Universität Bielefeld

ИВАНОВСКИЙ ГОСУДАРСТВЕННЫЙ ХИМИКО-ТЕХНОЛОГИЧЕСКИЙ УНИВЕРСИТЕТ 1918 CHIMIA EST VITA

Experimental and theoretical study of some aromatic molecules: results and challenges

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Seminar 29/05/2018

The objects:

Organic compounds

- acenaphthene
- naphthalene, anthracene
- rubrene
- *tris*(pentafluorophenyl)(phenylethyl)silane
- flexible *bis*-arenes: Ph-OC_2H_4O-Ph_f, Naph-OC_2H_4O-Ph_f, Anthr-OC_2H_4O-Ph_f

Organometallic compounds

- perfluoro-*ortho*-phenylene mercury
- gold(I) dithiocarboxylate complex

The methods:

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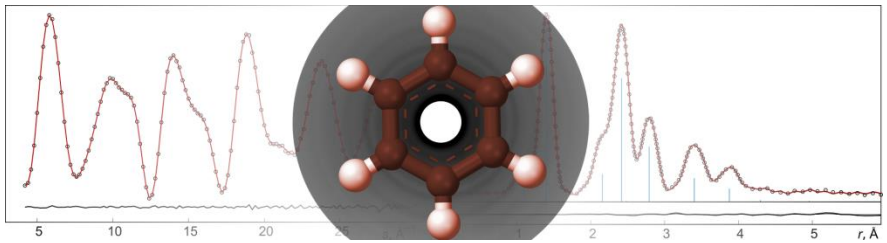


Gas-phase electron diffraction/
mass-spectrometry,
EMR-100/APDM-1, Ivanovo
(Prof. Dr. Georgiy V. Girichev,
Prof. Dr. Sergey A. Shlykov,
Dr. Vjacheslav M. Petrov)
EXPERIMENT

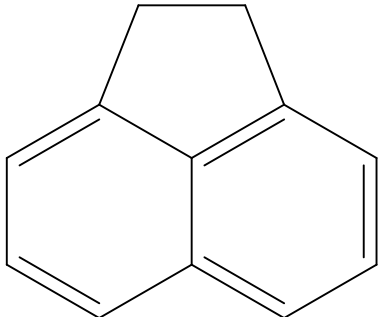
UNEX program (Dr. Yury V. Vishnevskiy)
REFINEMENT OF THE EXPERIMENTAL GED DATA

&

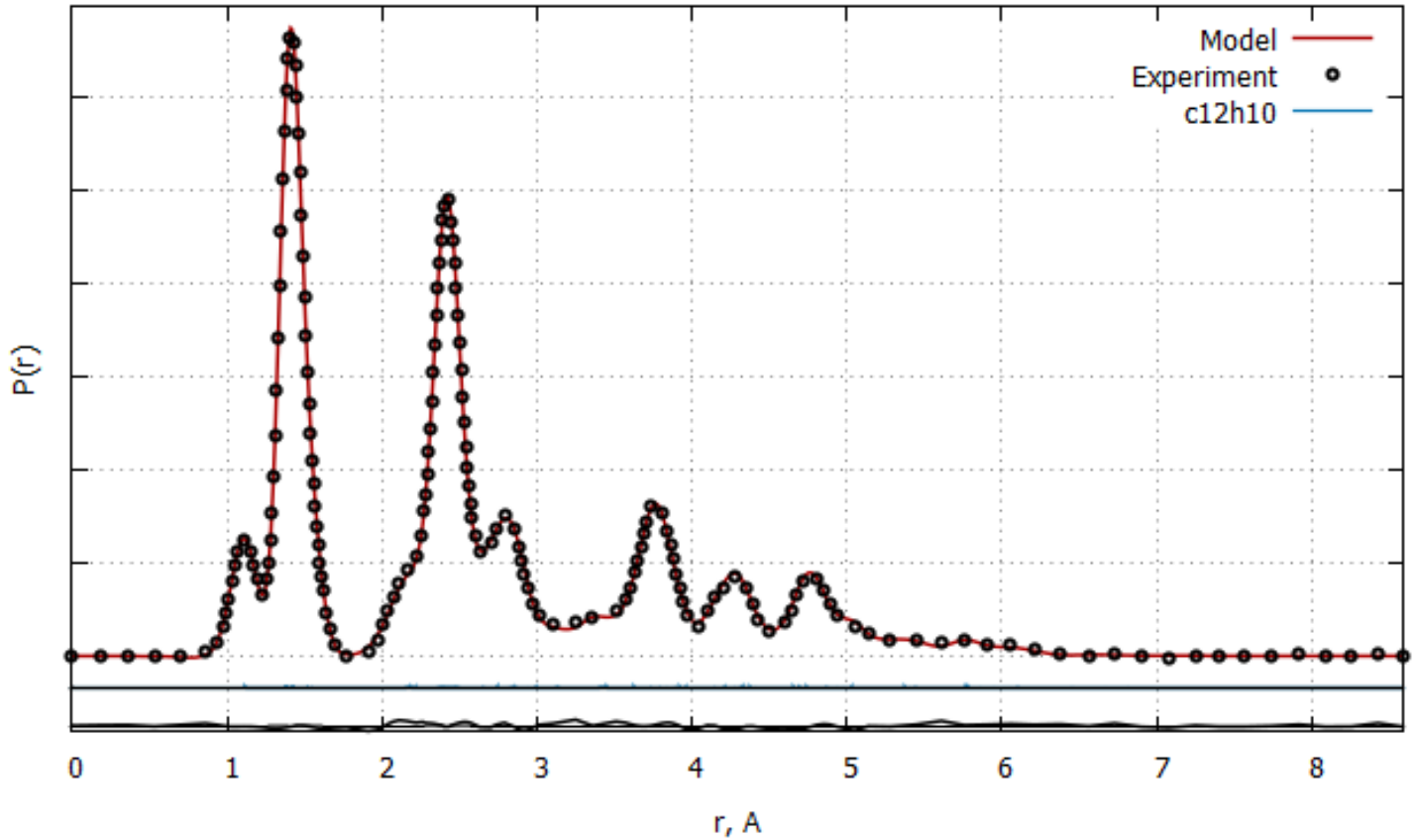
QUANTUM-CHEMICAL CALCULATIONS, including:

- **N**atural **B**ond **O**rbital analysis (NBO)
- **Q**uantum **T**heory of **A**toms **I**n **M**olecules (QTAIM)

Acenaphthene

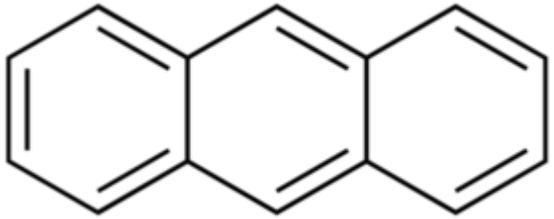


The first case of the **complete** refinement of GED experimental data from Ivanovo with use of UNEX program.

