SUNWAY UNIVERSITY

Non-conventional Interactions in Molecular Crystals

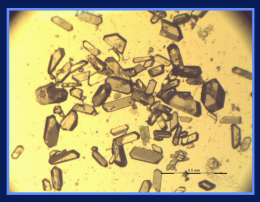
Edward R.T. Tiekink
Research Centre for Crystalline Materials

The 43rd Congress on Science and Technology of Thailand (STT 43)

Molecular packing

Well known…

Hydrogen bonding
Halogen bonding



"Emerging"

Secondary bonding
M···M interactions
M···H interactions
Interactions involving chelate rings

"Non-conventional", "Weak", "Second tier",
"Not really important cf. $(HB)^2$"

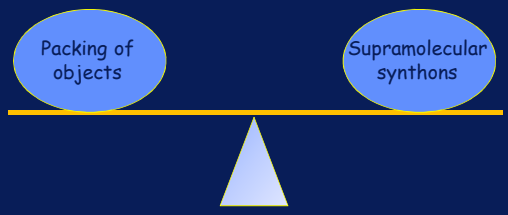
Factors that Control Molecular Packing

Supramolecular synthon approach

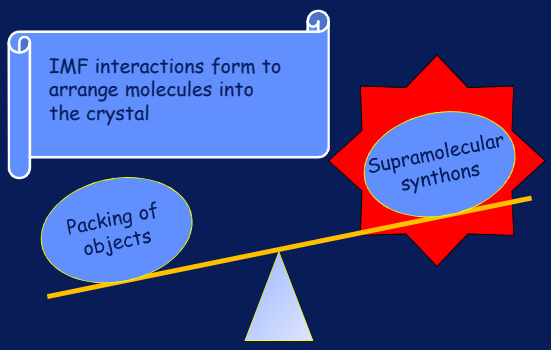
versus

Global crystal packing approach

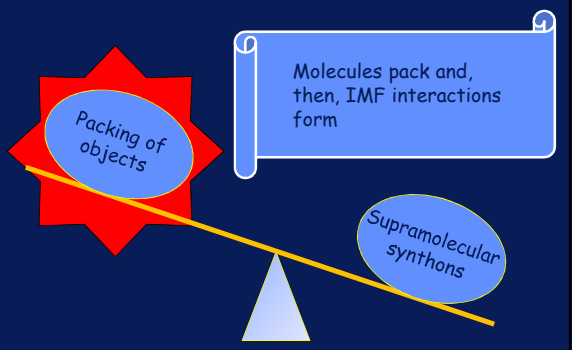
Factors that Control Molecular Packing



Factors that Control Molecular Packing



Factors that Control Molecular Packing



"Egg Causality Dilemma"

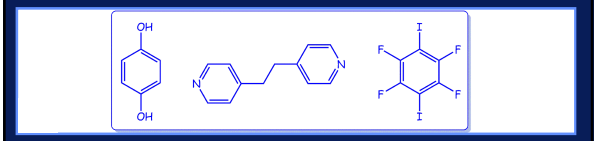
atom…atom or molecule…molecule interactions

Molecular packing

Well known…

Hydrogen bonding
Halogen bonding

Hydrogen Bonding versus Halogen Bonding

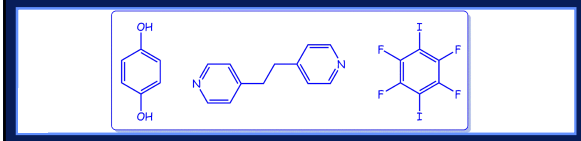


Halogen Bonding versus Hydrogen Bonding in Driving Self-Assembly Processes**

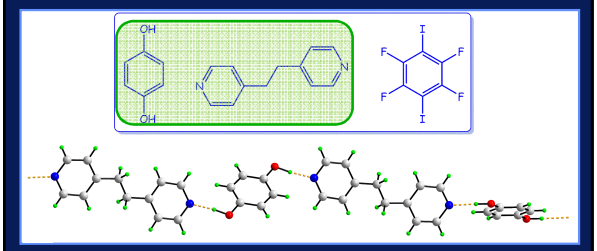
Eleonora Corradi, Stefano V. Meille, Maria T. Messina, Pierangelo Metrangolo,* and Giuseppe Resnati*

