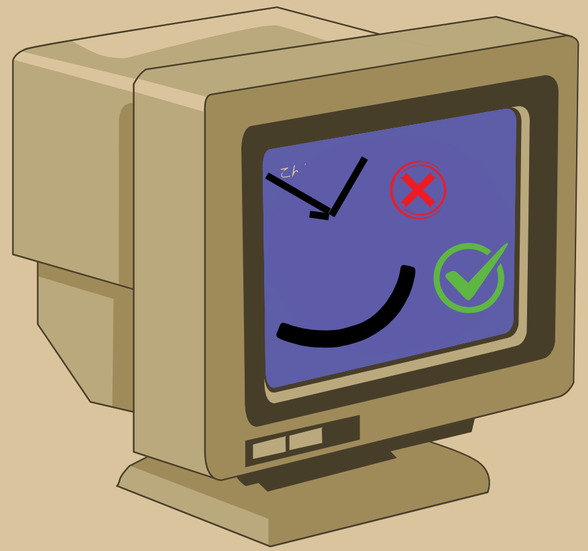
COMPUTATIONAL INVESTIGATION OF MECHANICAL PROPERTIES OF ORGANIC MOLECULAR CRYSTALS

TEA FREY, IVAN KODRIN



Functional crystalline materials

Optoelectronic

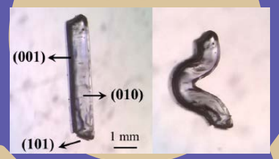
Biomimetics

Artificial mechanosensors

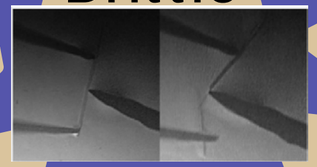
Pharmaceuticals

Molecular crystals

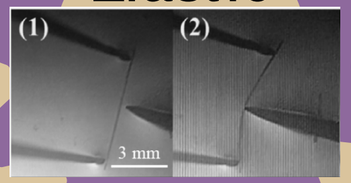
Plastic



Brittle



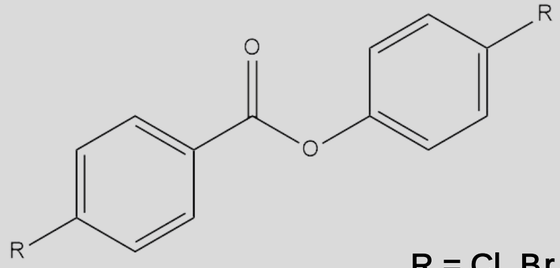
Elastic



- Chemical structure
- Intermolecular interactions
- Crystal Packing

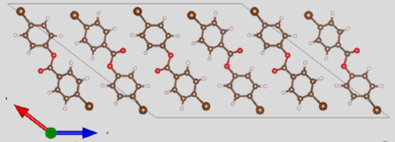
Periodic DFT

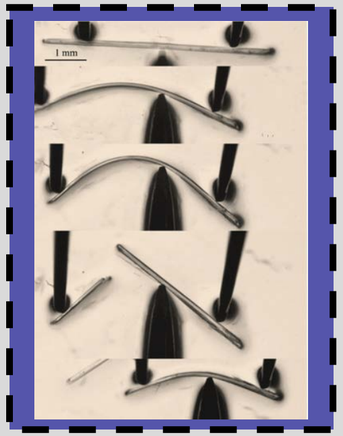
Model Systems



Form I

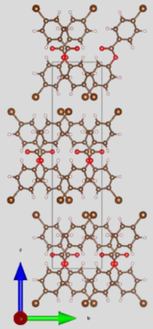
- Elastic
- Analog forms for bromine (1a) and chlorine (2)

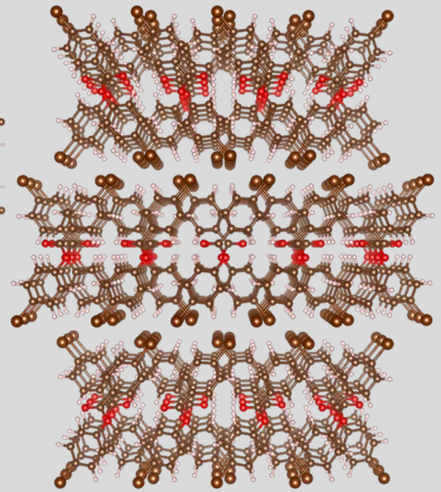


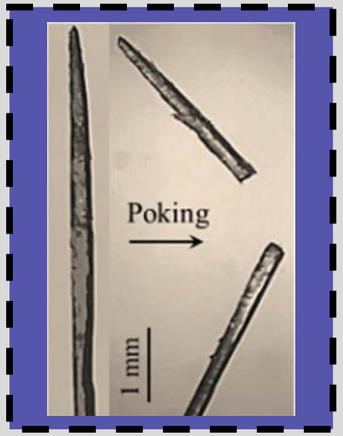


Form II

- Brittle
- Second polymorph form of bromine (1b)







S. Saha, G. R. Desiraju, *Chem. Commun.* 54 (2018.) 6348-6351

How to quantify mechanical properties?

