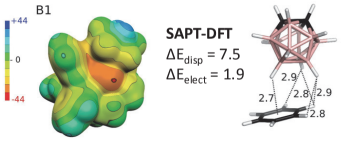
Table 1. Relevant computed B–H···π force constants and their coupling terms.[a]

Force constants	Zhang et al.[5]	This work
B–H···π	0.189	0.061
H_2O···H_2O	0.087	0.180
B–H···π coupling	–	0.003
O–H···π coupling	–	−0.7

[a] See the text for details. Values are given in mdyn Å^{-1}.

Grunenberg, *Chem. Eur. J.* 2016, **22**, 18678 - 18681

… and the interaction might have different origin



Hobza et al. *Phys. Chem. Chem. Phys.*, 2017, **19**, 18194 - 18200

HYDROGEN BONDING

⚠CAUTION

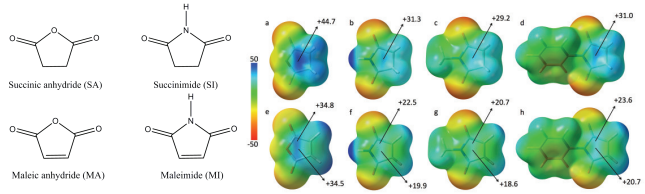
Computational tools are useful to study NCIs

but…

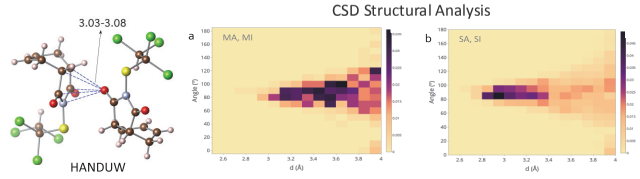
much care must be taken when they are used to interpret new phenomena !

