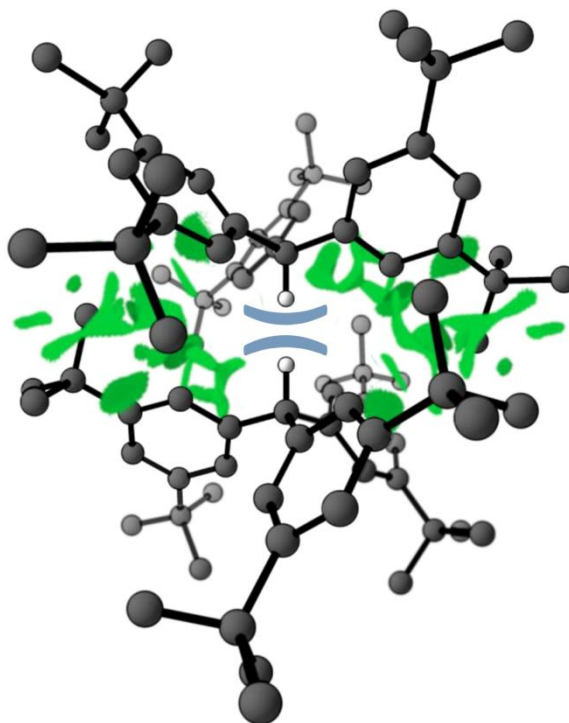


Undercutting short H···H contact limits by *i n t e r* molecular dispersion interactions

Seminar talk presented by
Sören Rösel

March 24st, 2017

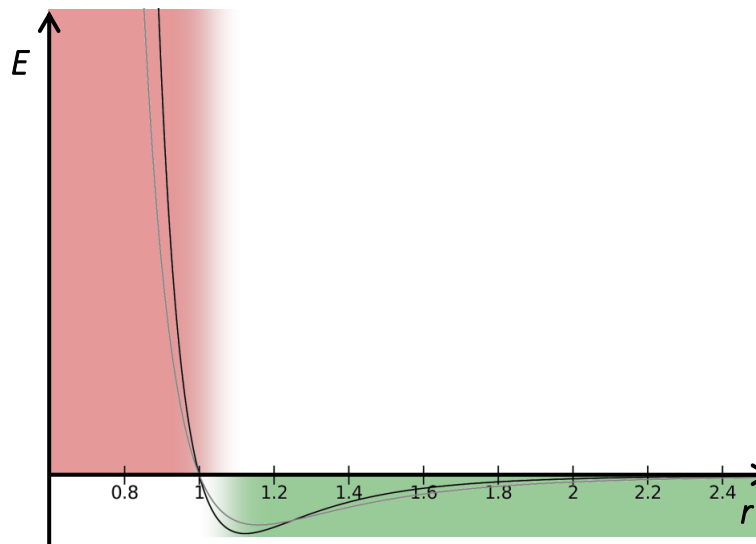
AG Schreiner
Institute of Organic Chemistry
Justus-Liebig University Giessen



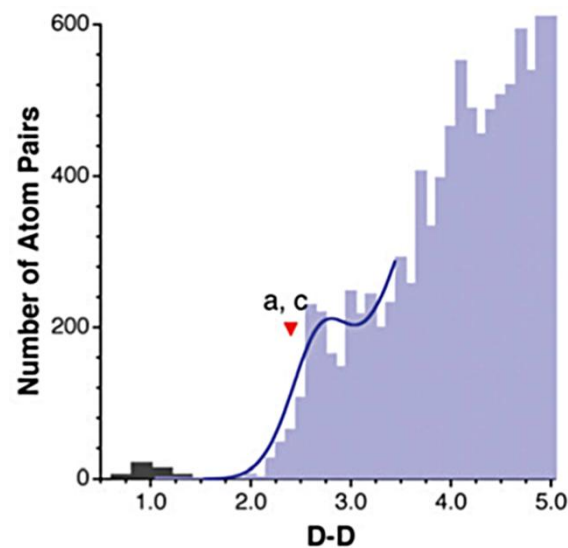
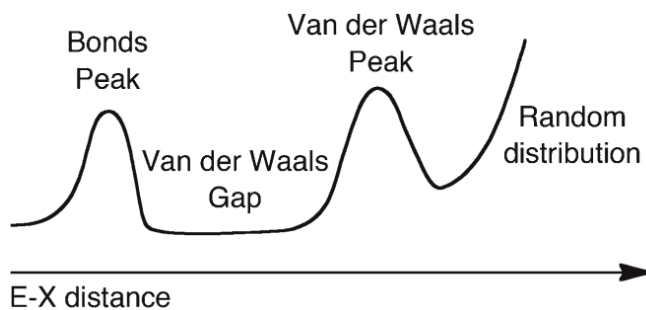
Intermolecular forces in chemistry

The Lennard-Jones potential:

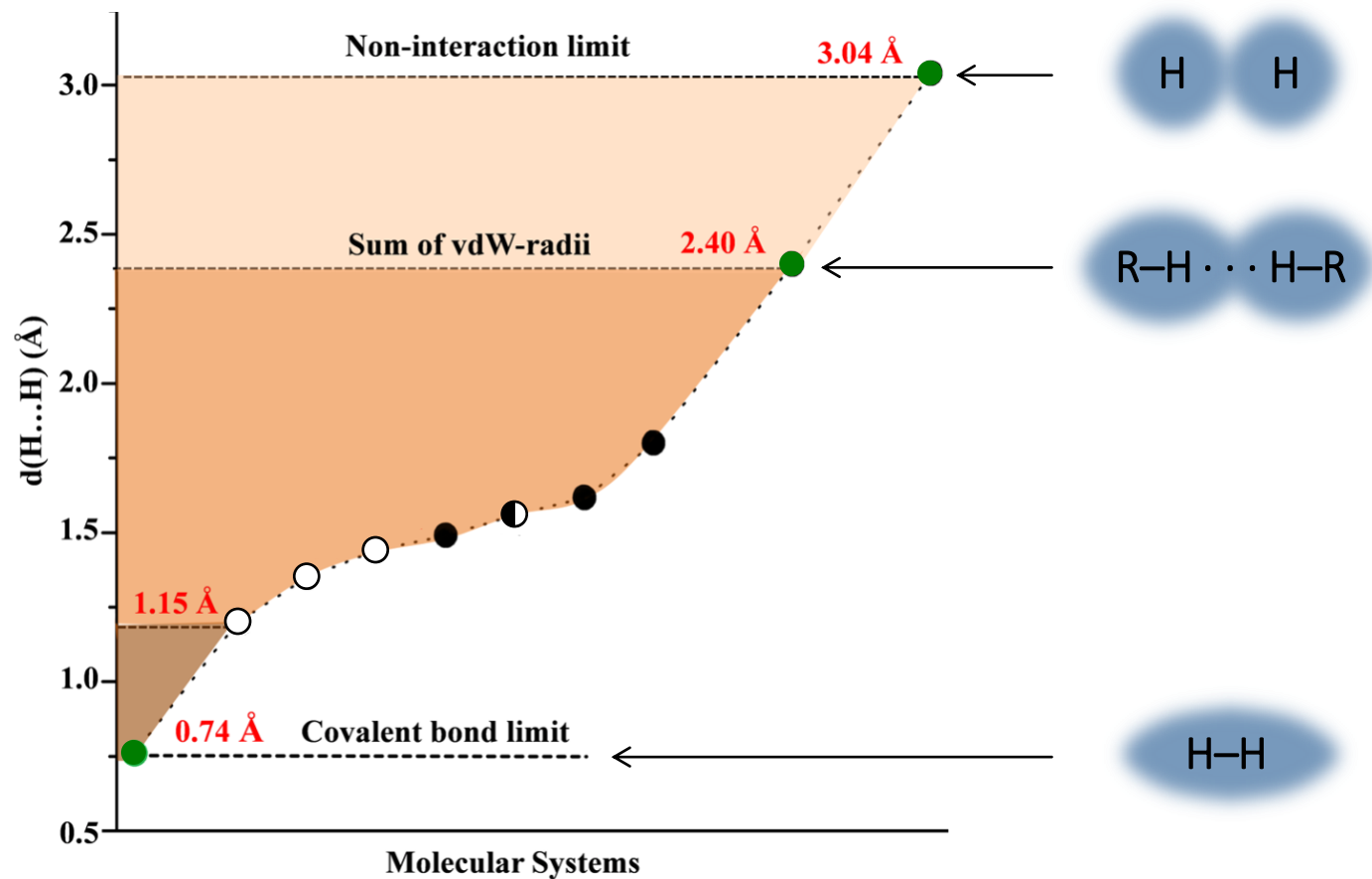
$$E(r) = C_{12}r^{-12} - C_6r^{-6}$$



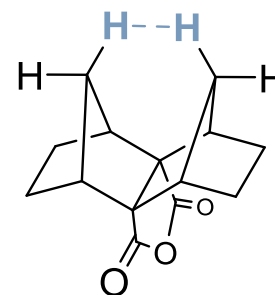
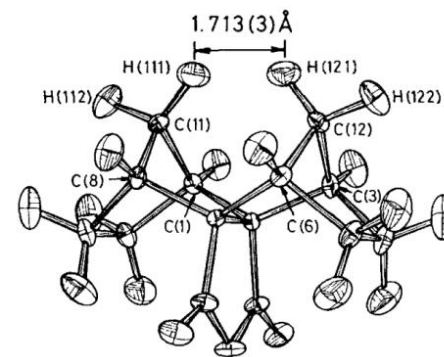
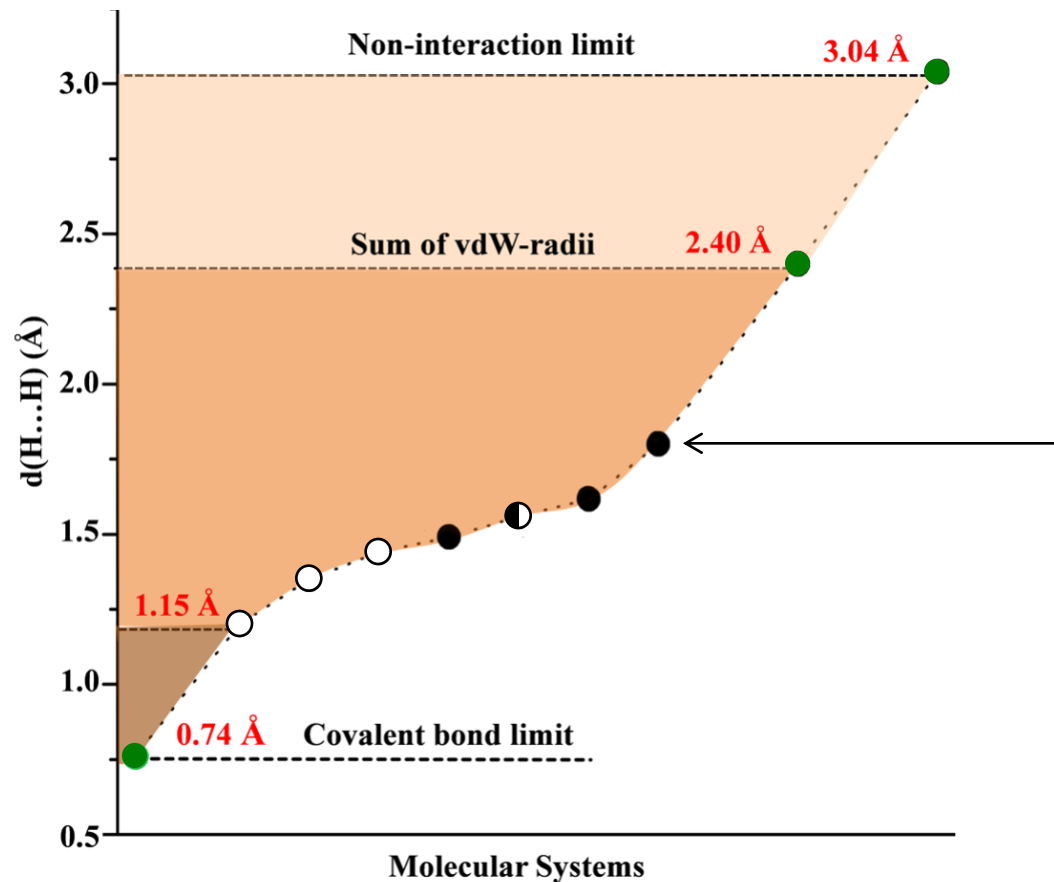
The van-der-Waals radius:



The H...H contact region



The H...H contact region



3
 $R_{\text{H}\cdots\text{H}} = 1.713(3) \text{ Å}$

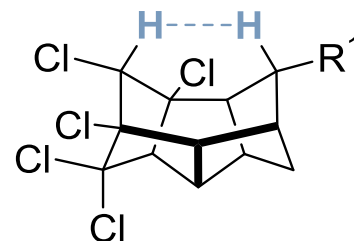
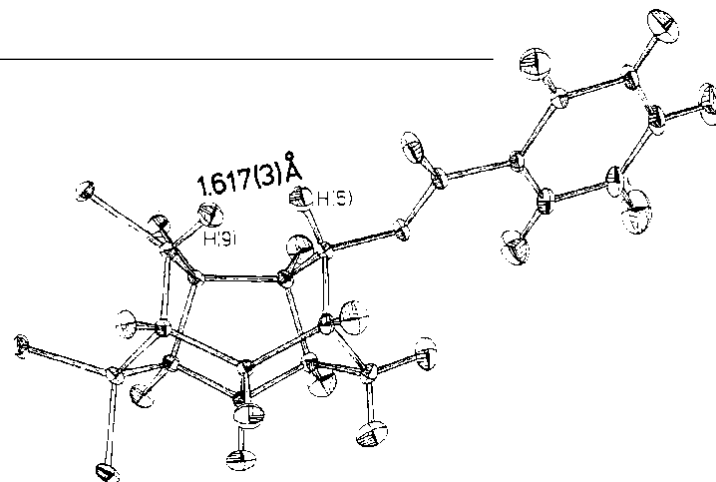
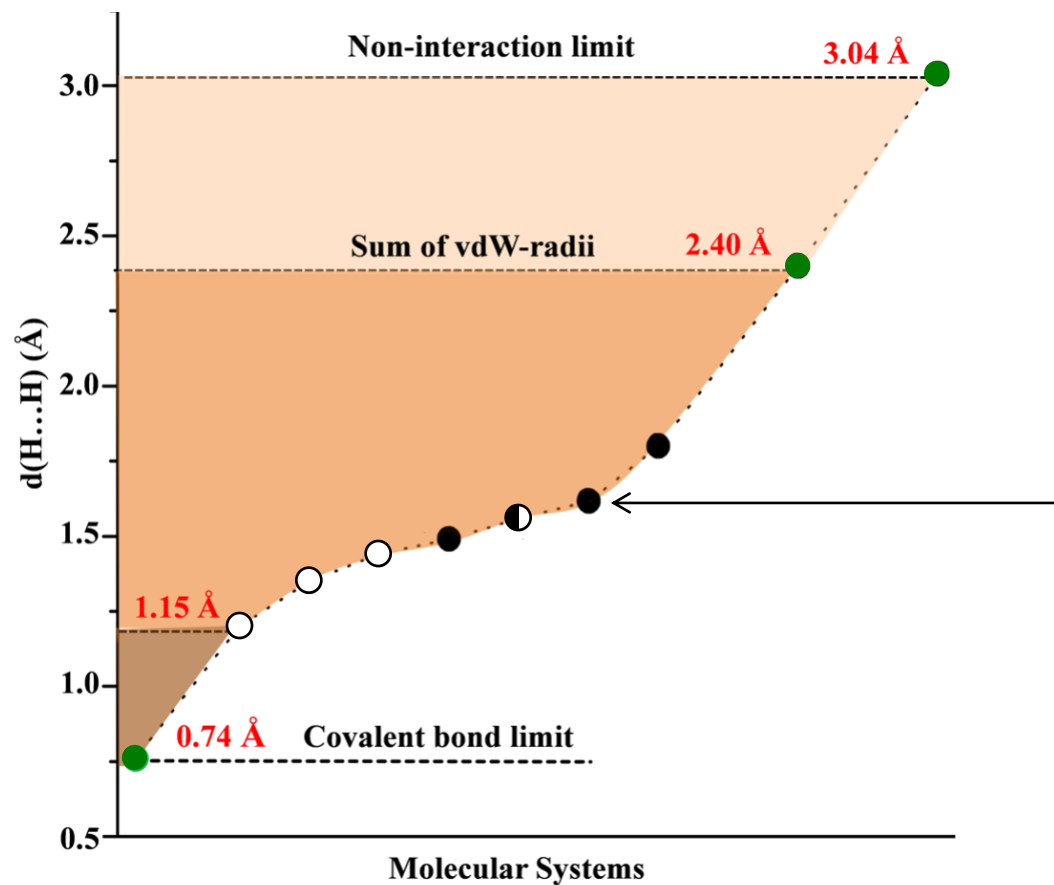
NRD-structure

$\Delta r_{\text{vdW}}(\text{H}\cdots\text{H}) = -0.69 \text{ Å}$

$r(\text{C}-\text{H}) = 1.088/1.089 \text{ Å}$

$\nu(\text{C}-\text{H}) = 3052 \text{ cm}^{-1} [+3\%]$

The H...H contact region



$$R_{\text{H}\cdots\text{H}} = 1.617(3) \text{ \AA}$$

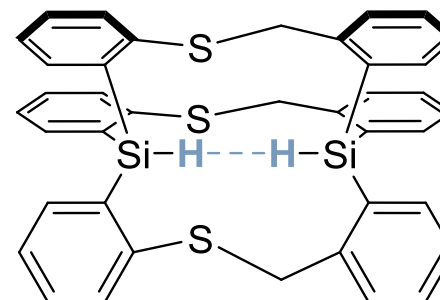
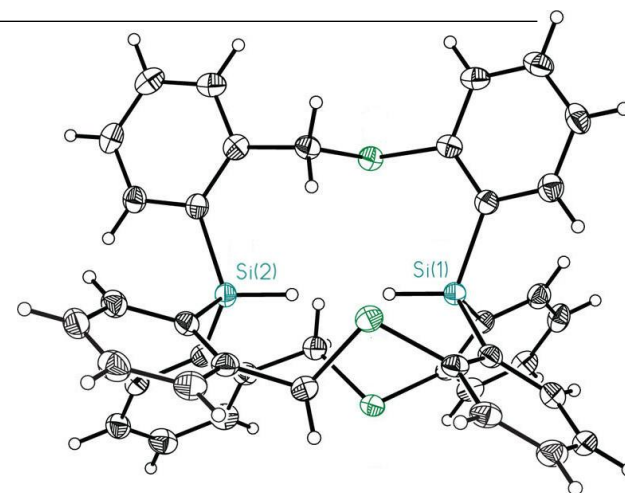
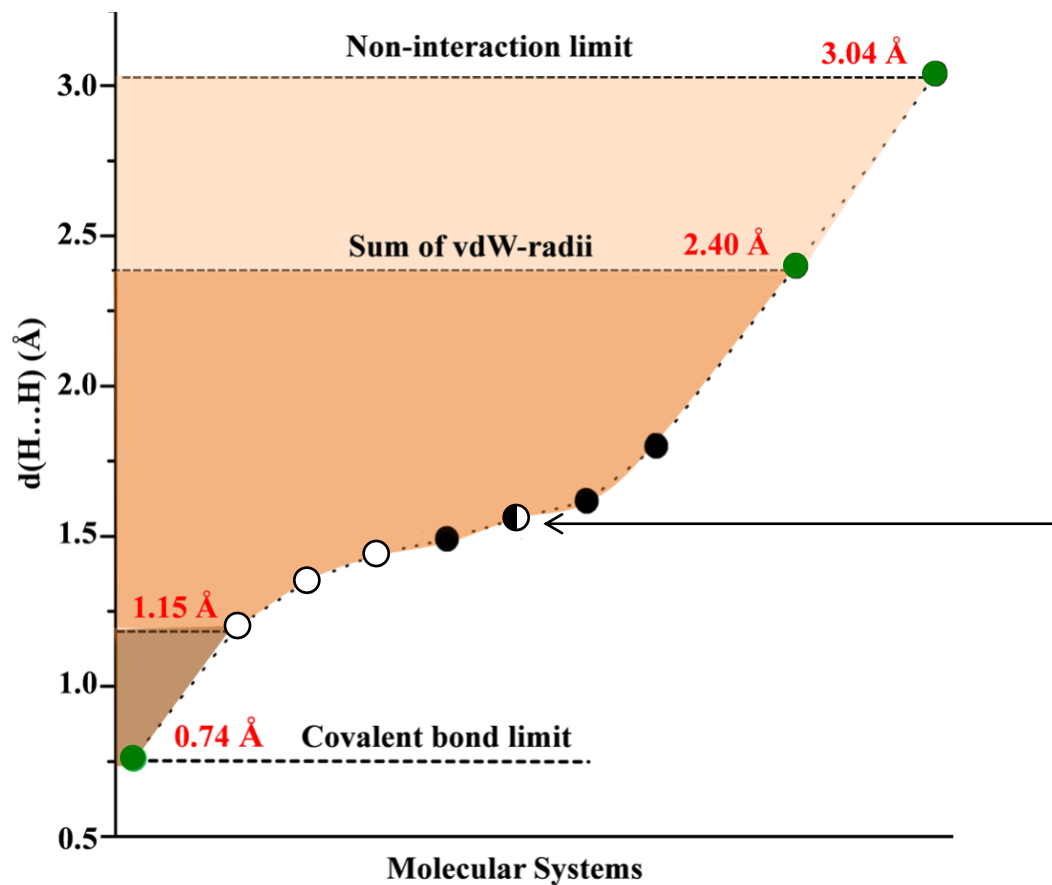
NRD-structure

