Neambijentalna mjerenja:
Termoodskočni efekt –
primjer sinergije difrakcijskih, termičkih, spektroskopskih i teorijskih metoda

My trip to *jumping crystals*…

Kansai international airport, Osaka, Japan

(artificial island, opened in 1994, 4 km x 2.5 km, total cost $20 billion, sinking rate currently 7 cm/year)

大阪大学
OSAKA UNIVERSITY

Osaka University

established in 1724, 3000 academic staff,
9000 administrative staff, 26000 students, area 1.6 km^2

Panče Naumov

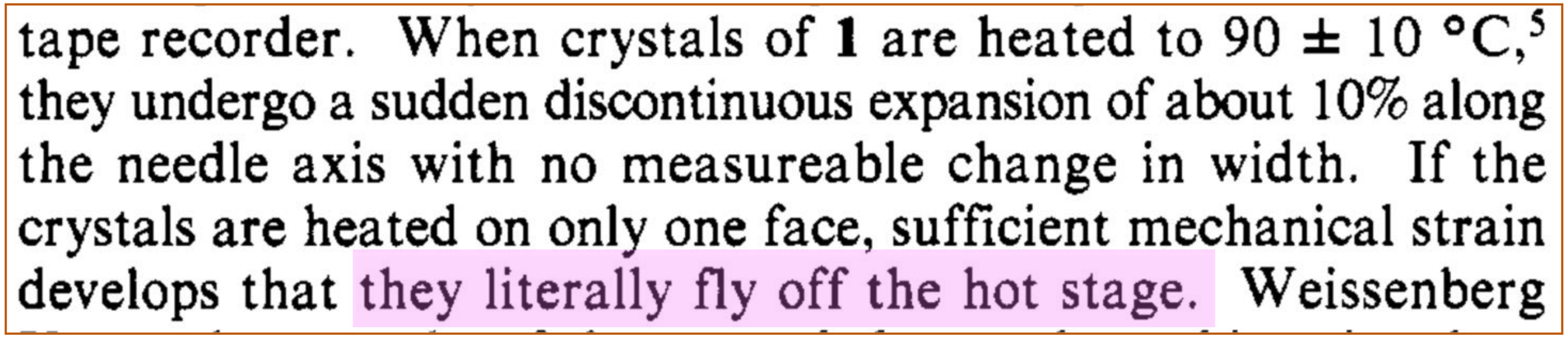
(giving lecture at the ECM29, Rovinj, 2015)

Merry Christmas!

(Osaka, 2010)

Thermosalient materials - jumping crystals

- first reported in 1983. by Etter and Siedle (*J. Am. Chem. Soc.,* 1983, **105**, 641.)
  Solid-state rearrangement of (Phenylazophenyl)Palladium Hexaflouroacetylacetonate



tape recorder. When crystals of **1** are heated to 90 ± 10 °C,[5] they undergo a sudden discontinuous expansion of about 10% along the needle axis with no measureable change in width. If the crystals are heated on only one face, sufficient mechanical strain develops that they literally fly off the hot stage. Weissenberg

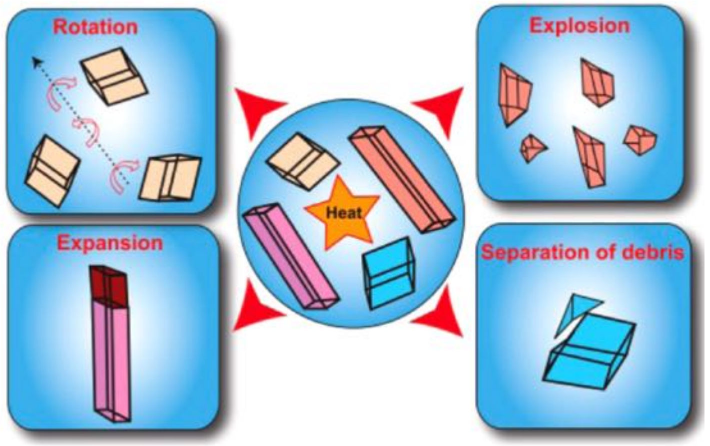
By 2009. there were less than dozen reported thermosalient systems!

1. Gigg et al., *J. Chem. Soc., Perkin Trans. 1*, 1987, 2411. - (±)-3,4-di-*O*-acetyl-1,2,5,6-tetra-*O*-benzyl-*myo*-inositol
2. Ding and Herbst, *Acta Cryst.*, 1991, **B47**, 739. - *trans,trans,anti,trans,trans*-perhydropyrene
3. Lieberman et al., *Mol. Cryst. Liq. Cryst.*, 1994, **242**, 79. - Terephtalic acid
4. Zamir et al., *Mol. Cryst. Liq.Cryst.,* 1994, **242**, 193. - Oxitropium bromide
5. Corbett and Dickman, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.,* 1996, **52**, 1851. - 4,5-Bis(flourodinitromethyl)-2-methoxy-1,3-dioxolane
6. Crottaz et al., *J. Mater. Chem.*, 1997, **7(1)**, 143. - $NiCr_2O_4$ and $CuCr_2O_4$
7. Lieberman et al., *Chem. Mater.*, 2000, **12**, 490. - 1,2,4,5 tetrabromobenzene
8. Yasutake et al., *Tetrahedron Lett.*, 2000, **41**, 7933. - [3_6]-superphane
9. Ferndandes et al., *Acta Cryst.,* 2004*,* **B60**, 300. - *Ortho*-ethoxy-*trans*-cinnamic acid
10. Siegrist et al., *Adv. Mater.,* 2007, **19**, 2079. - Pentacene

Thermosalient materials, or more colloquially called *jumping crystals*, are materials that during heating/cooling undergo a polymorphic phase transition, which is so sudden and energetic that crystals jump off the stage to distances much bigger than the crystal dimensions.