π-hole interactions

Noncovalent interactions in succinic and maleic anhydride derivatives

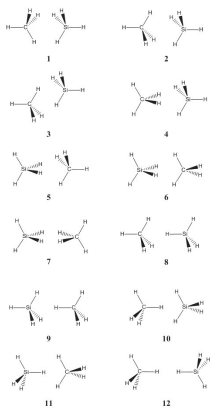


CSD Structural Analysis



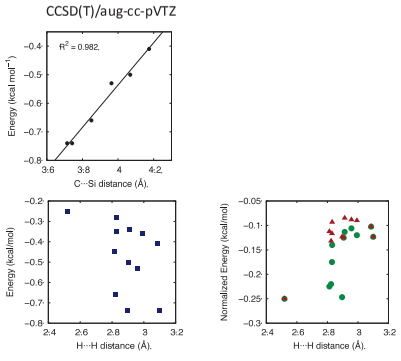
Echeverría; unpublished results

σ-hole interactions



The silane-methane dimer revisited

CCSD(T)/aug-cc-pVTZ

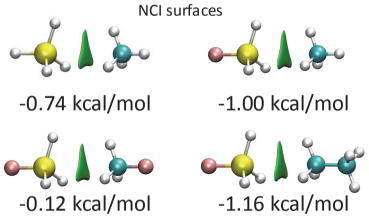


Echeverría, *Phys. Chem. Chem. Phys.* 2017, DOI: 10.1039/c7cp07241d

σ-hole interactions

The silane-methane dimer revisited

NCI surfaces



-0.74 kcal/mol -1.00 kcal/mol

-0.12 kcal/mol -1.16 kcal/mol

σ-donors in C / σ-attractors in Si

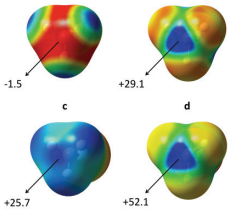
↓

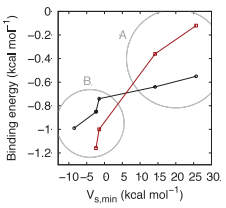
Strengthen the interaction

Echeverría, *Phys. Chem. Chem. Phys.* 2017, DOI: 10.1039/c7cp07241d

σ-hole interactions

The silane-methane dimer revisited





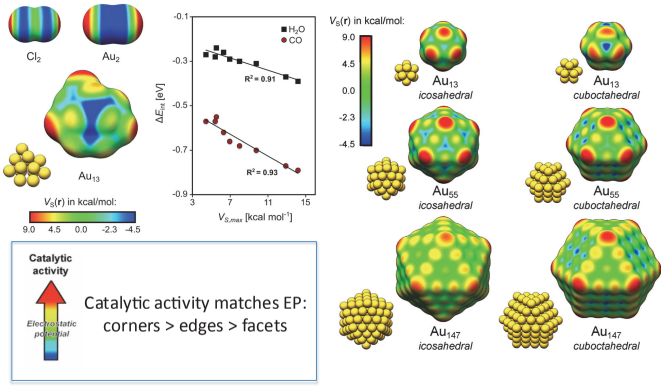
ALMO-EDA (B3LYP-D3)

Dimer	Topol.	ΔE_{Pauli}	ΔE_{Elec}	ΔE_{Disp}	ΔE_{Pol}	ΔE_{CT}	ΔE_{int}
$CH_4\cdots SiH_4$	**1**	2.381	-1.51 (48)	-1.37 (44)	-0.04 (1)	-0.20 (7)	-0.74
$FCH_3\cdots SiH_4$	**1**	2.034	-1.02 (38)	-1.36 (51)	-0.09 (3)	-0.18 (7)	-0.61
$FCH_3\cdots SiH_3F$	**1**	2.096	-0.58 (25)	-1.43 (61)	-0.14 (6)	-0.18 (8)	-0.23
$H_3C\text{-}CH_3\cdots SiH_3F$	**1**	3.558	-2.39 (51)	-1.80 (38)	-0.16 (3)	-0.37 (8)	-1.18
$CH_4\cdots SiH_4$	**12**	0.953	-0.58 (47)	-0.49 (40)	-0.01 (1)	-0.14 (12)	-0.27

Echeverría, *Phys. Chem. Chem. Phys.* 2017, DOI: 10.1039/c7cp07241d

Hole interactions in catalysis

Extending the σ-hole concept to metals: Au and Pt nanostructures



Catalytic activity

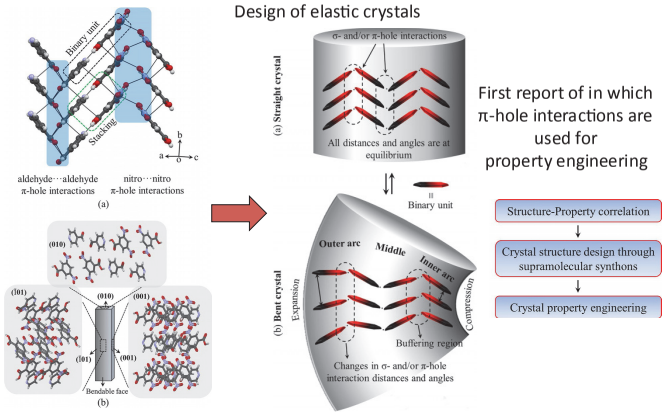
Electrostatic potential

Catalytic activity matches EP: corners > edges > facets

Brinck et al. *J. Am. Chem. Soc.* 2017, **139**, 11012–11015

π/σ-hole interactions

Design of elastic crystals



First report of in which π-hole interactions are used for property engineering

Structure-Property correlation

↓

Crystal structure design through supramolecular synthons

↓

Crystal property engineering

Desiraju et al. *Chem. Eur. J.* 2017, **23**, 4936 – 4943

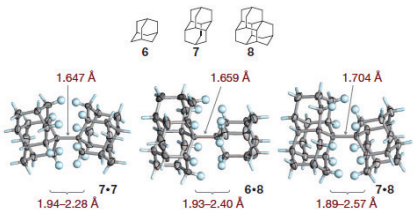
London dispersion

LETTER

doi:10.1038/nature10367

Overcoming lability of extremely long alkane carbon–carbon bonds through dispersion forces

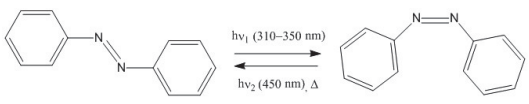
Peter R. Schreiner[1], Lesya V. Chernish[2], Pavel A. Gunchenko[2], Evgeniya Yu. Tikhonchuk[2], Heike Hausmann[1], Michael Serafin[3], Sabine Schlecht[3], Jeremy E. P. Dahl[4], Robert M. K. Carlson[4] & Andrey A. Fokin[1,2]