$$\Delta r_{\text{vdW}} = -0.78 \text{ \AA}$$

$$r(\text{C}-\text{H}) = 1.095/1.078 \text{ \AA}$$

$$\nu(\text{C}-\text{H}) = 3119 \text{ cm}^{-1} [+(-2-5)\%]$$

The H...H contact region



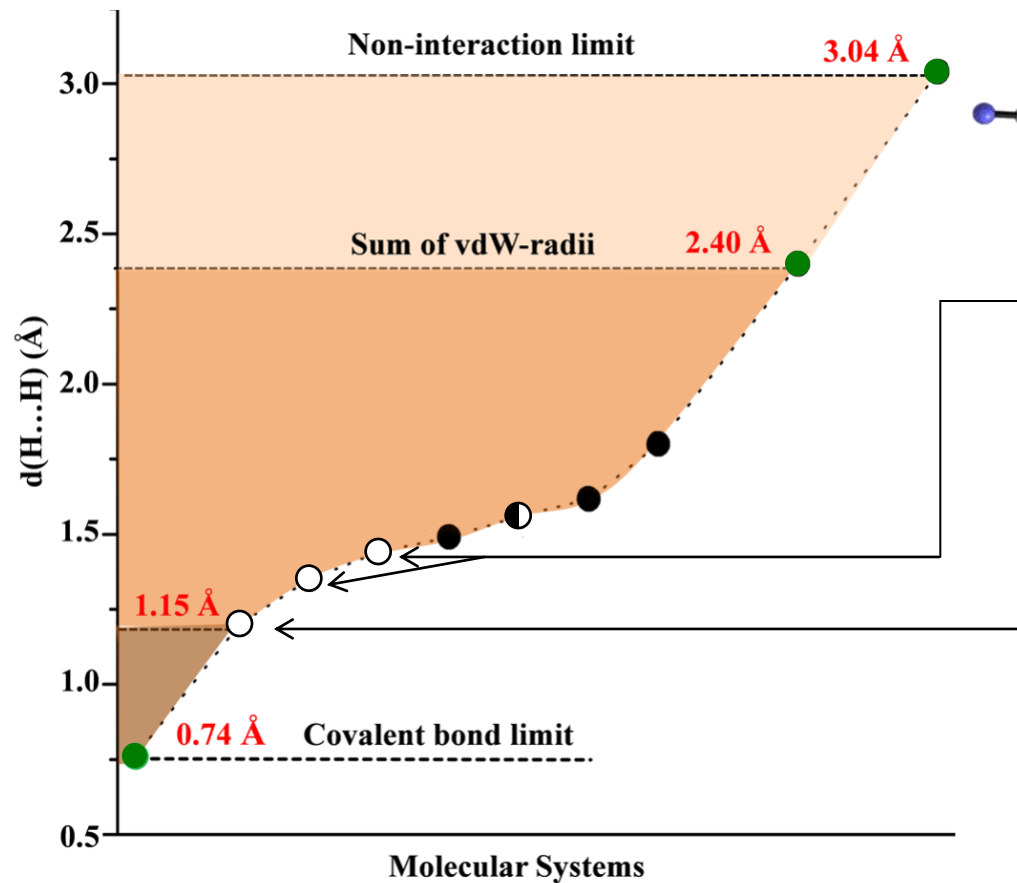
$$R_{\text{Si}\cdots\text{Si}} = 4.433(2) \text{ \AA}$$

$$R_{\text{H}\cdots\text{H}} (\text{Comp.}) = 1.556 \text{ \AA}$$

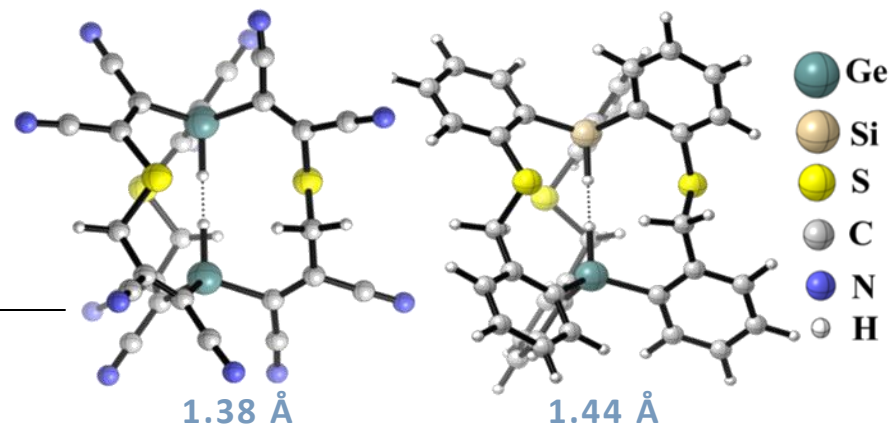
XRD-structure
 (H...H data: MP2(FC)/6-31G(d))
 $\Delta r_{\text{vdW}} = -0.84 \text{ \AA}$

$$\nu(\text{Si-H})_{\text{exp.}} = 2325 \text{ cm}^{-1} [+7\%]$$

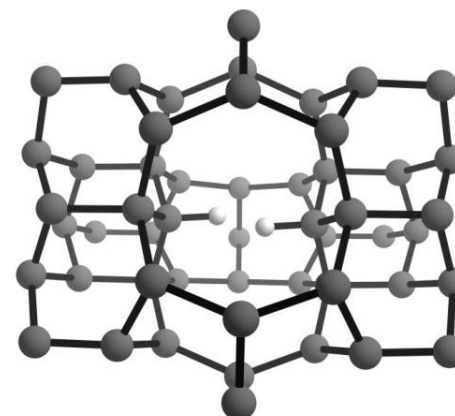
The H...H contact region



Computational predictions:



M06-2X/6-31G(d)

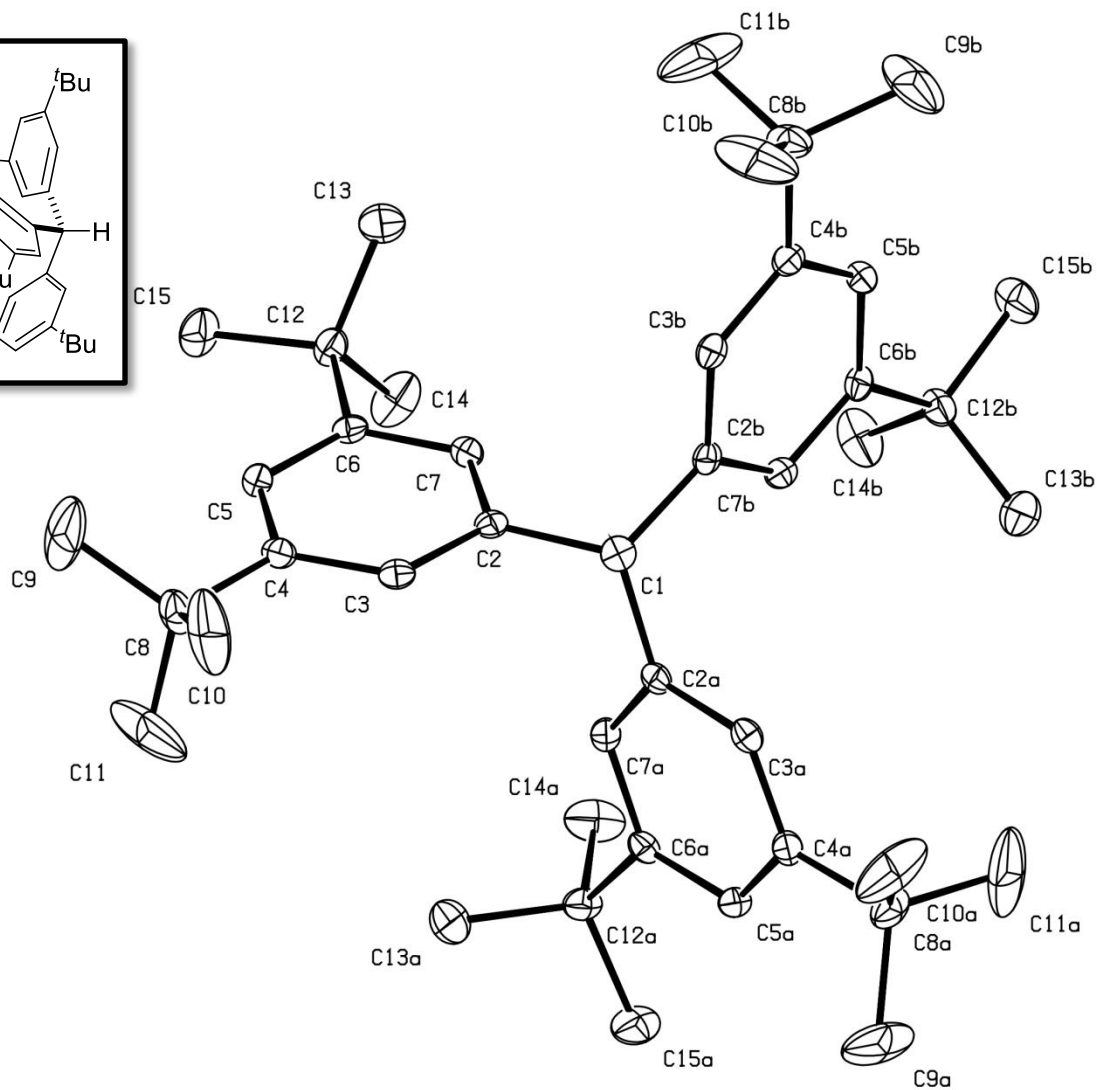
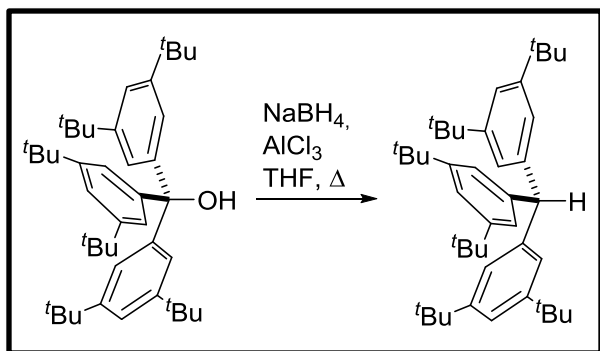


1.15 Å

B97D/6-31G(d)

Bears an Euler modulus!