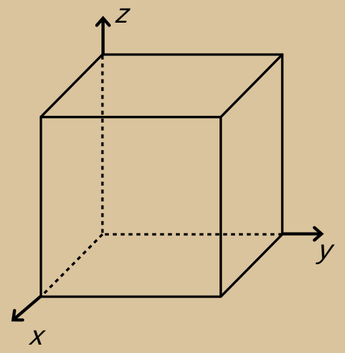
Hooke's law:

Young modulus

$$E = \frac{\sigma}{\varepsilon}$$

Tensile stress

Tensile strain



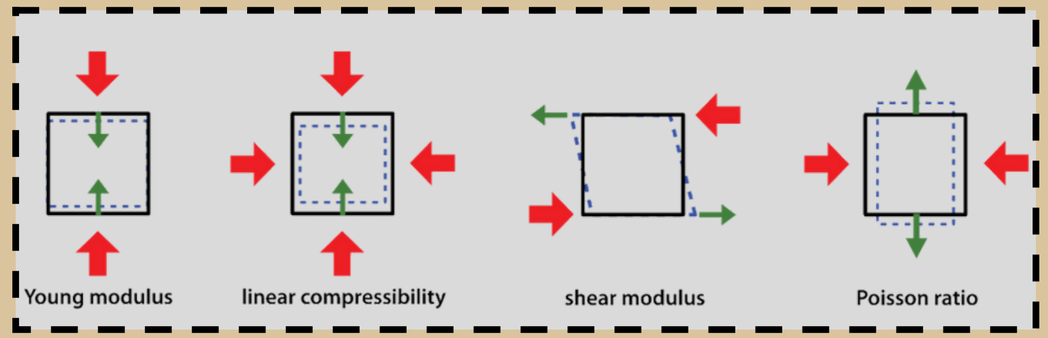
Crystal anisotropy

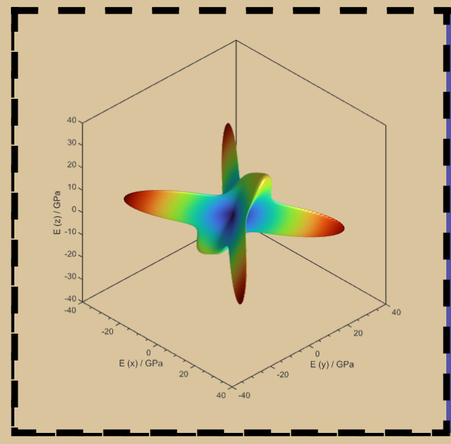
Elastic tensors

$$\sigma_{ij} = \sum_{kl} C_{ijkl}\epsilon_{kl} \ , i,j,k,l = x,y,z$$

Second Order Elastic Constants (SOEC)

$$\begin{bmatrix}\sigma_1\\ \sigma_2\\ \sigma_3\\ \sigma_4\\ \sigma_5\\ \sigma_6\end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16}\\ c_{21} & c_{22} & c_{23} & c_{24} & c_{25} & c_{26}\\ c_{31} & c_{32} & c_{33} & c_{34} & c_{35} & c_{36}\\ c_{41} & c_{42} & c_{43} & c_{44} & c_{45} & c_{46}\\ c_{51} & c_{52} & c_{53} & c_{54} & c_{55} & c_{56}\\ c_{61} & c_{62} & c_{63} & c_{64} & c_{65} & c_{66}\end{bmatrix} \begin{bmatrix}\epsilon_1\\ \epsilon_2\\ \epsilon_3\\ 2\epsilon_4\\ 2\epsilon_5\\ 2\epsilon_6\end{bmatrix}$$





Complete 3D overview of mechanical properties of a crystal!