  0570-0833/00/3910-1782 $ 17.50+.50/0 *Angew. Chem. Int. Ed.* **2000**, *39*, No. 10

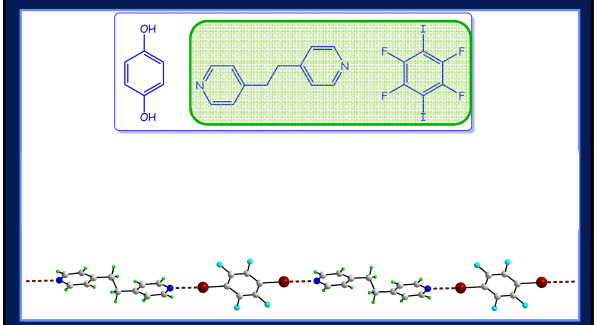
Hydrogen Bonding versus Halogen Bonding



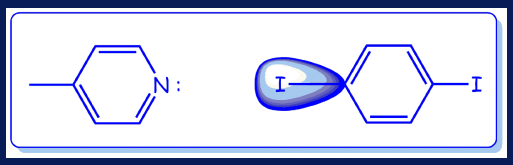
Hydrogen Bonding versus Halogen Bonding



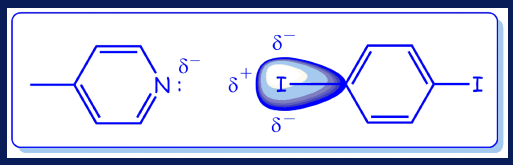
Hydrogen Bonding versus Halogen Bonding



? Halogen Bonding ?

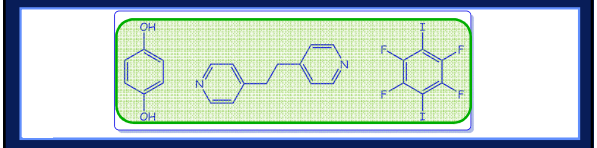


? Halogen Bonding ?