Tri(3,5-di-*tert*-butylphenyl)methane



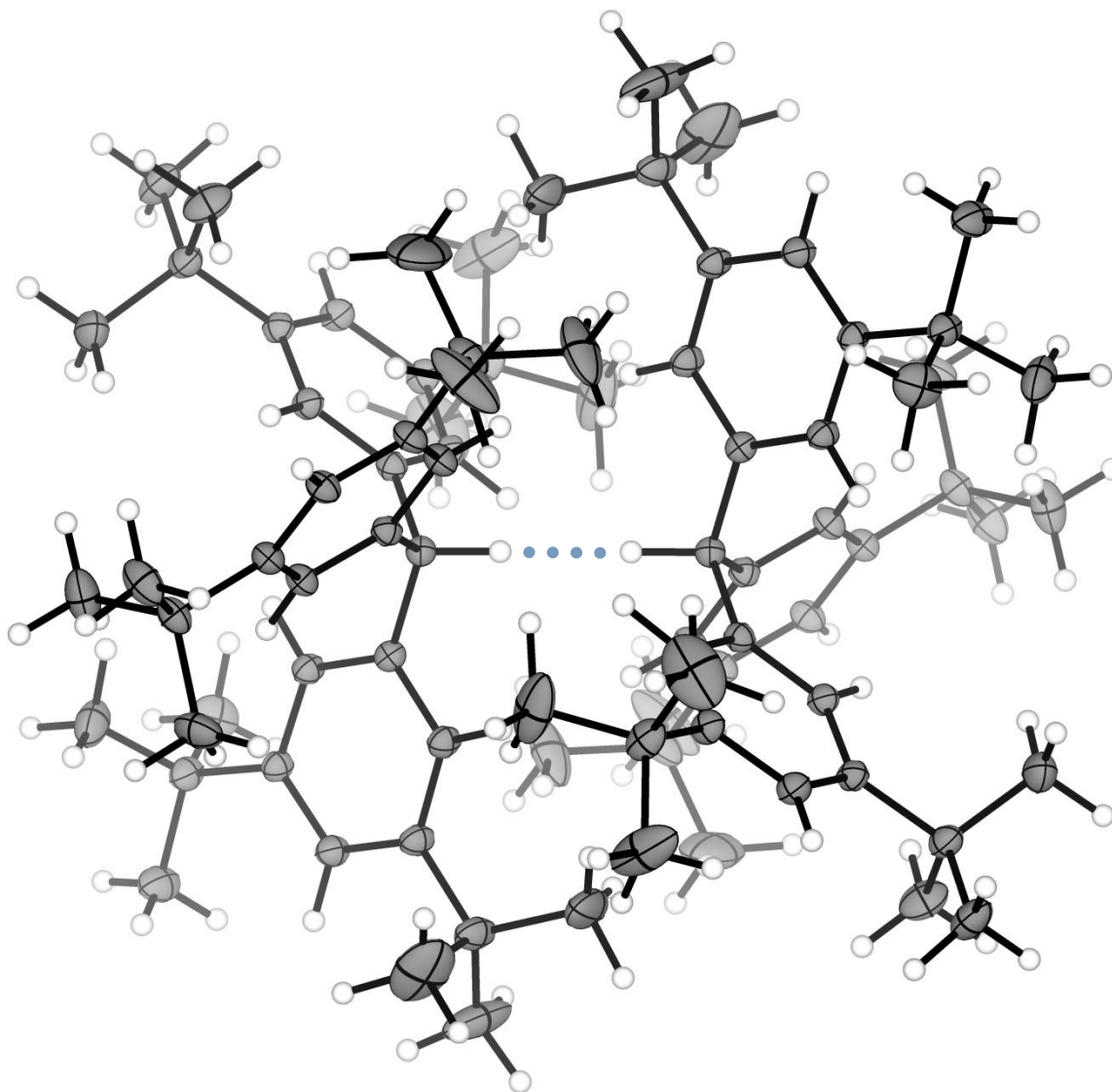
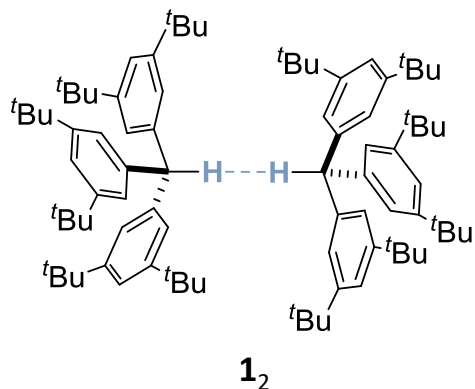
Tri(3,5-di-*tert*-butylphenyl)methane

XRD-structure Pa-3

$$r(\text{H}\cdots\text{H}) = 1.71(11) \text{ \AA}$$

$$\Delta r_{\text{vdW}} = -0.69 \text{ \AA}$$

$$r(\text{C}-\text{H}) = 1.03(4) \text{ \AA}$$



Tri(3,5-di-*tert*-butylphenyl)methane

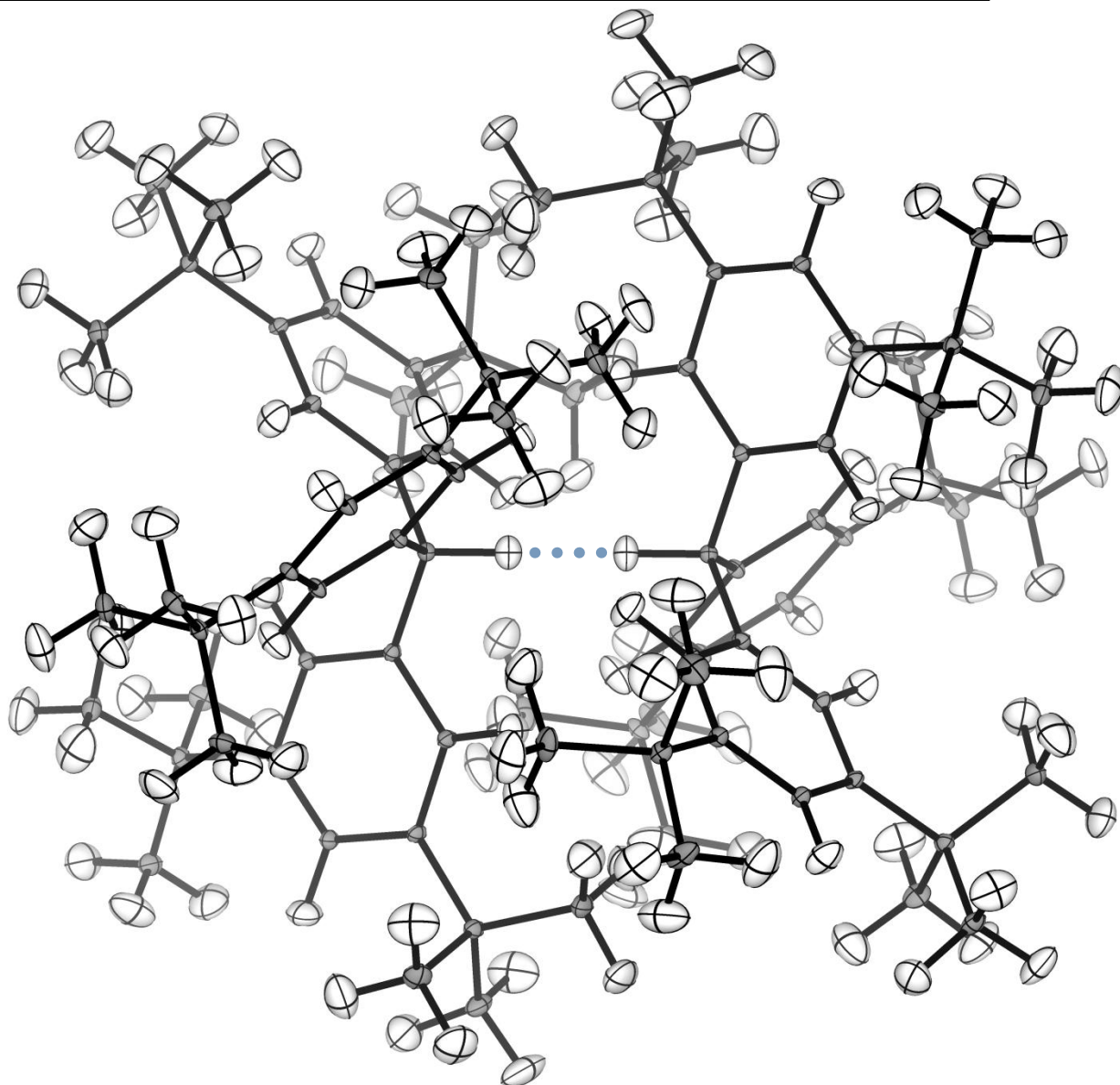
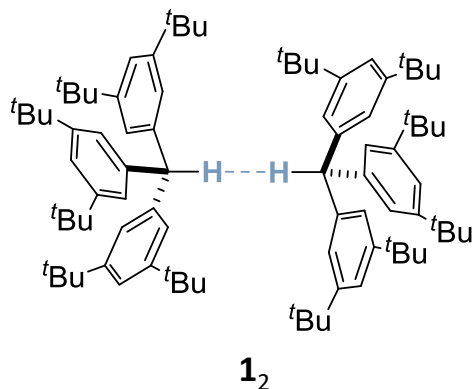
NRD-structure P2₁3

$$r(\text{H}\cdots\text{H}) = 1.567(1) \text{ \AA}$$

$$\Delta r_{\text{vdW}} = -0.84 \text{ \AA}$$

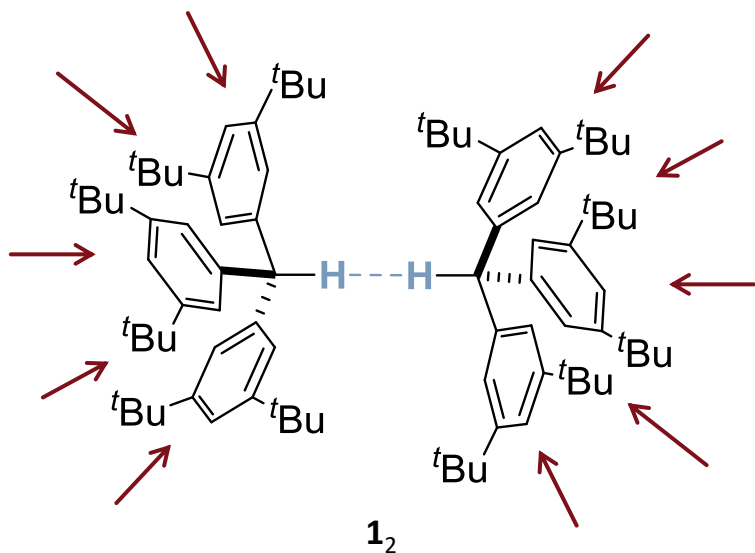
$$r(\text{C}-\text{H}) = 1.088(5) \text{ \AA}$$
$$1.098(5) \text{ \AA}$$

$$R\text{-value} = 0.031$$



Rationalizing the H...H Contact

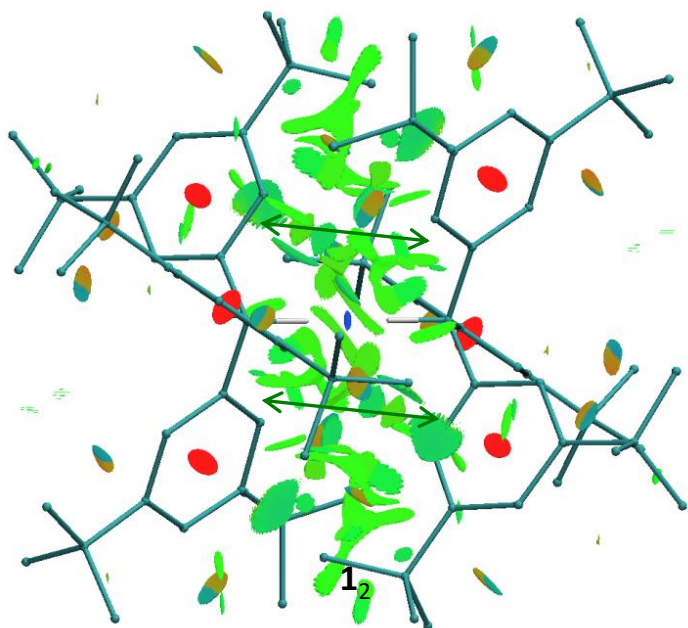
Crystal packing?



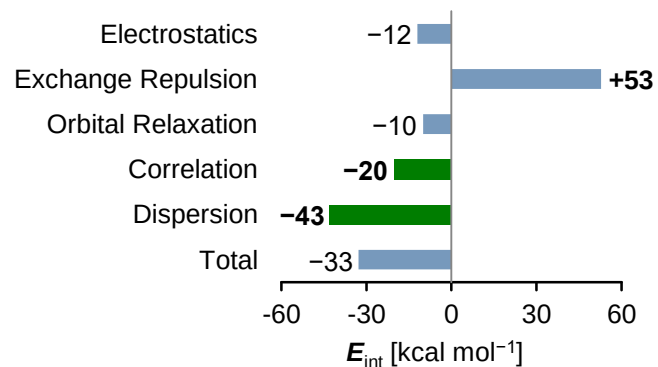
	NRD	HSE-3c	
T [K]	20	0	0
(state)	(s)	(s)	(g)
$H_{\alpha} \cdots H_{\alpha}'$	1.567(1)	1.562	1.634
$C_{\alpha}-H_{\alpha}$	1.093(5) ^{c,d}	1.089	1.092
$H_{\alpha}-C_{\alpha}-C_i$	106.0(1) ^c	106	104.9
$H_{\alpha}-C_{\alpha}-C_i-C_o$	39.8	39.9	45.2

Rationalizing the H...H Contact

London Dispersion!