Periodic DFT methods

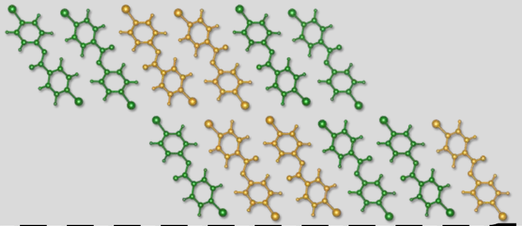
Optimization of known crystal structures:

- DFT method
- PBE-D3 functional
- pob-TZVP-rev2 basis set
- Default convergence criteria

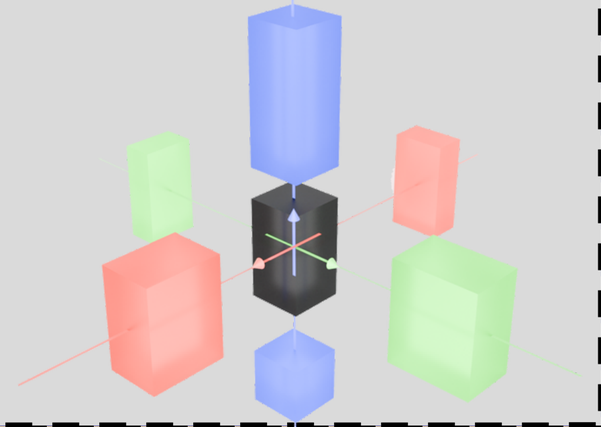
Reoptimization with stronger convergence criteria

1. Calculating SOEC using a fully automated procedure
   - keyword ELASTCON

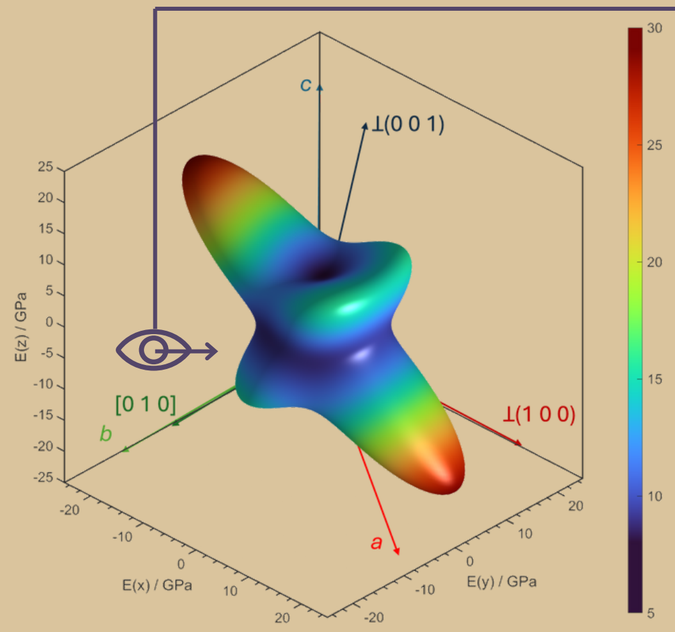
2. Calculating Interaction energies between fragments within unit cell