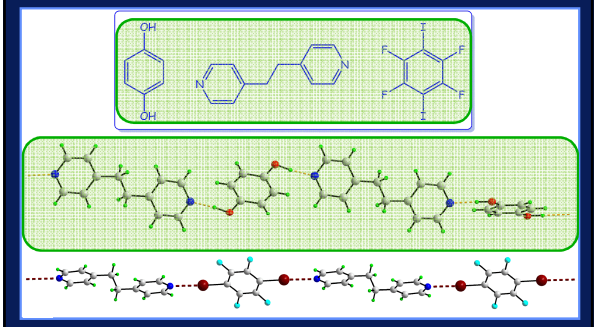


polar gap, σ-hole

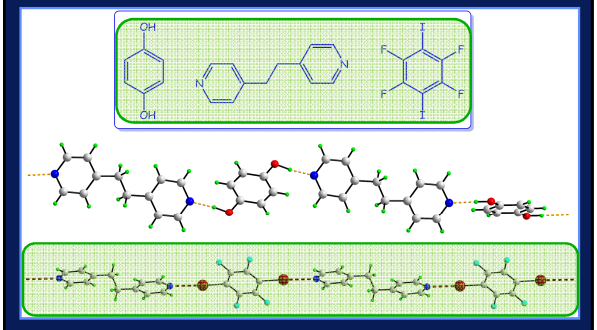
Hydrogen Bonding versus Halogen Bonding



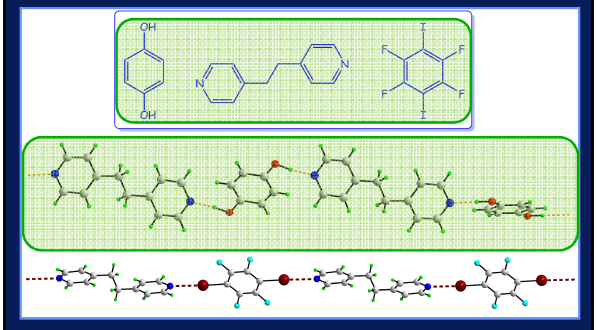
Hydrogen Bonding versus Halogen Bonding



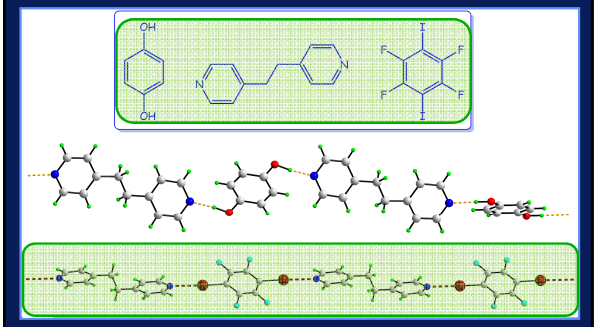
Hydrogen Bonding versus Halogen Bonding



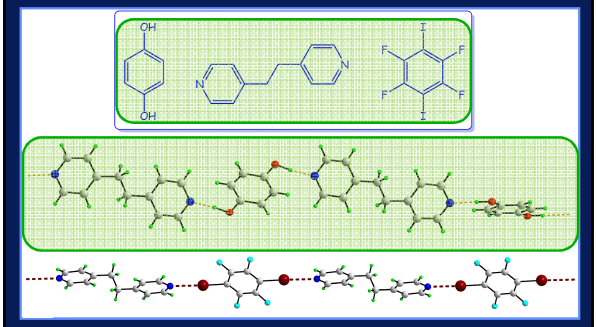
Hydrogen Bonding versus Halogen Bonding



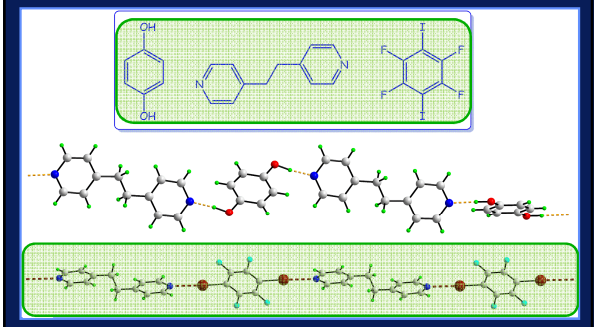
Hydrogen Bonding versus Halogen Bonding



Hydrogen Bonding versus Halogen Bonding



Hydrogen Bonding versus Halogen Bonding



Molecular packing

Well known…

Hydrogen bonding
Halogen bonding

HB[2]: Similar in energy = 5 – 15 kcal/mol

Molecular packing

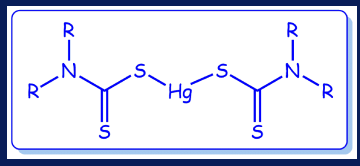
Well known…

Hydrogen bonding
Halogen bonding

"Emerging"

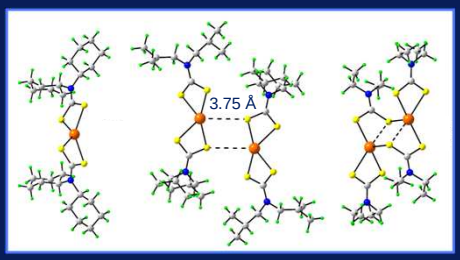
Secondary bonding
M···M interactions
M···H interactions
Interactions involving chelate rings

Steric effects and Secondary Bonding



"$Hg(S_2CNR_2)_2$"

Steric effects and Secondary Bonding



"$Hg(S_2CNR_2)_2$"
Sum of the van der Waals radii for Hg and S = 3.35 Å

← increasing size of R

Inherently weak interactions

How weak?

Inherently weak interactions

How weak?

Repackaging:

Tetrel, pnictogen and chalcogen bonds

Electrophilic sites from Groups 14, 15 & 16, resp.