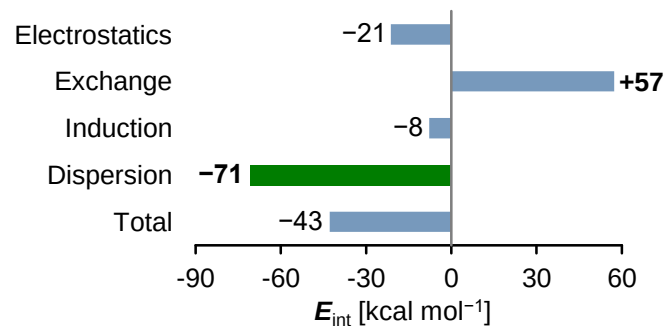


Energy Decomposition Analysis



B3LYP-D3(BJ)/def2-TZVPP.

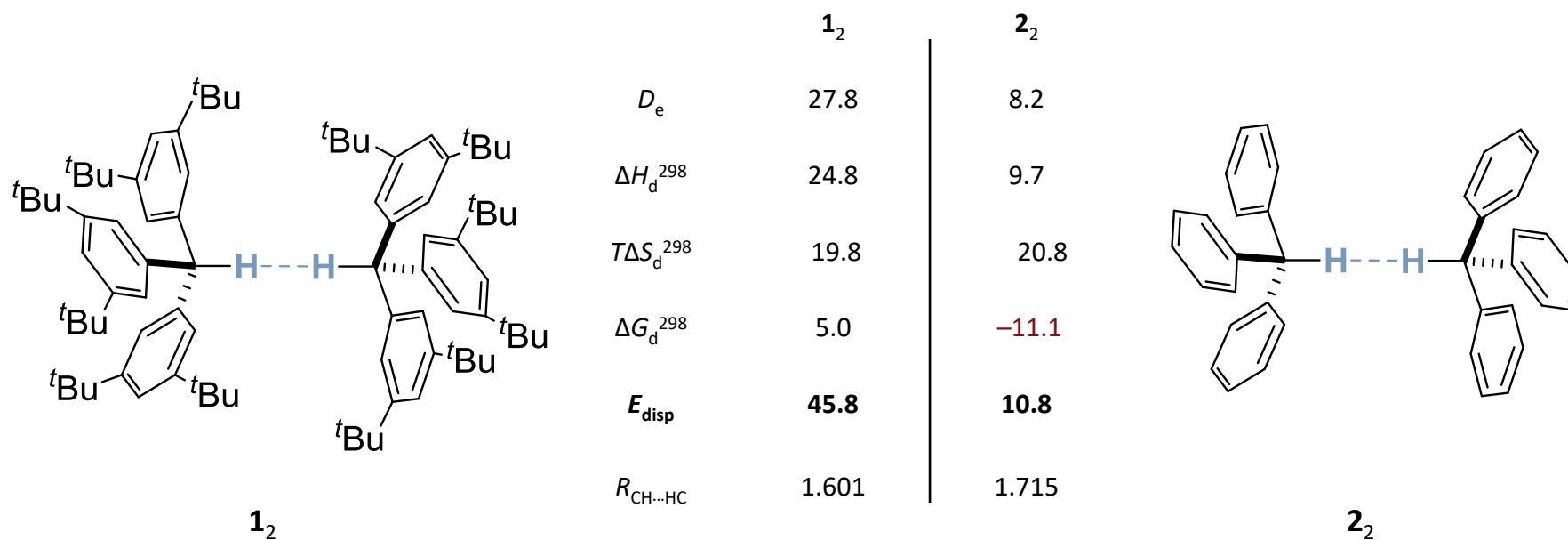
SAPT (0)



SAPT(0)/aug-cc-pVDZ.

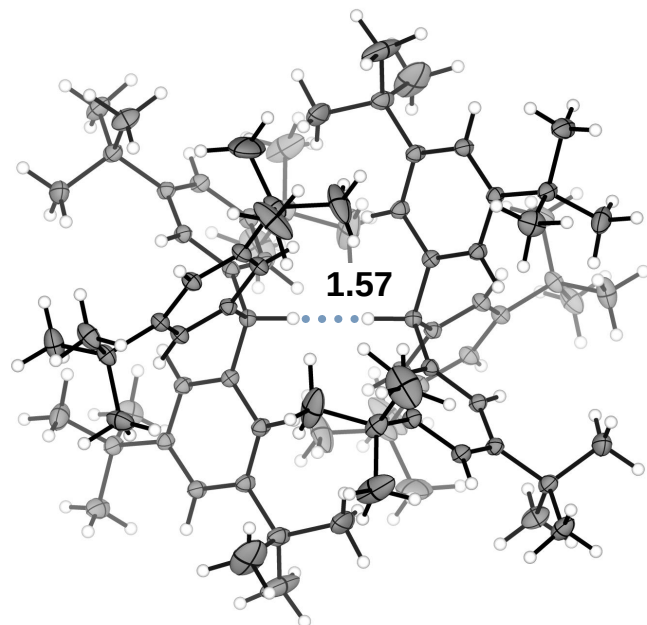
Rationalizing the H...H Contact

London Dispersion through *t*Bu-groups

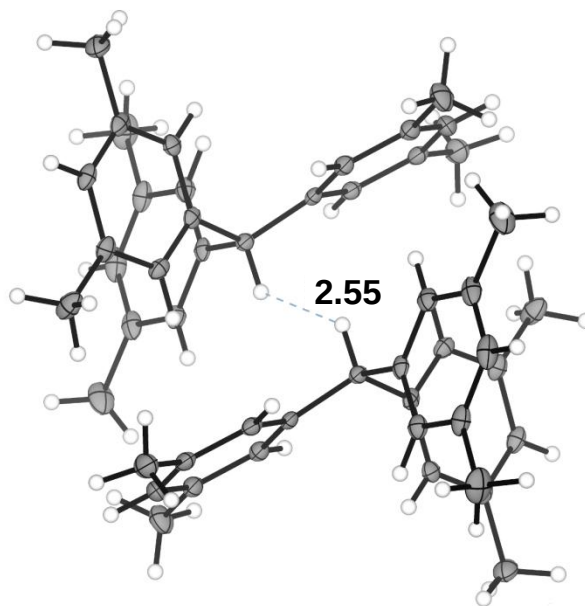


Rationalizing the H...H Contact

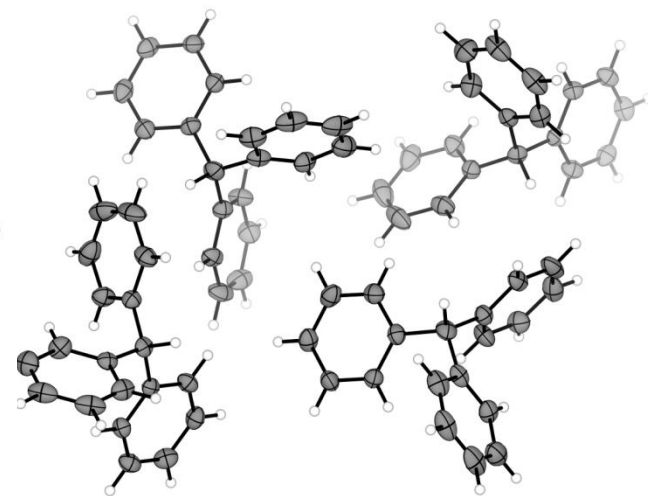
Special arrangement lost without ^tBu-groups



^tBu



Me



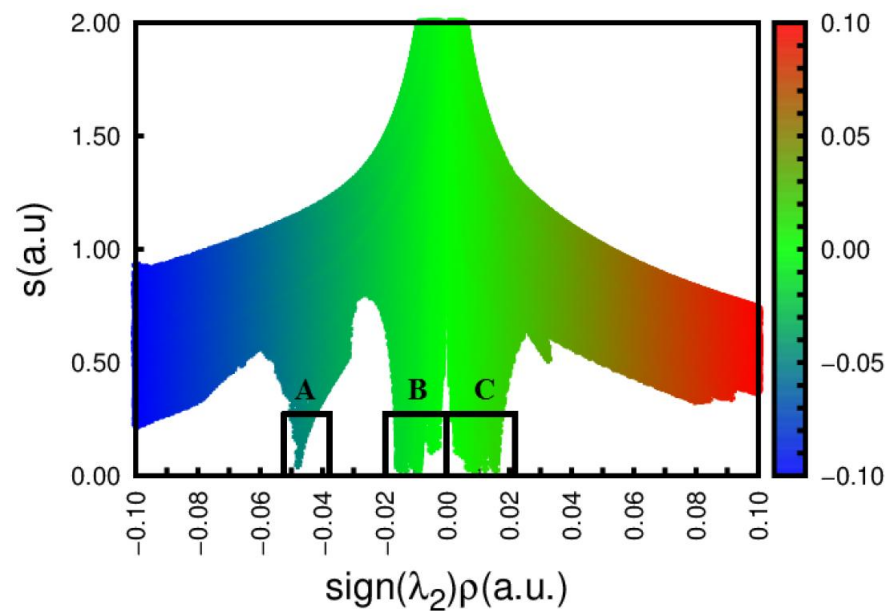
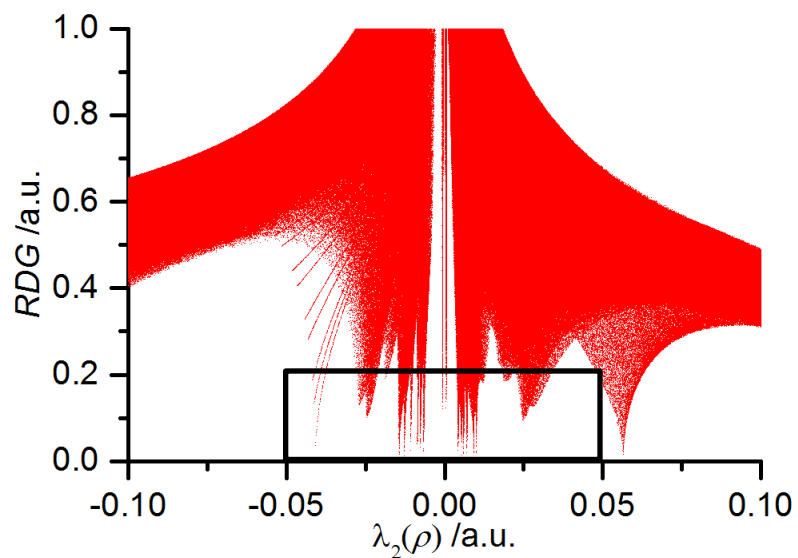
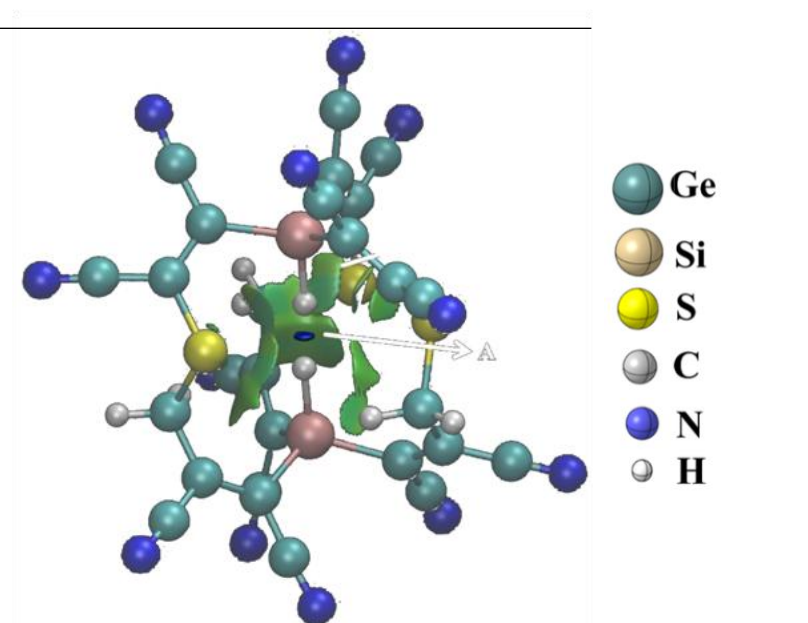
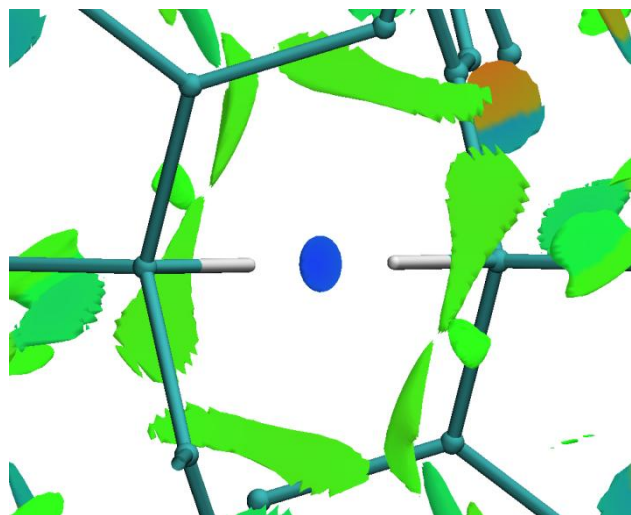
H