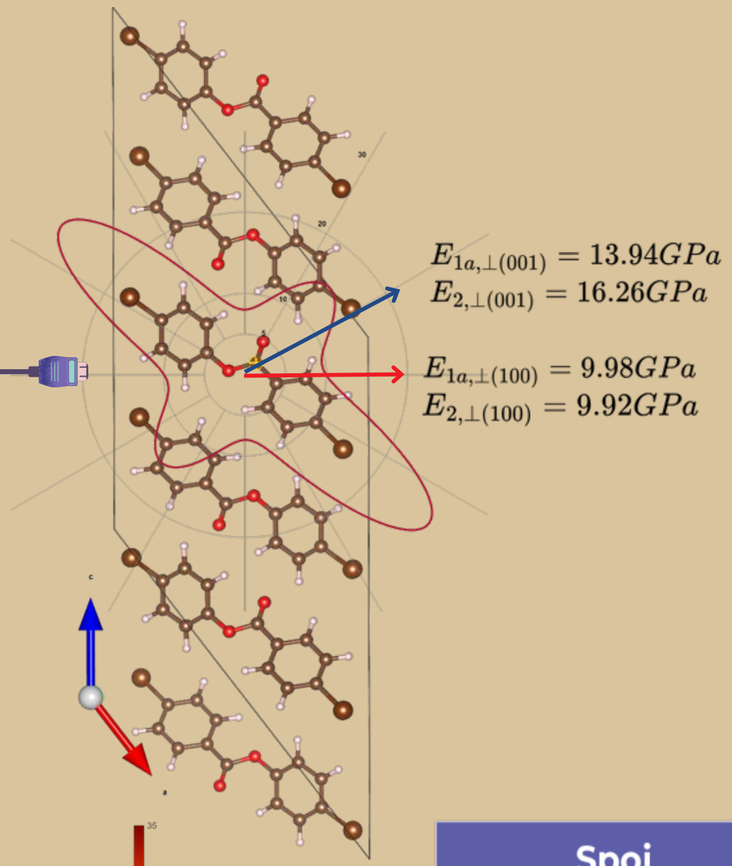
3. Virtual Tensile tests



Results and analysis



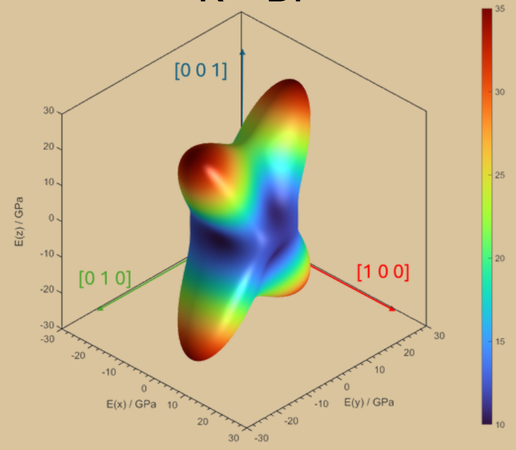
Form I
Elastic
R = Cl, Br



$E_{1a,\perp(001)} = 13.94GPa$
$E_{2,\perp(001)} = 16.26GPa$

$E_{1a,\perp(100)} = 9.98GPa$
$E_{2,\perp(100)} = 9.92GPa$

Form II
Brittle
R = Br

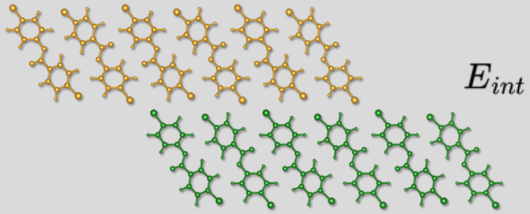


Spoj	Young modulus (E) / GPa
1a (Form I , R = Br)	13.10
1b (Form II , R = Br)	16.99
2 (Form I , R = Cl)	15.09