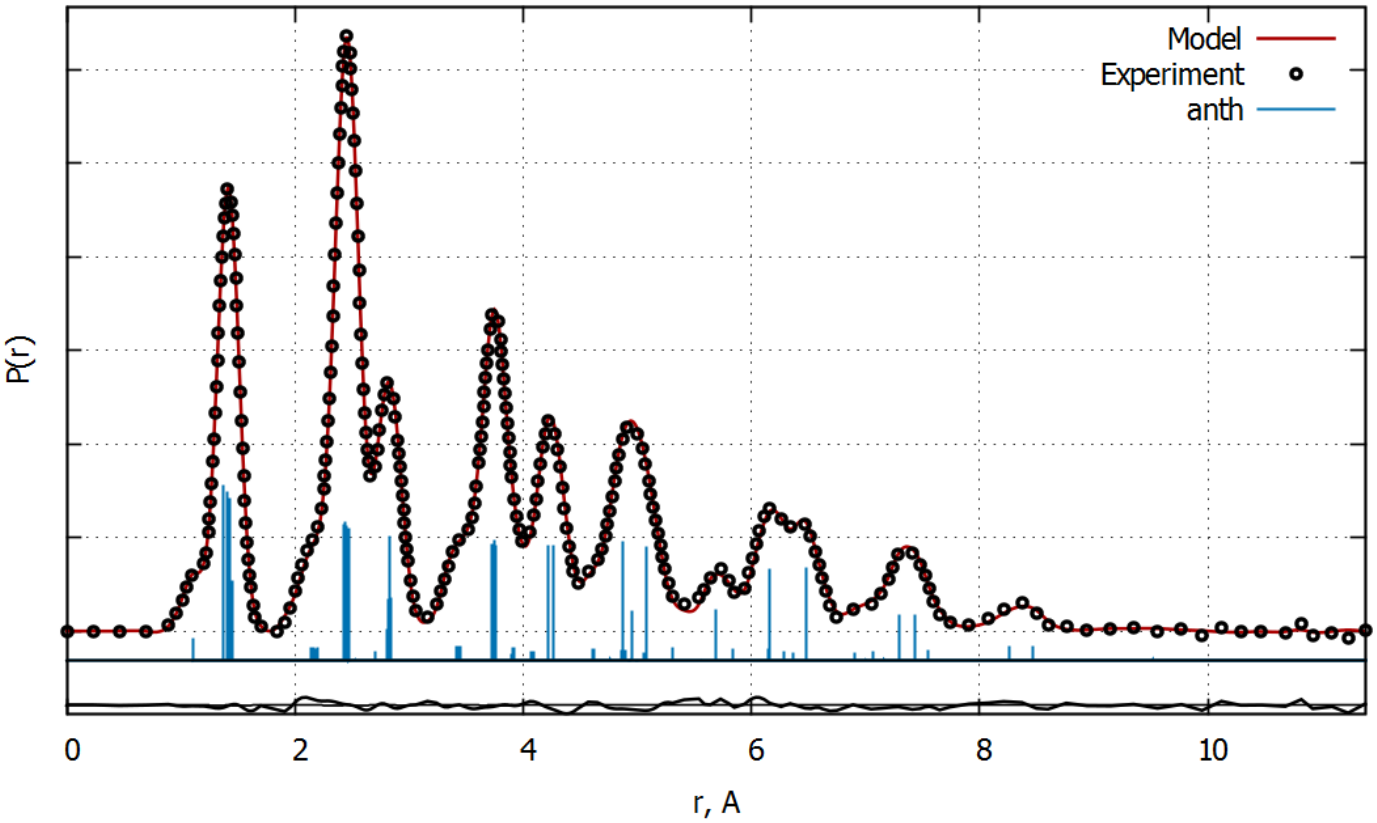


- R_f = 3.92 % (GED)
- R_f = 3.86 % (GED+MW)

Anthracene

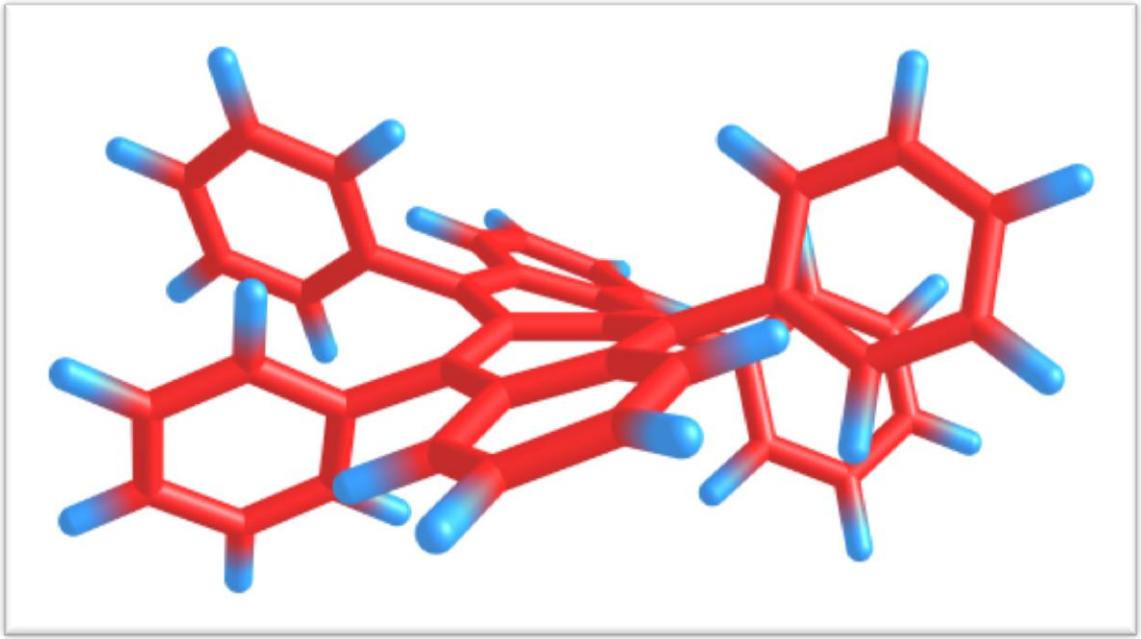


Very simple molecule, but challenging for the previous GED studies…



- R_f = 4.36 % (GED)