QTAIM analysis



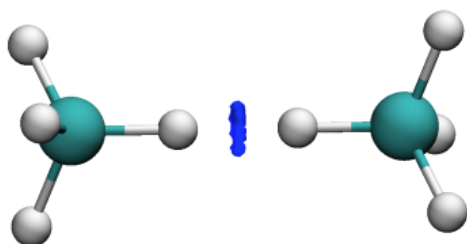
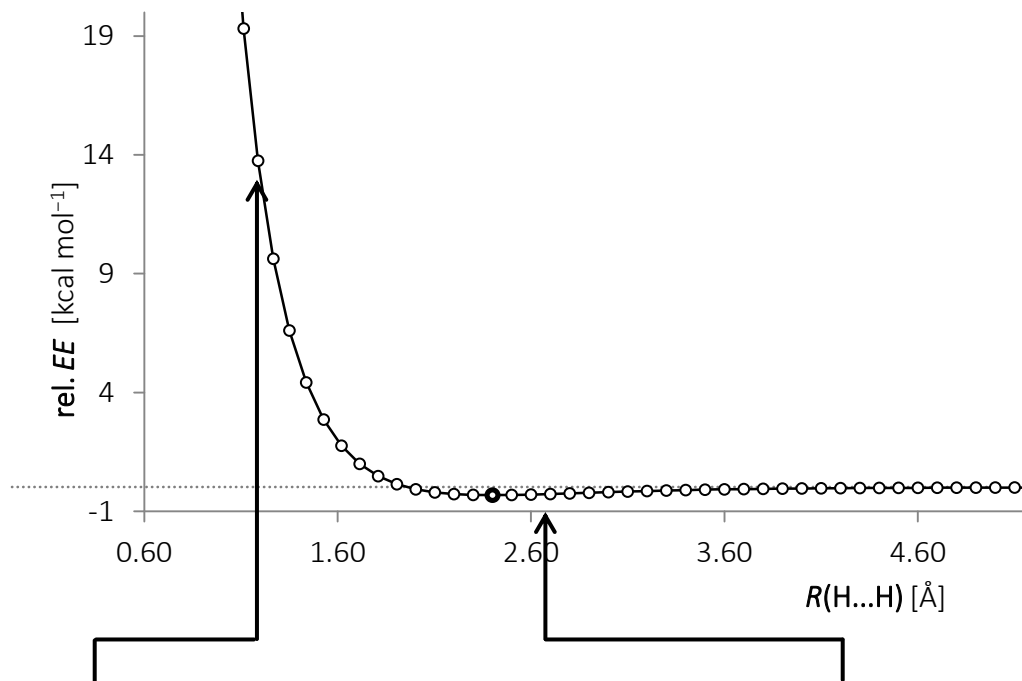
Contact Type

NCI analysis

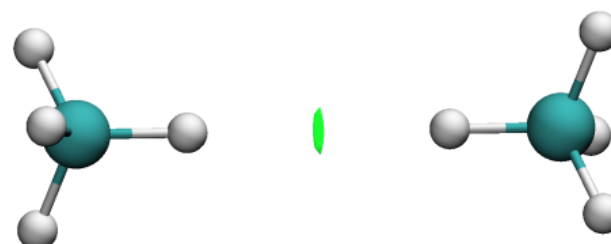


Contact Type

NCI analysis – model system



$r(\text{H}\cdots\text{H}) = 1.19 \text{ \AA}$
 $\text{rel. } EE = 13.8 \text{ kcal mol}^{-1}$



$r(\text{H}\cdots\text{H}) = 2.66 \text{ \AA}$
 $\text{rel. } EE = -0.3 \text{ kcal mol}^{-1}$

Contact Type

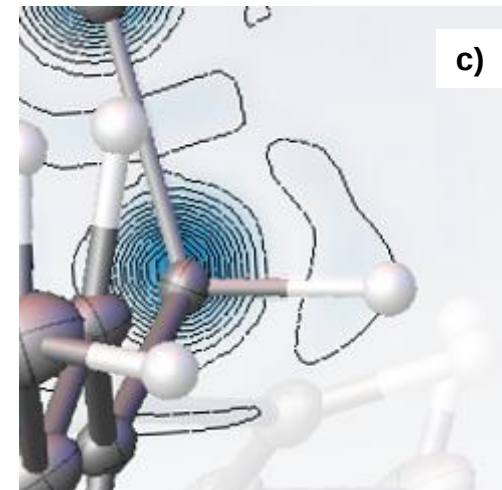
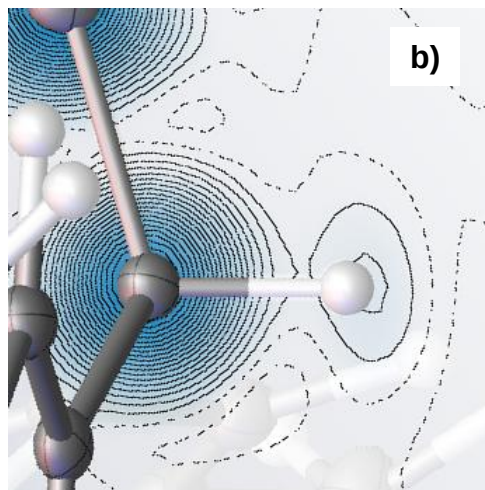
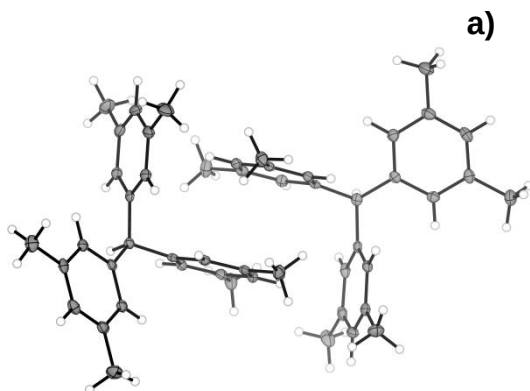
Electron density analysis

Resolution:
R

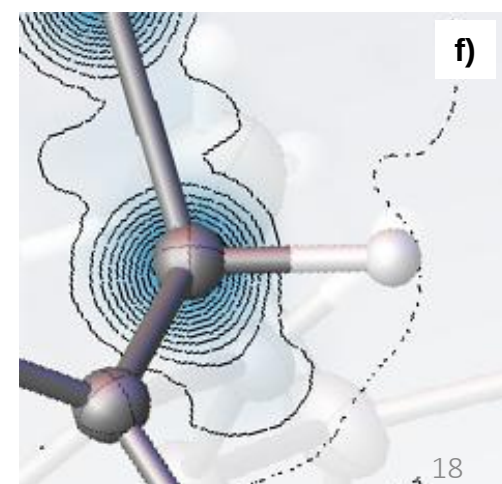
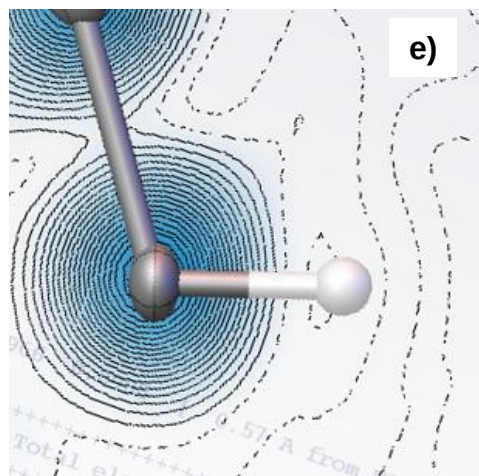
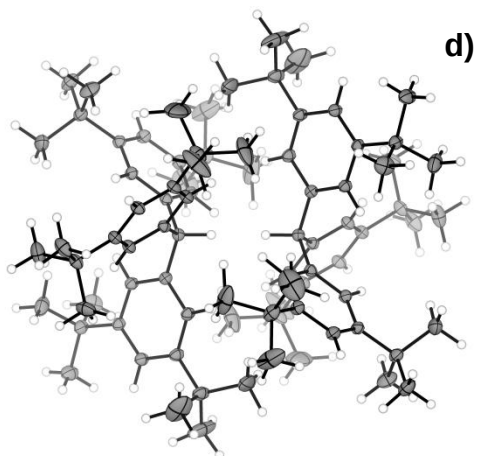
1.01 Å