Results and analysis

Interaction energies

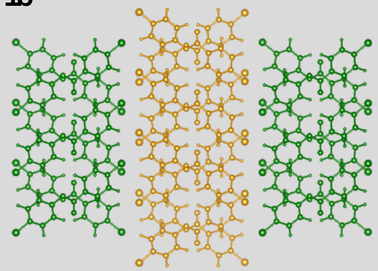
1a



$E_{int} = -111 kJmol^{-1}$

C–H···Br
C–Br···Br

1b

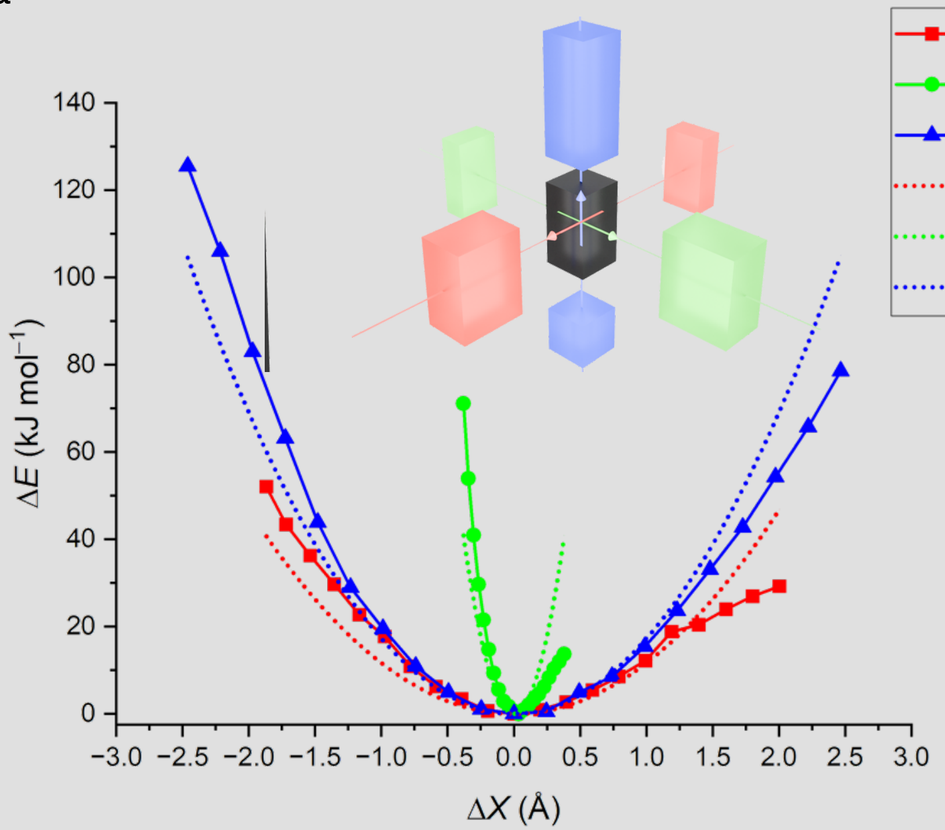


$E_{int} = -124 kJmol^{-1}$

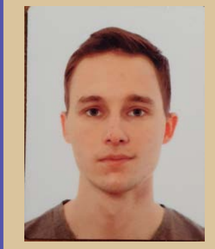
C–H···Br
C–Br···Br

Virtual tensile tests

1a



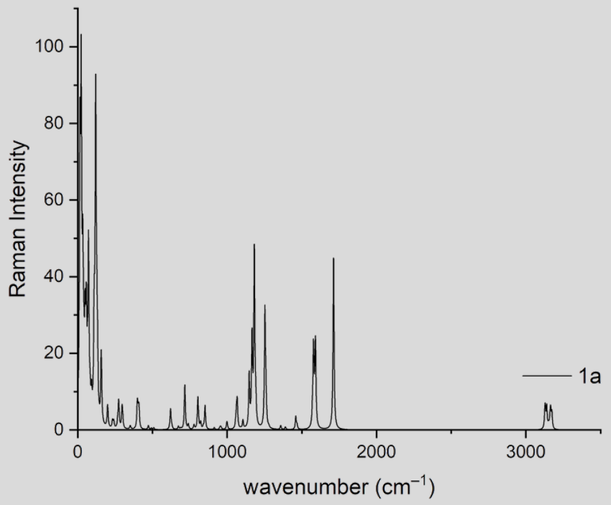
Direction	form I - elastic k / kJ mol^{-1} Å^{-2}	form II - brittle k / kJ mol^{-1} Å^{-2}
a	23.3	172.5
b	567.3	173.9
c	34.5	17.4



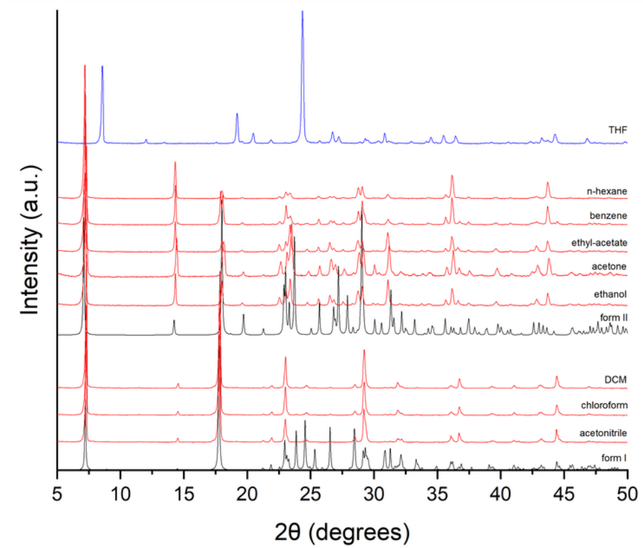
IGOR KERŠ

On the next episode...

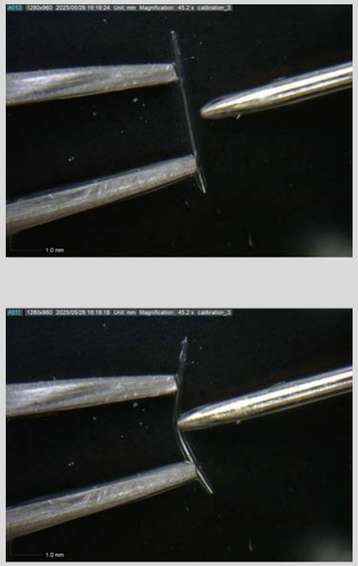
- Calculating Raman spectra at different points of deformation



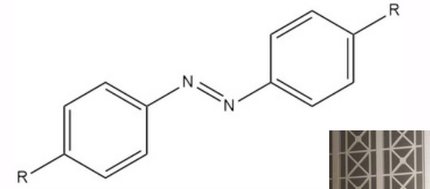
- Discovery and analysis of new polymorphs



- Experimental tests



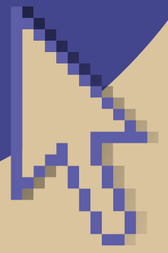
- New model systems



STIPE BLAŽEVIĆ

COMPUTATIONAL CHEMISTRY DAY 2025

THANK YOU FOR LISTENING!



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- Igor Kerš, bacc. chem.

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