Rubrene

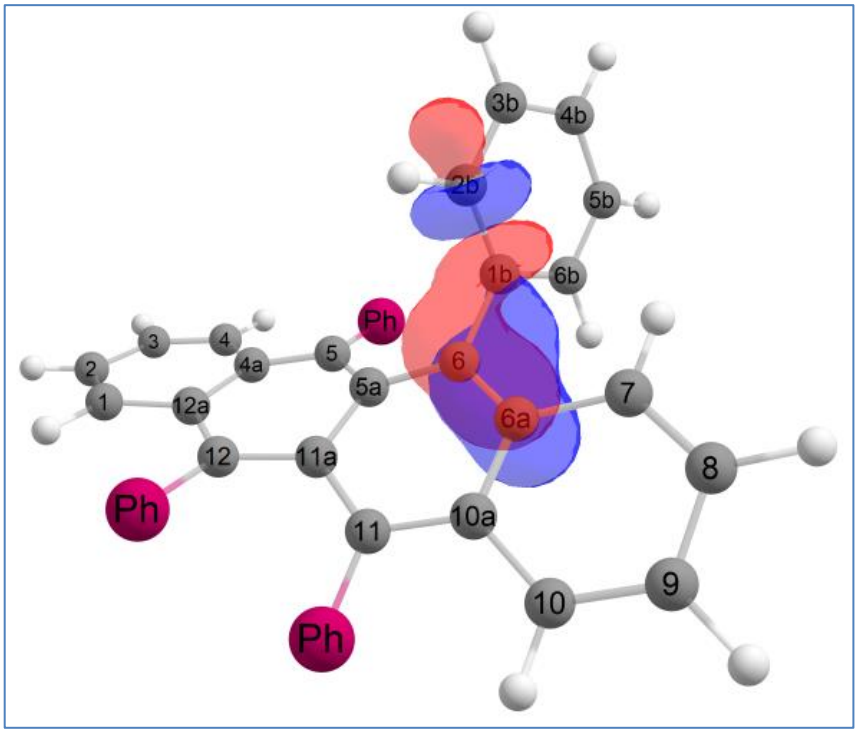


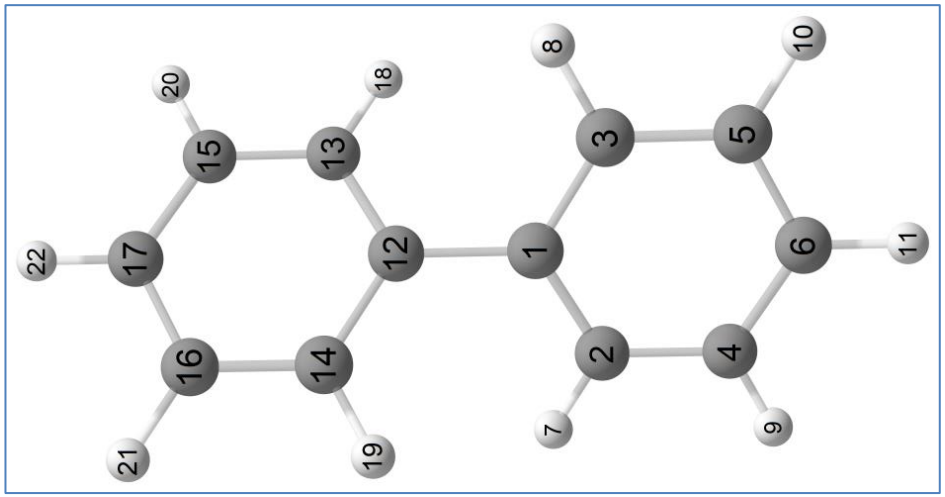
Equilibrium structure is *twist*-distorted

@ B3LYP/cc-pVTZ

Structure	D_{2h}	C_{2h}	D_2
ΔE, kJ mol^{-1}	28.3	16.3	0.0
# of imaginary frequencies	2	1	0

NBO-analysis and comparison with Ph-Ph:

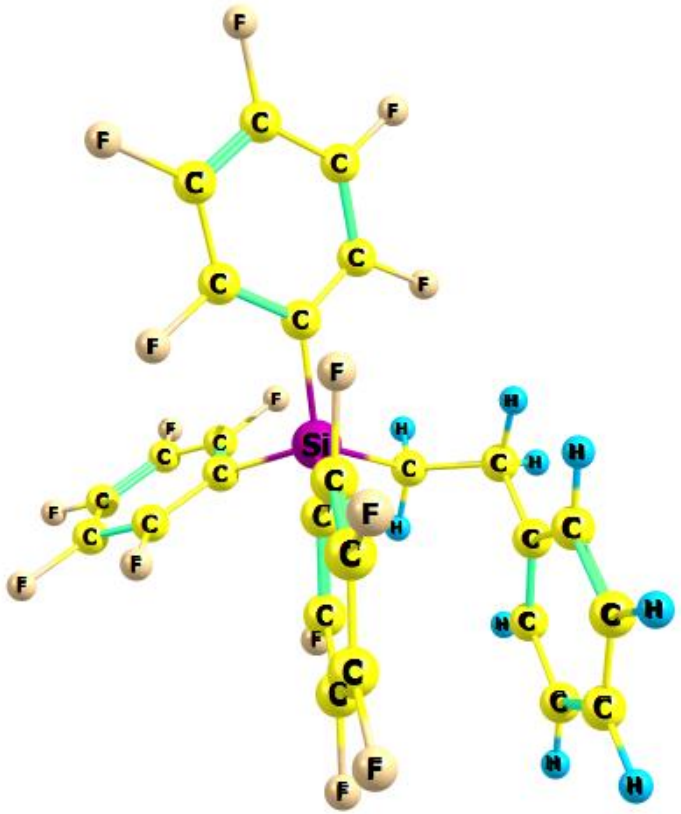


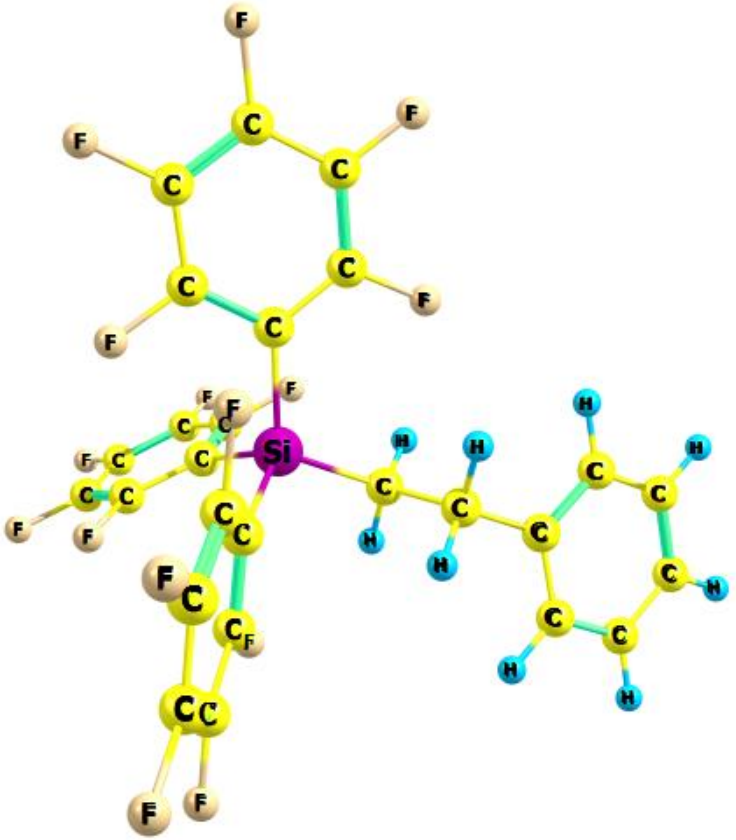


$E^{(2)}_{sum}$ = 25.6 kcal mol^{-1}

Ph-Ph			
τ/ °	0°	**40°**	90°
$E^{(2)}_{sum}$ / kcal mol^{-1}	42.4	**34.6**	22.1
ΔE / kcal mol^{-1}	10.2	**0.0**	9.3

tris(pentafluorophenyl)(phenylethyl)silane





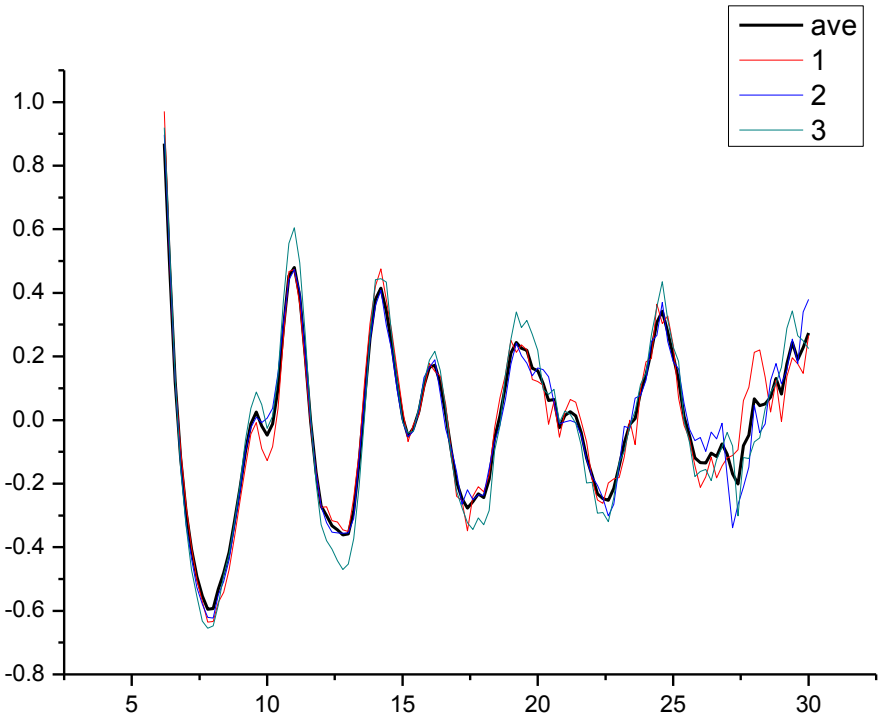
	A	**B**
ΔE, kJ mol^{-1}	**0**	**9.2**

@ PBE0-D3/cc-pVTZ

tris(pentafluorophenyl)(phenylethyl)silane

GED expirement, Bielefeld

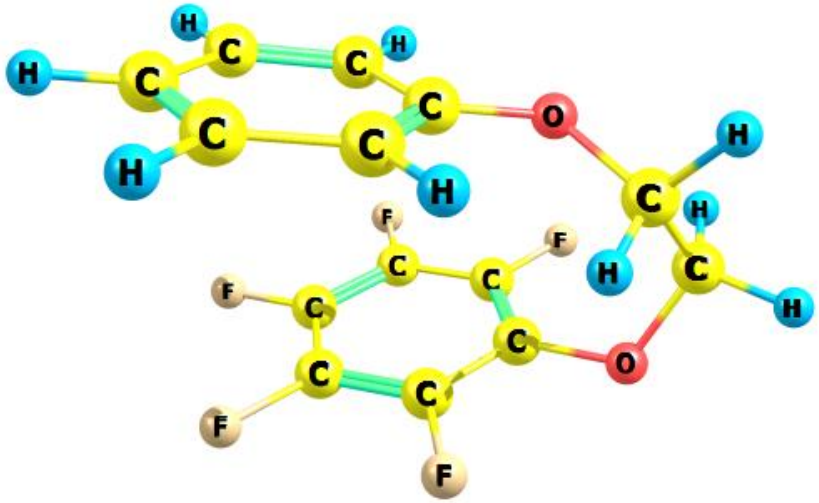
	Long distance	Medium distance
$R_{f,\,exp}$ / %	3.5	**16.6**



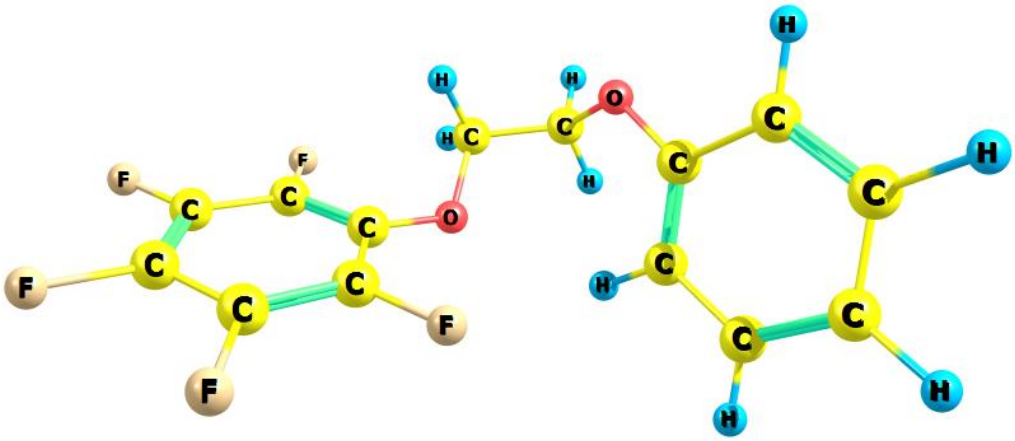
will be remeasured

3 sM(s) curves differ significantly from one another and the average curve

1-(pentafluorophenoxy)-2-(phenoxy)ethane ($Ph\text{-}OC_2H_4O\text{-}Ph_f$)