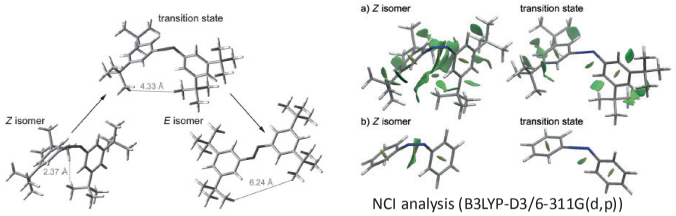


Nature 2011, **477**, 308 - 311

London dispersion

Controlling azobenzene switches



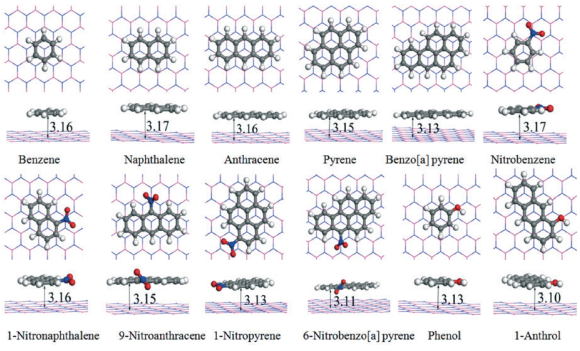


NCI analysis (B3LYP-D3/6-311G(d,p))

Wegner et al. *Angew. Chem. Int. Ed.* 2015, **54**, 13436 - 13439

Noncovalent interactions in 2D materials

Capturing aromatic POPs with h-BN nanosheets

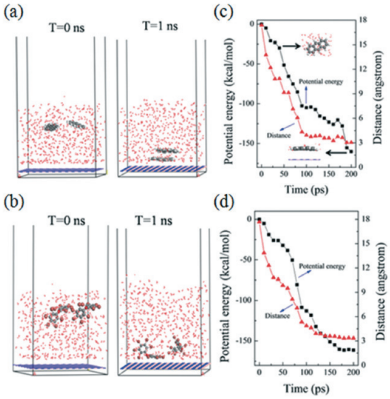


Interaction energies: 15 – 33 kcal/mol

Chen et al. *Environ. Sci.: Nano*, 2016, **3**, 1493 – 1503

Noncovalent interactions in 2D materials

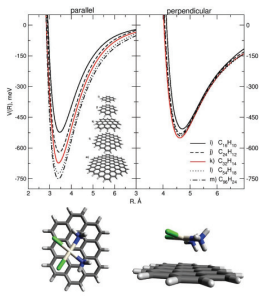
Capturing aromatic POPs with h-BN nanosheets



Chen et al. *Environ. Sci.: Nano*, 2016, **3**, 1493 – 1503

Noncovalent interactions in 2D materials

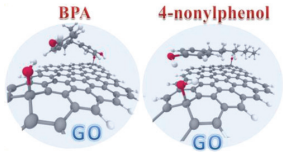
Cisplatin supported on graphene



ΔE_{ads} = 20 kcal/mol
Avoids solubility and toxicity problems

J. Comput. Chem. 2017, DOI: 10.1002/jcc.24920

Adsorption of 4-n-Nonylphenol and bisphenol-A on graphene oxides:



12 kcal/mol 16 kcal/mol

Removal of EDCs from wastewaters

Environ. Sci. Technol. 2015, **49**, 9168 – 9175

Summary

- NCIs are everywhere, they are subtle but not faint
- Important when working additively or cooperatively
- They can affect properties of materials, crystal packing, surface adsorption, etc.
- Useful for property engineering
- In calculations, look for trends to rationalize

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Dr. Gabriel Aullón

Prof. Santiago Alvarez

GOBIERNO DE ESPAÑA MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD
SEVENTH FRAMEWORK PROGRAMME
European Commission

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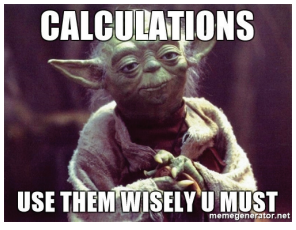

"The purpose of computing is insight, not numbers"
Richard Hamming (1915 – 1998)

THANK YOU FOR YOUR ATTENTION