THE JOURNAL OF PHYSICAL CHEMISTRY A — Article — pubs.acs.org/JPCA

Systematic Elucidation of Factors That Influence the Strength of Tetrel Bonds

Steve Scheiner*

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300, United States

DOI: 10.1021/acs.jpca.7b01030
J. Phys. Chem. A 2017, 121, 5581−5588

$TH_{(4-n)}F(n)$ + $:NH_3$

T = C, Si, Ge & Sn

n = 0	0.9 kcal/mol
n = 1*	6 – 9 kcal/mol
SnF_4	25.5 kcal/mol

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HB^2: Similar in energy = 5 – 15 kcal/mol

$TH_{(4-n)}F(n)$ + $:NH_3$

T = C, Si, Ge & Sn

n = 0	0.9 kcal/mol
n = 1*	6 – 9 kcal/mol
SnF_4	25.5 kcal/mol

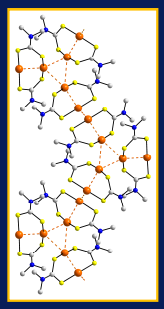
Aurophilic interactions

Au···Au separations in molecular Crystal structures: 2.50 ~ 3.50 Å

Radius from ccp-Au: 2.89 Å

Sum of van der Waals radii: 3.80 Å

$5d^{10}$ closed shell interactions - relativistic effects



Yam *et al. Inorg. Chim. Acta* **358** (2005) 4191.

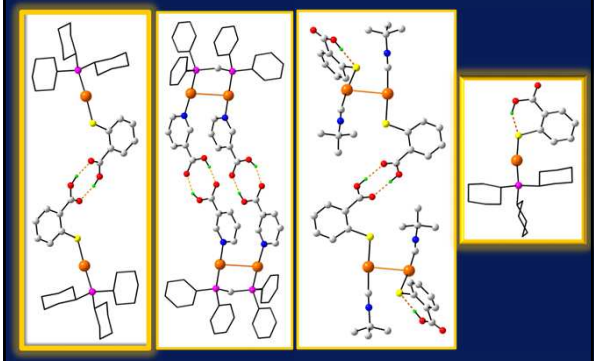
Gold Chemistry

Competition between

i) Au···Au and hydrogen bonding

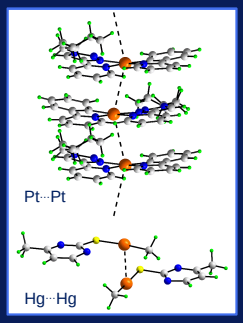
Comparable in energy

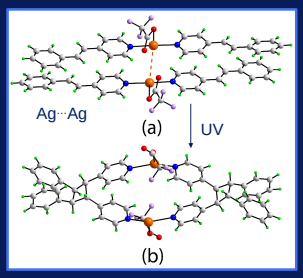
Gold structures with carboxylic acids



Coordination Chemistry Reviews, 275 (2014) 130 – 153

Heterometallophilic (M···M') interactions





Krikorian *et al.*, 2014; Bravo *et al.*, 1986; Chu *et al.*, 2005

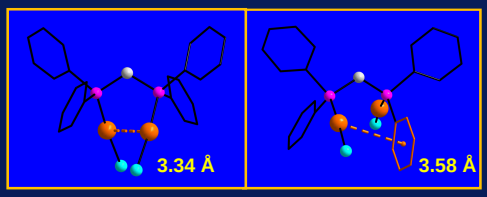
Gold Chemistry

Competition between

i) Au···Au and hydrogen bonding

ii) Au···Au and Au···π(arene)

Polymorphs of $(dppm)(AuCl)_2$

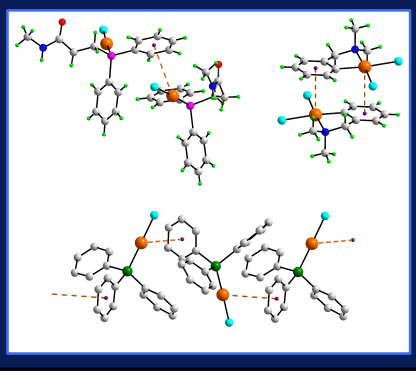


Schmidbaur *et al.* (1977) Healy (2003)