A

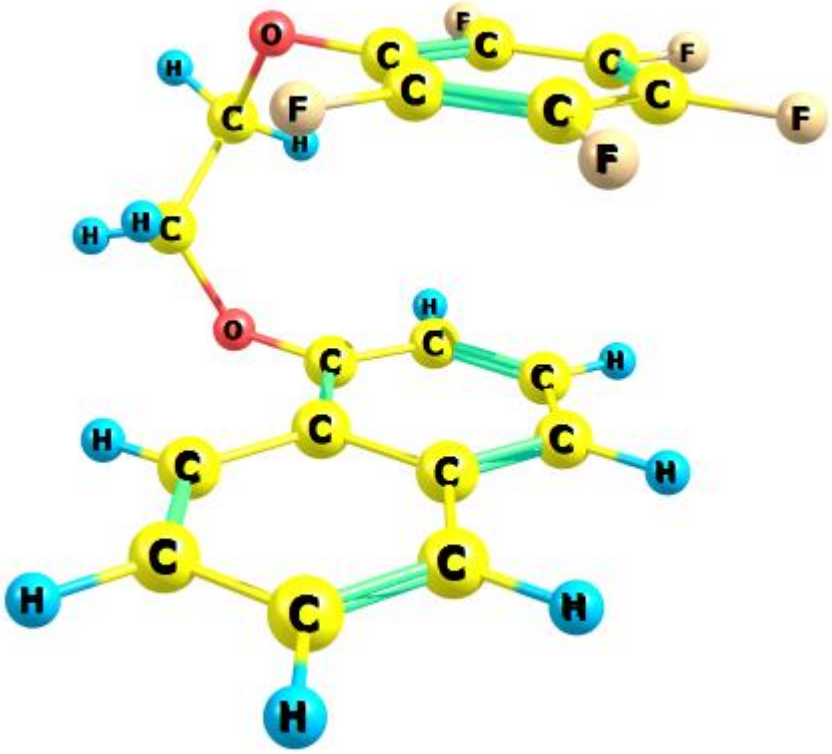


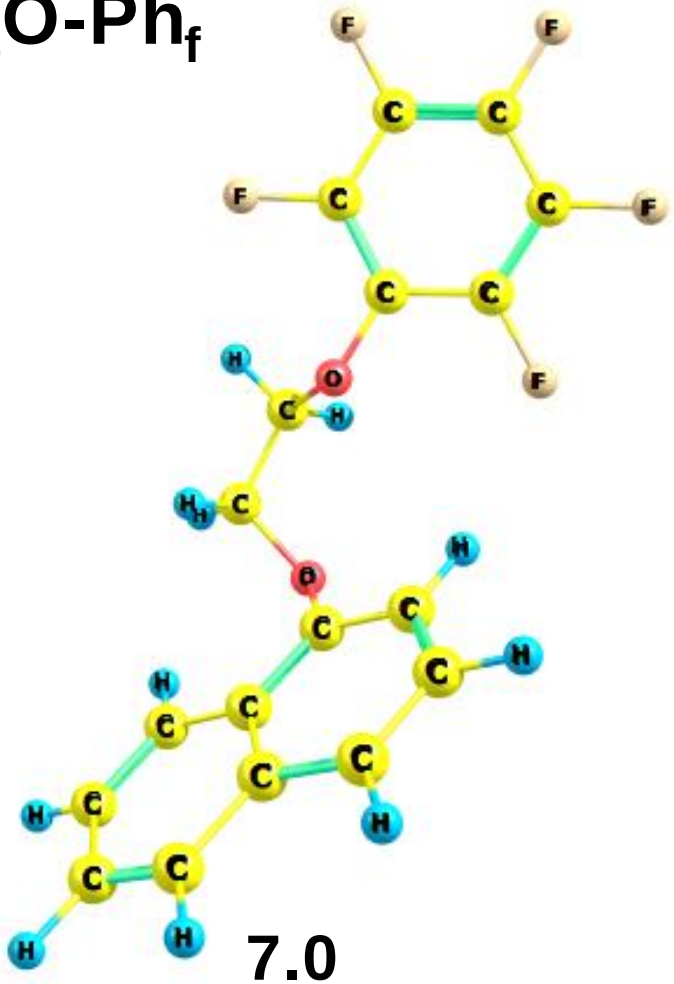
B

ΔE, kJ mol^{-1}	**0**	**9.2**

@ PBE0-D3/cc-pVTZ

Naph-OC_2H_4O-Ph_f

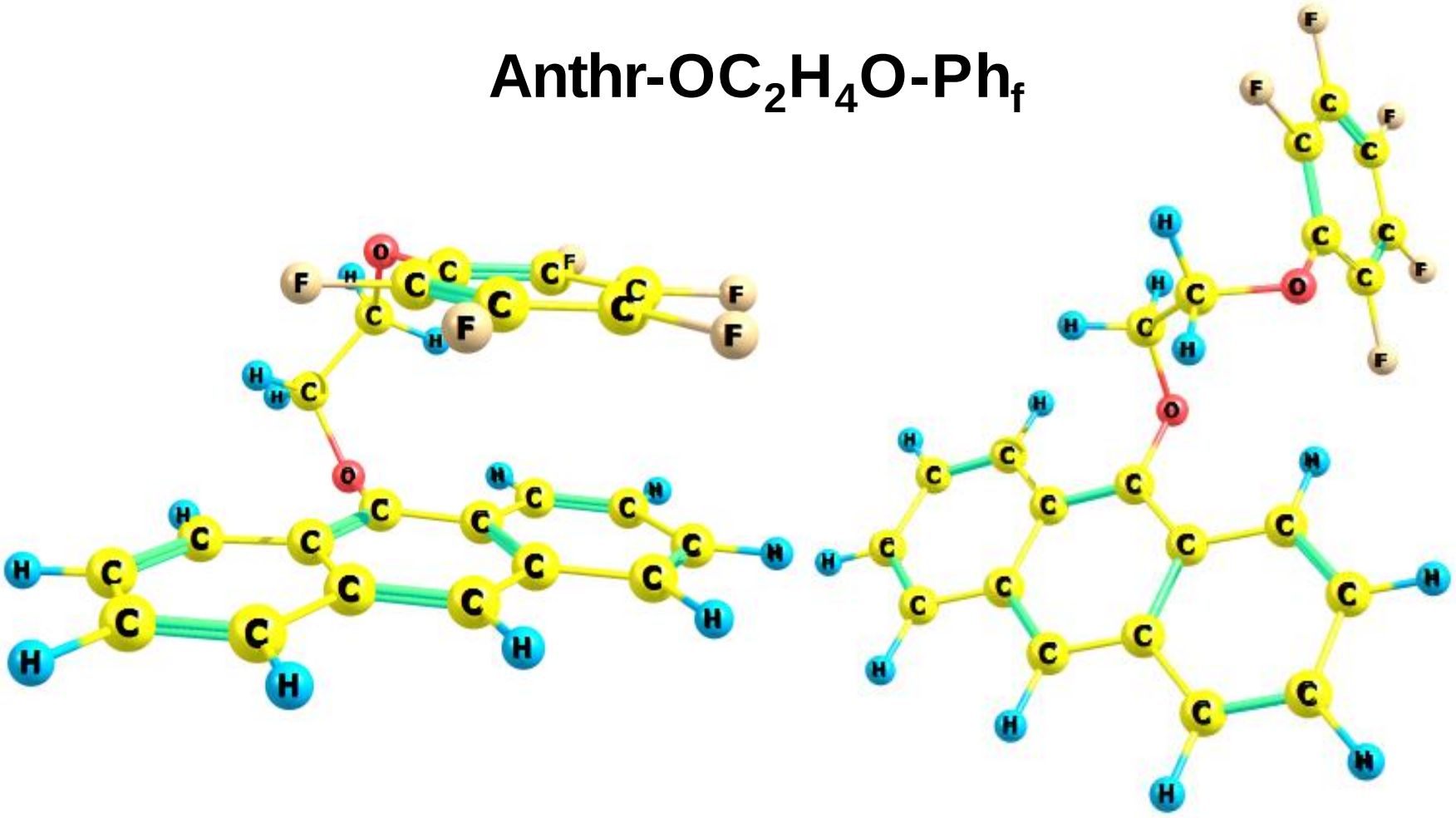




ΔE, kJ mol^{-1} **0** **7.0**

@ PBE0-D3/cc-pVTZ

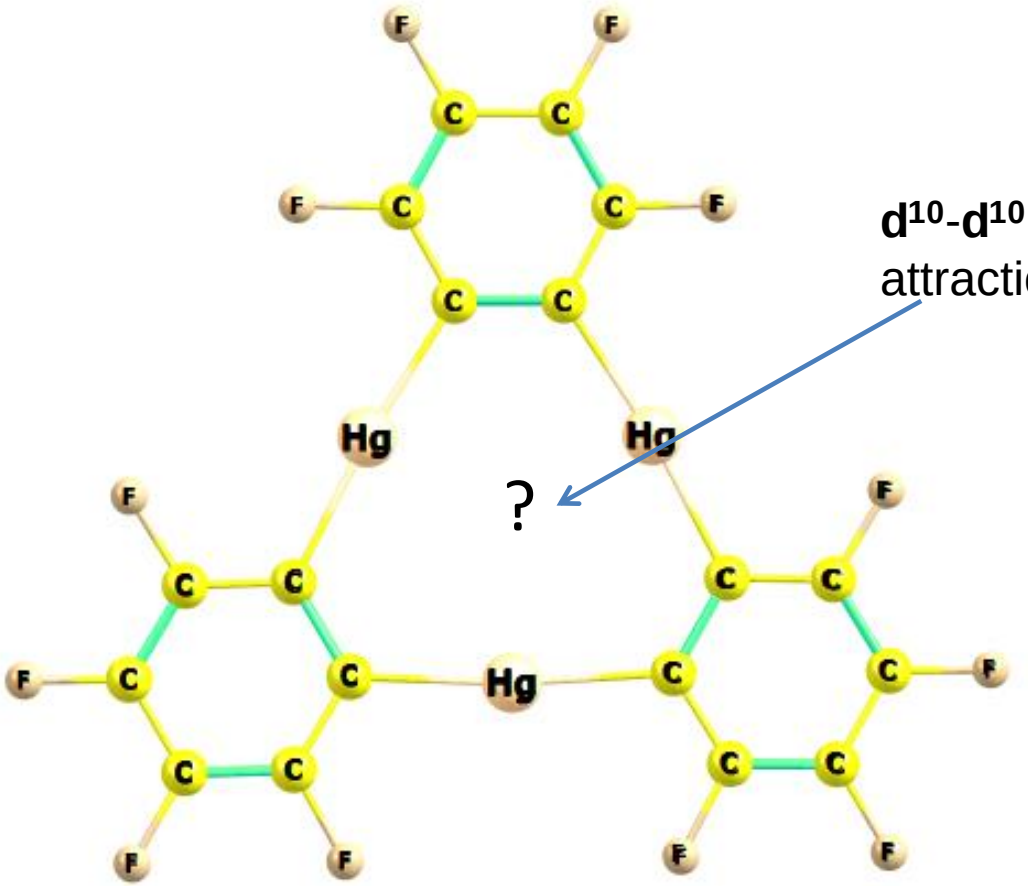