0.37 Å

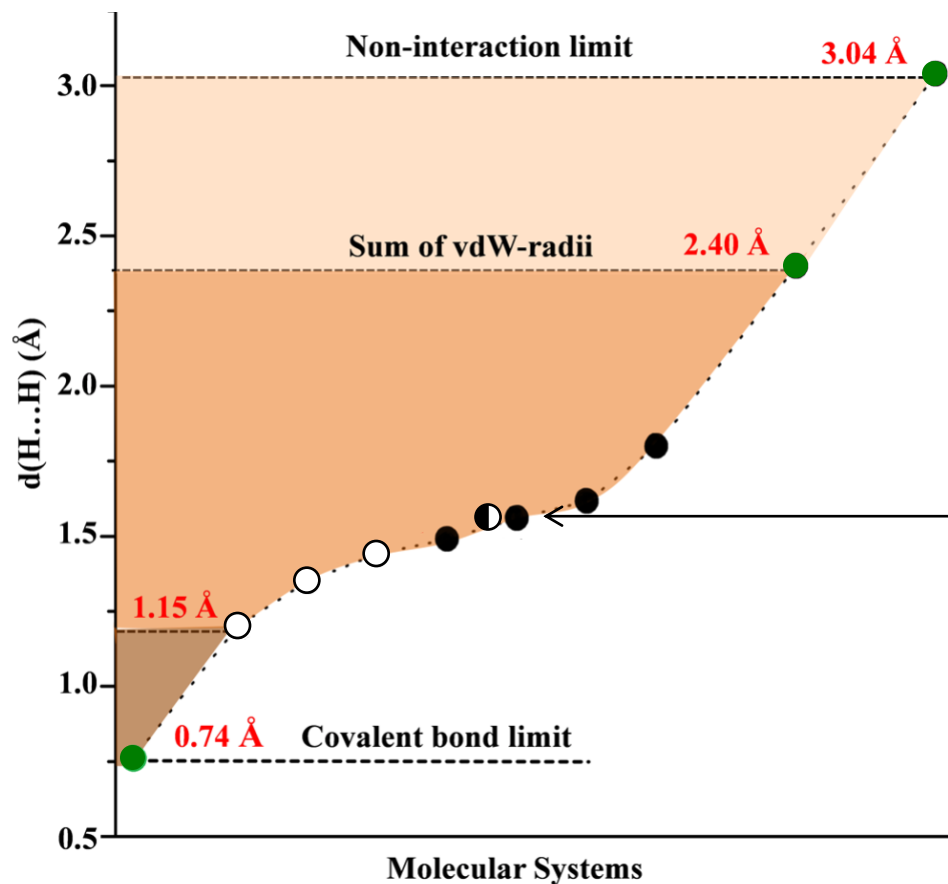
Me



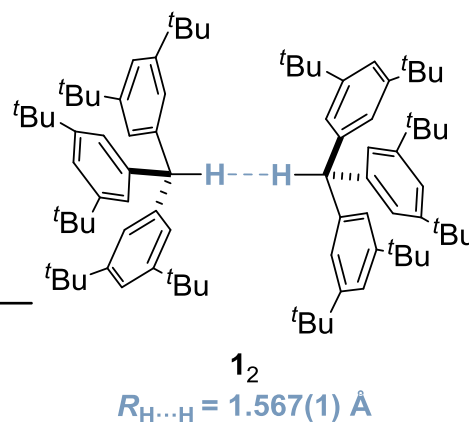
^tBu



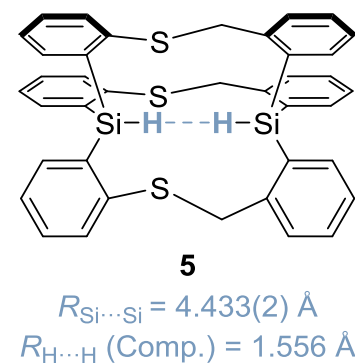
Tri(3,5-di-*tert*-butylphenyl)methane – a new record build on dispersion



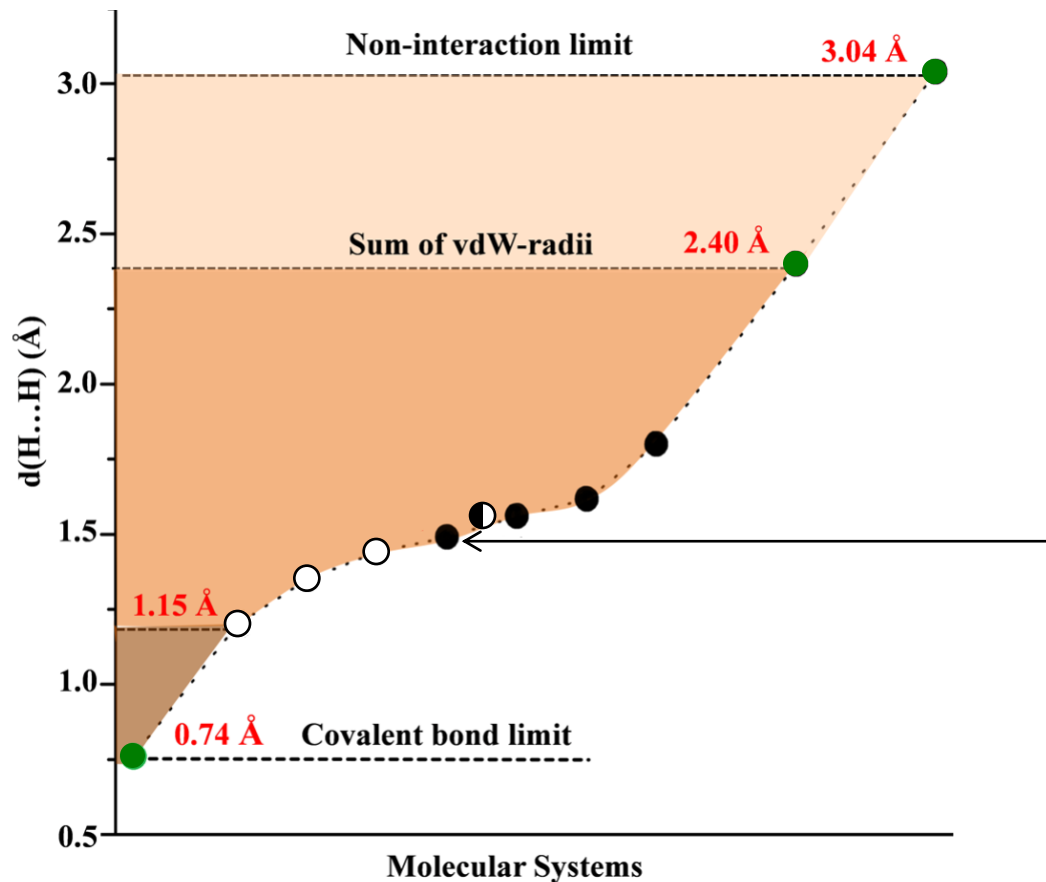
London
Dispersion
bond
dimer



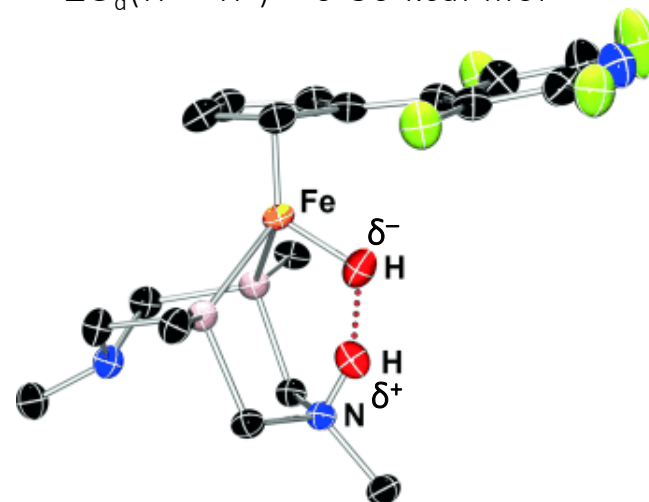
Three times
covalent
bond
cage



Bonding Hydride-Proton ($\text{H}^- \rightarrow \text{H}^+$) interaction



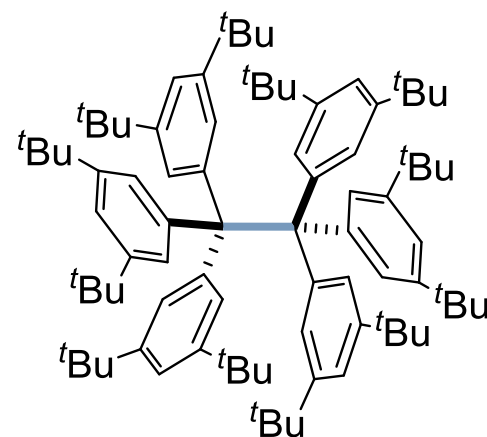
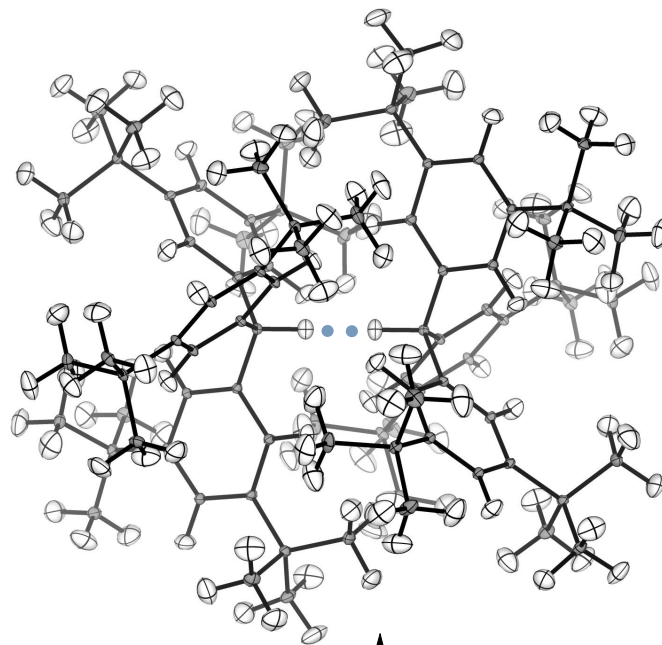
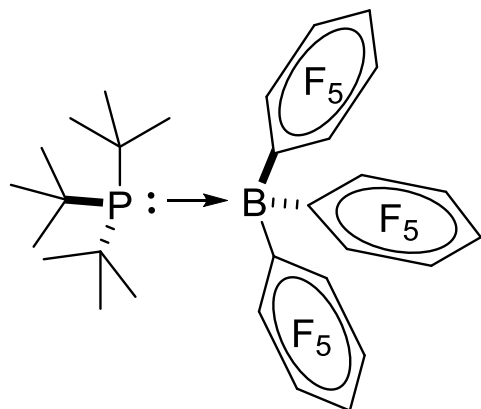
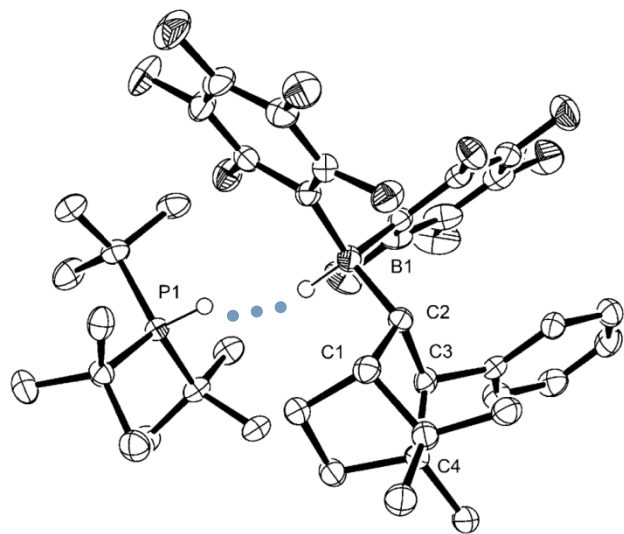
Bonding Hydride-Proton interaction
 $\Delta G_d(\text{H}^- \rightarrow \text{H}^+) = 0\text{-}30 \text{ kcal mol}^{-1}$