Intermolecular Au···π(arene) interactions

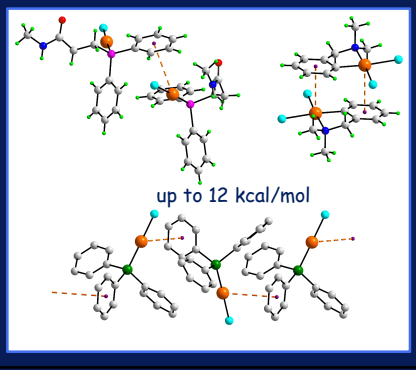
0-D

1-D



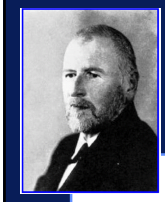
Intermolecular Au···π(arene) interactions

0-D

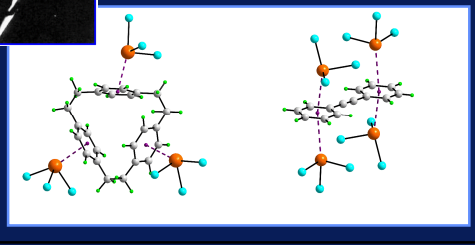


1-D

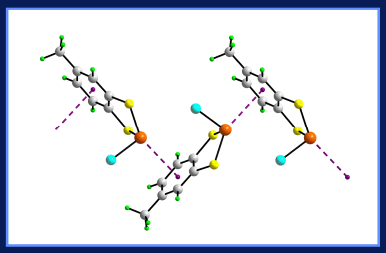
Intermolecular M(lp)···π(arene) interactions



"Menšutkin complexes"



Intermolecular M(lp)···π(arene) interactions



cf. polar gap, σ-hole

Inorg. Chim. Acta, 2008, **361**, 427.

Energy?

ChemComm

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Cite this: *Chem. Commun.*, 2016, 52, 3500

Received 17th December 2015,
Accepted 27th January 2016

DOI: 10.1039/c5cc10363k

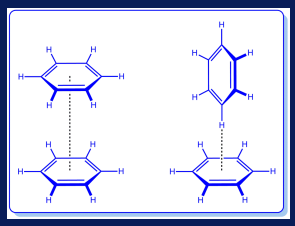
On the nature of the stabilisation of the E···π pnicogen bond in the $SbCl_3$···toluene complex†

Rabindranath Lo,[a] Petr Švec,[b] Zdeňka Růžičková,[b] Aleš Růžička[b] and Pavel Hobza*[ac]

$SbCl_3$ + C_6H_6 7.7 kcal/mol
C_6H_5Me 9.6 kcal/mol
C_6Me_6 15.5 kcal/mol

π-Systems in Supramolecular Chemistry

Classic π-systems/interactions

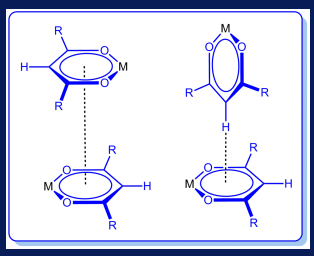


face-to-face edge-to-face

π-Systems in Supramolecular Chemistry

TM Chelate π-systems/interactions

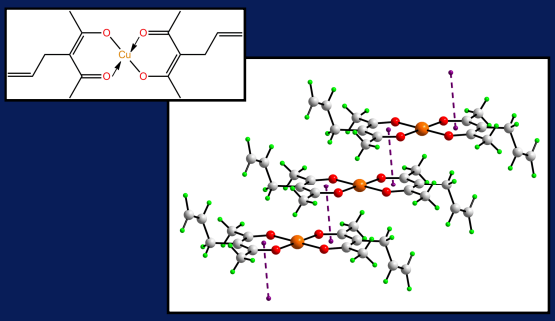
Snezana Zarić



face-to-face edge-to-face

Cryst. Growth Des., 2010, **10**, 3901; *Inorg. Chem.*, 2006, **45**, 4755.