Anthr-OC_2H_4O-Ph_f



ΔE, kJ mol^{-1} **0** **13.1**

@ PBE0-D3/cc-pVTZ

(perfluoro-*orho*-phenylene) mercury



d^{10}-d^{10} attraction?!

- Quantum chemistry:

NO

- AIM:

NO

- GED:

???

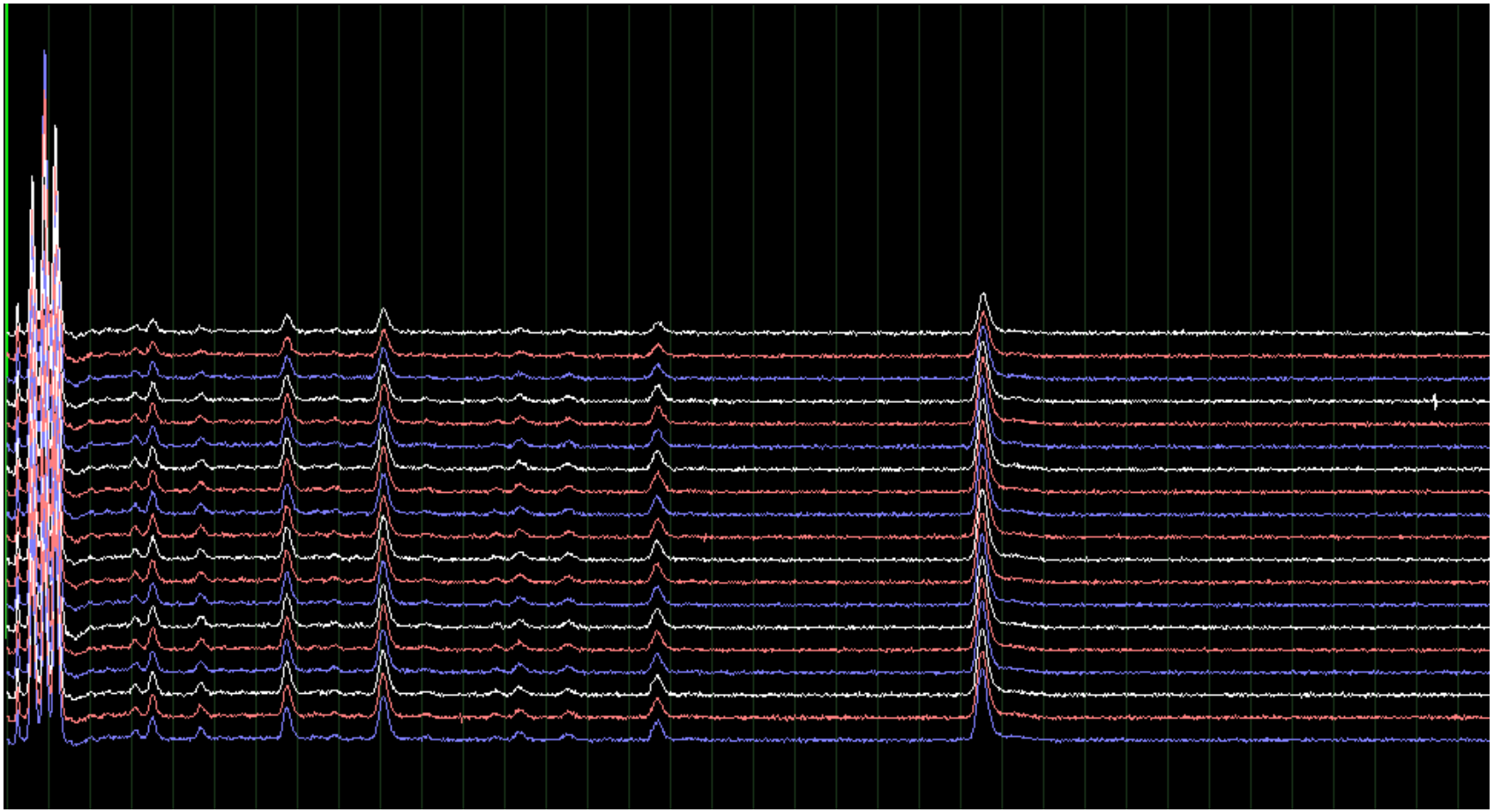
Problems of the GED refinement:

	Long distance	Short distance
$R_{f,\,exp}$ / %(photometric treatment)	25.7	54.6
$R_{f,\,exp}$ / %(scanner treatment)	13.8	15.1

these very large values make
a successful refinement impossible
from the beginning…

What is the reason of these disagreements within the sets of the experimental data?

Vapor composition during the GED/MS experiment

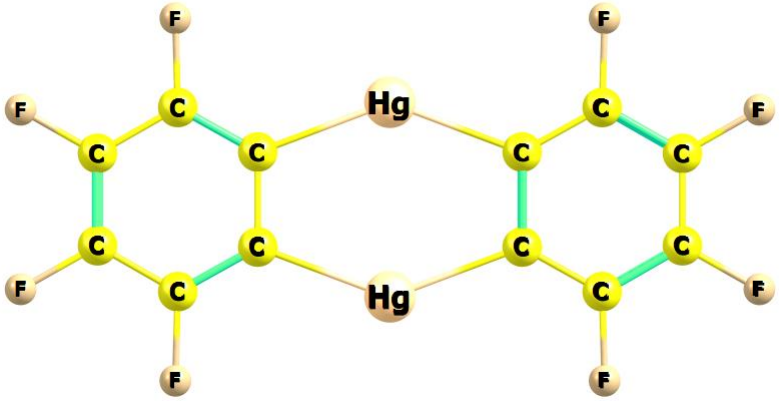


Mass-spectrum is highly reproducible

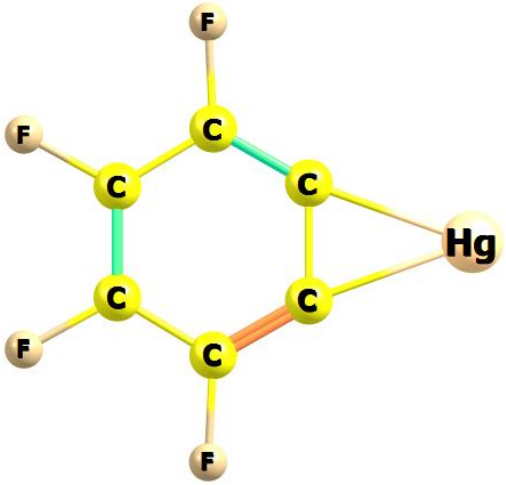
Any products of thermal decomposition in the vapor?