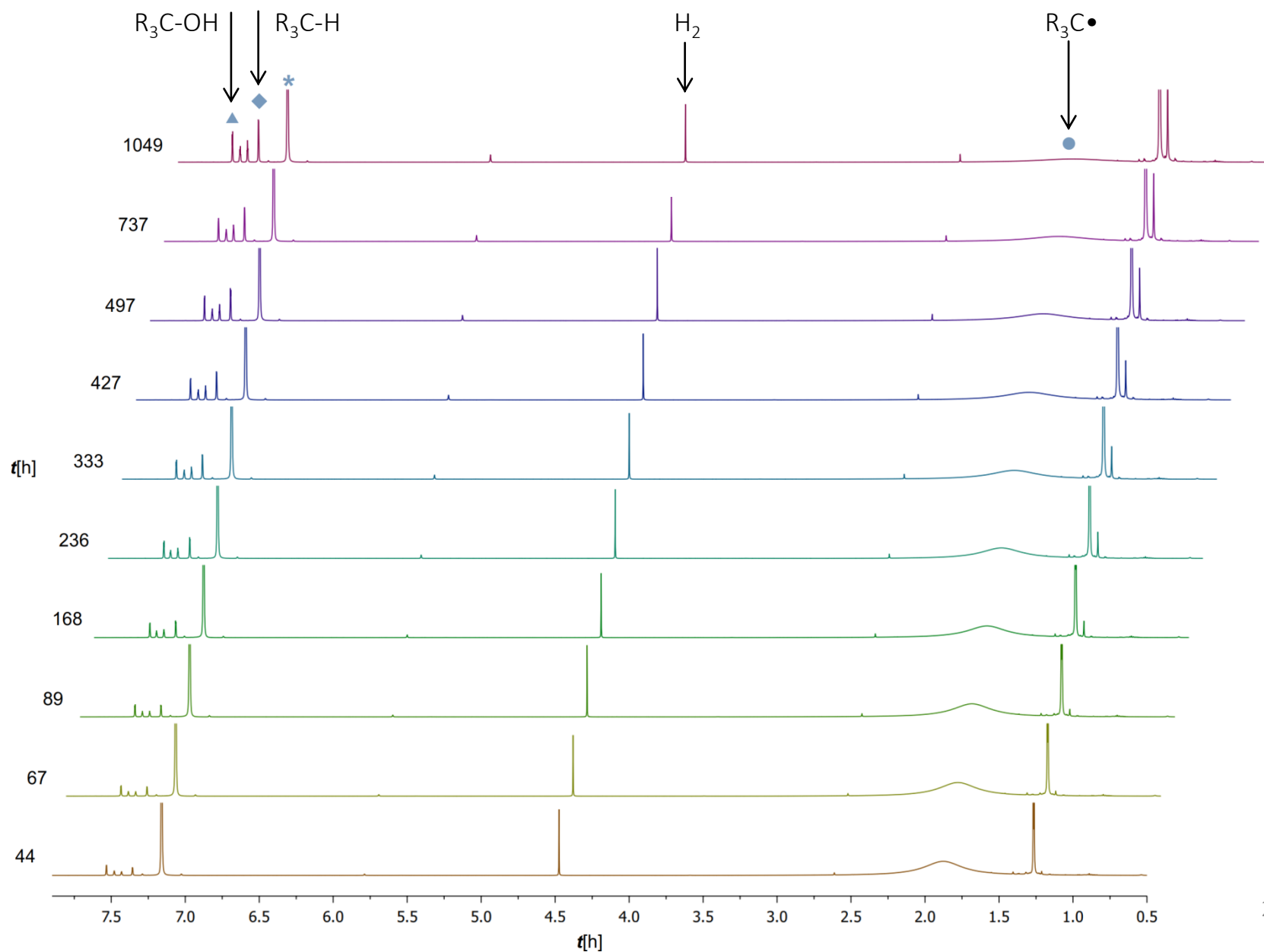
NRD-structure
 $r_{\text{H} \rightarrow \text{H}} = 1.489(10) \text{ Å}$

observed after H_2 splitting

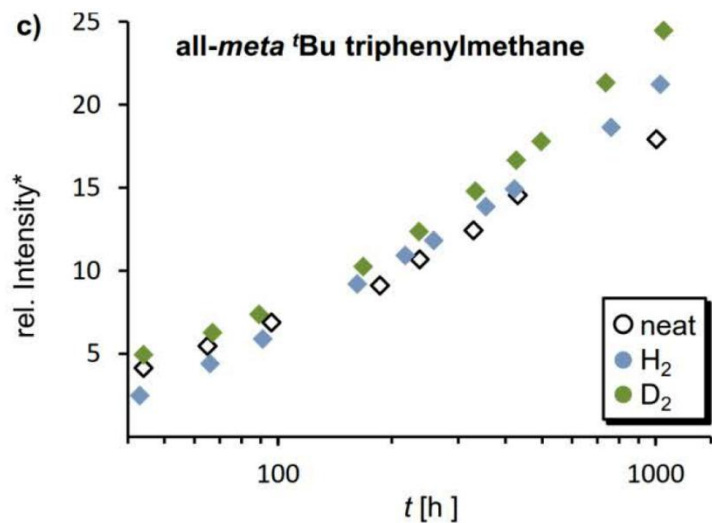
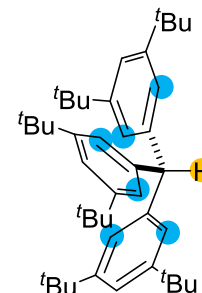
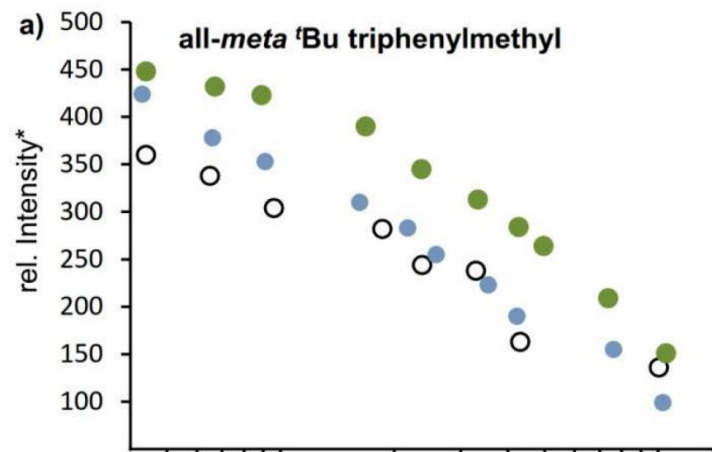
Frustrated Lewis Pairs appear as isoelectronic structures



Hydrogen activation by the all-*meta* *t*Bu-trityl radical

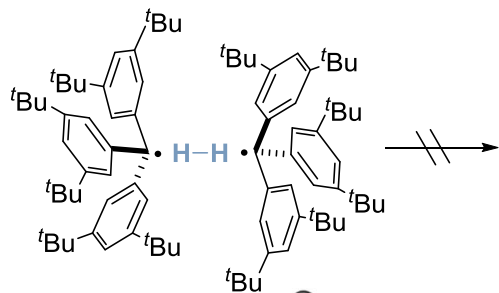


Hydrogen activation by the all-*meta* *t*Bu-trityl radical

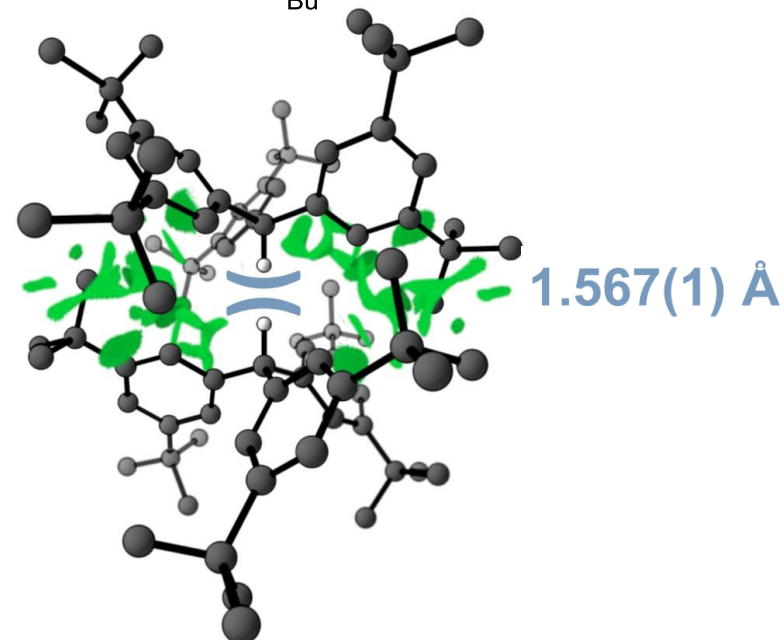


Experiment	Ratio H_o/H_α
theroretical	6
control	6.5(8)
H_2	6.3(4)
D_2	7.0(5)

Conclusions

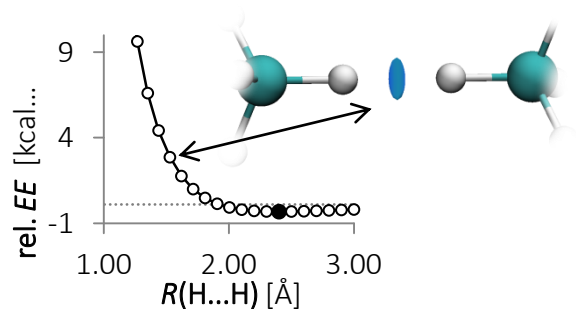


System inapt to split dihydrogen

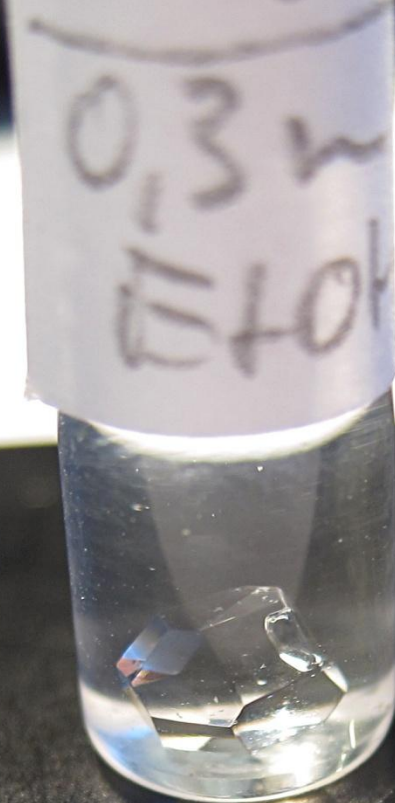


Shortest exp. reported $\text{H}\cdots\text{H}$ contact
 $\Delta R_{\text{vdW}} = -0.83 \text{ \AA}$

Dispersion bound dimer containing
 $E_{\text{disp}} = 70 \text{ kcal mol}^{-1}$



Contact situation uncertain
 -bonding by QTAIM and NCI
 -repulsive by exp. e^- -density and comput. energy



Acknowledgment

Prof. P.R. Schreiner

H. Quanz

Dr. C. Logemann

Dr. E. Mossou

E.Caldeweyher