TM π(chelate)···π(chelate) interactions



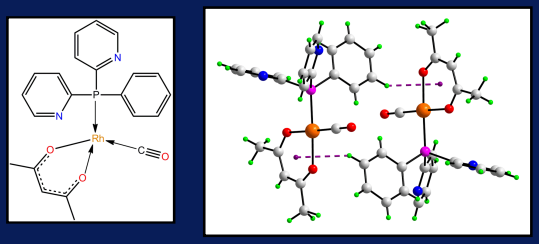
Acta Cryst. C, 1983, **39**, 591.

π(chelate)···π(chelate) interactions

π(chelate)···π(arene) ~ 6 kcal/mol

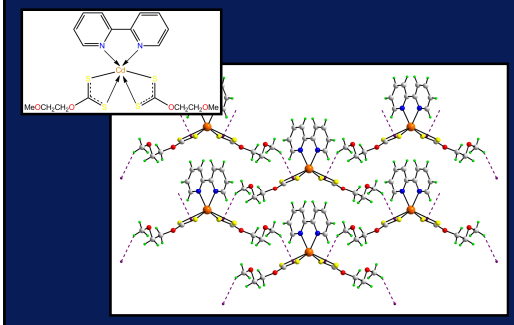
π(chelate)···π(chelate) ~ 9 kcal/mol

TM arene-H···π(chelate) interactions



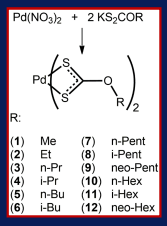
Bull. Pol. Acad. Sci. Chem., 1994, **42**, 205.

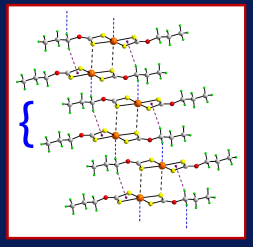
Main group arene-H···π(chelate) interactions



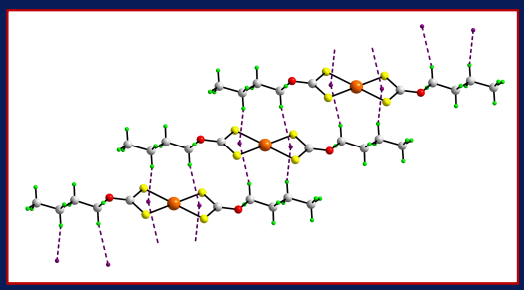
Z. Kristallogr., 2002, **218**, 747.

C—H···π(chelate) interactions:

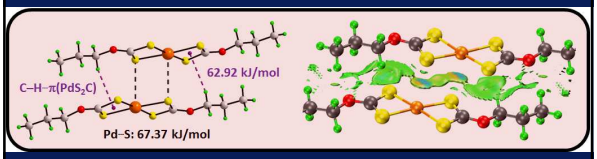




C—H···π(chelate) interactions:

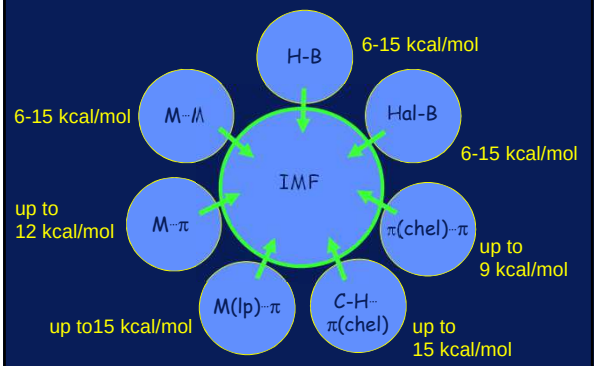


Intermolecular interactions involving chelate rings



Pd···S	16 kcal/mol
C–H···π(chelate)	15 kcal/mol

Overview



Conclusions

More than $(HB)^2$

Energies of "emerging" interactions similar

Sunway University

Fortuna Eruditis Favet ("*Fortune favours the prepared mind*")