⇩

incompleteness of the model

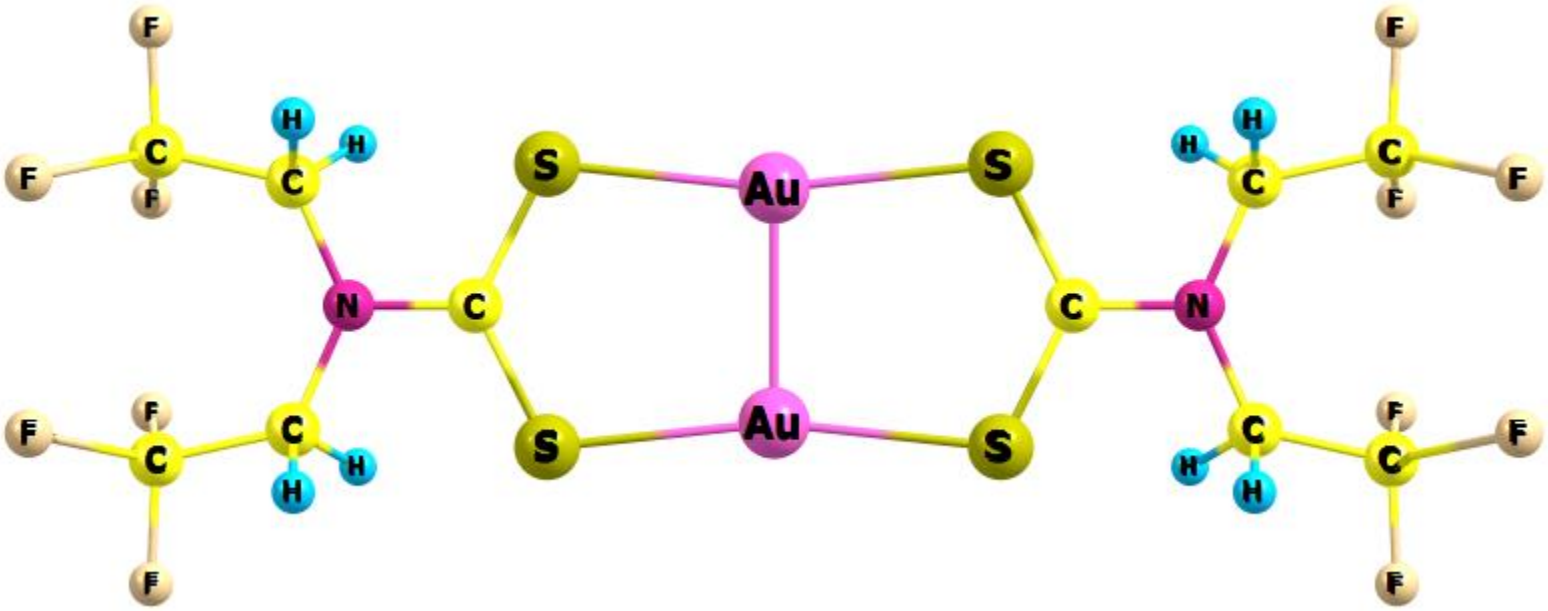


or

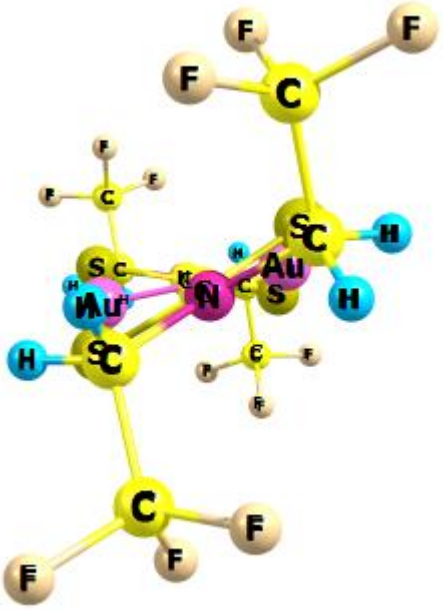


including of these species to the model did not result in improvement of the R_f

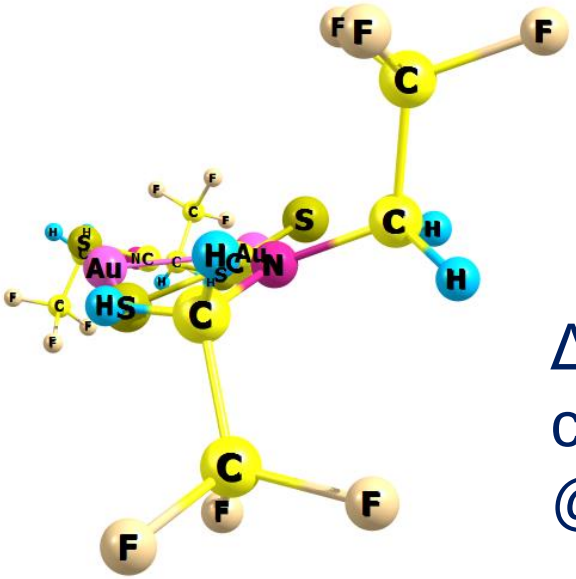
Gold(I) dithiocarboxylate complex



Another promising candidate for
d^{10}-d^{10} attraction in the gas phase

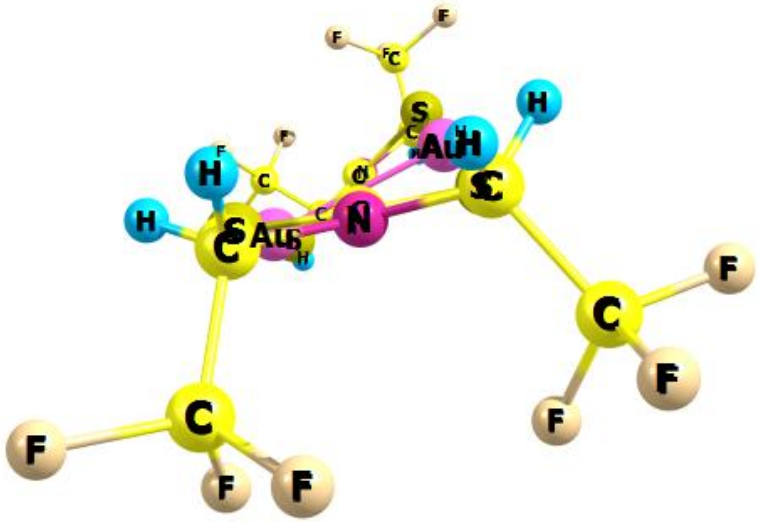


1) **D_2** (0 kcal mol^{-1}; 36 %)

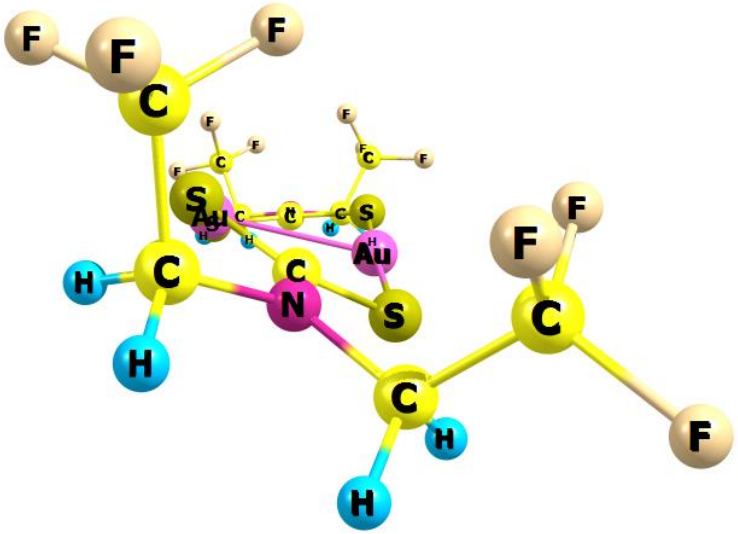


2) **C_2** (0.54 kcal mol^{-1}; 64 %)

ΔE and conformer ratio @ 453 K



3) **C_2** (7.87 kcal mol^{-1}; 0 %)



4) **C_2** (8.00 kcal mol^{-1}; 0 %)

Molecule(s)	What has been done	Current state
Acenaphthene	GED,GED+MW, QC (+NBO), MS	manuscript in preparation
Naphthalene, **anthracene**	GED (Ivanovo), QC (+NBO)	GED+MW refinement in progress…; GED (Bielefeld) is to follow
Rubrene	QC (+NBO)	GED/MS (Ivanovo) and GED (Bielefeld?!) is to follow
***tris*(pentafluorophenyl)(phenylethyl)silane**	QC, preliminary treatment of the GED data	GED (Bielefeld, MD) is to follow
Ph-OC_2H_4O-Ph_f; **Naph-OC_2H_4O-Ph_f;** **Anthr-OC_2H_4-Ph_f**	QC	GED (Ivanovo) is to follow

Molecule(s)	What has been done	Current state
perfluoro-*ortho*-phenylene mercury	GED/MS (failed), QC (+AIM)	MS study at different U_{ion} is to follow…
Gold (I) dithiocarboxylate	GED (Bielefeld), QC (preliminary results)	GED refinement of the 2-conformer mixture is in progress…

Thank you for your attention!