Thermosalient transition takes place on the time scale of several milliseconds (or even less!) and is accompanied by the large and anisotropic change of the unit-cell dimensions (up to 25%).

Why is it interesting?



- simply, it is visually extremely attractive phenomenon
- they provide impressive demonstration of macroscopic conversion of thermal energy to mechanical work
- these actuating or mechanically responsive materials are candidates for future dynamically active elements such as smart medical devices or implants, artificial muscles, biomimetic kinematic devices, electromechanical devices, actuators, thermal sensors…
- single crystals have many advantages and superior performance in comparison to polymers (faster responses and more rapid relaxation to the original state, easier control of locomotion)

Advantages

- Rapid energy transfer
- Efficient energy conversion
- Extraordinary strains
- Favorable elastic constants
- Facile fabrication
- Advantages of crystal engineering

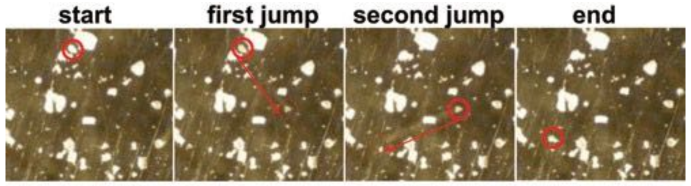
Aplications

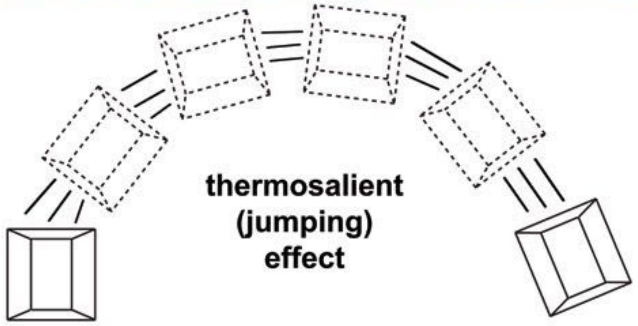
- Microfluidic valves/gates
- Energy harvesting
- Mechanically tunable optical elements
- Actuation materials (artificial muscles)
- Switchable reflector elements
- Tunable contact printing

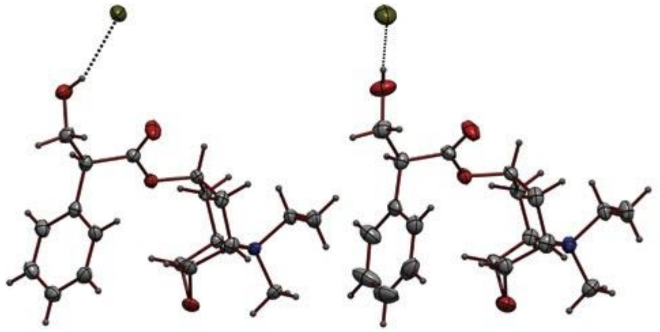
Any problems?

1. still today, the mechanism is not fully resolved
2. why some compounds jump, and other do not?
3. in most cases quality of crystals during the phase transition is decreased; crystals deform, bend or break; sublimation of crystals ⇒ structural analysis is impossible

Out of those 11 systems only in 5 cases the crystal structures of both phases was determined!



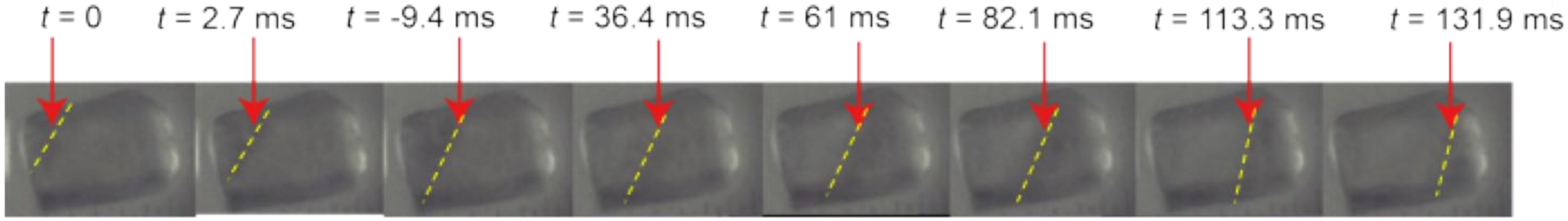




Facts:

- thermosalient phases have similar crystal structures with identical symmetry and space groups
- process is related with relatively small, albeit distinct changes in overall packing and in the unit cell parameters
- extremely fast phase transformation (~ ms)
- collective movement of the molecules, somewhat similar to martensic transformation

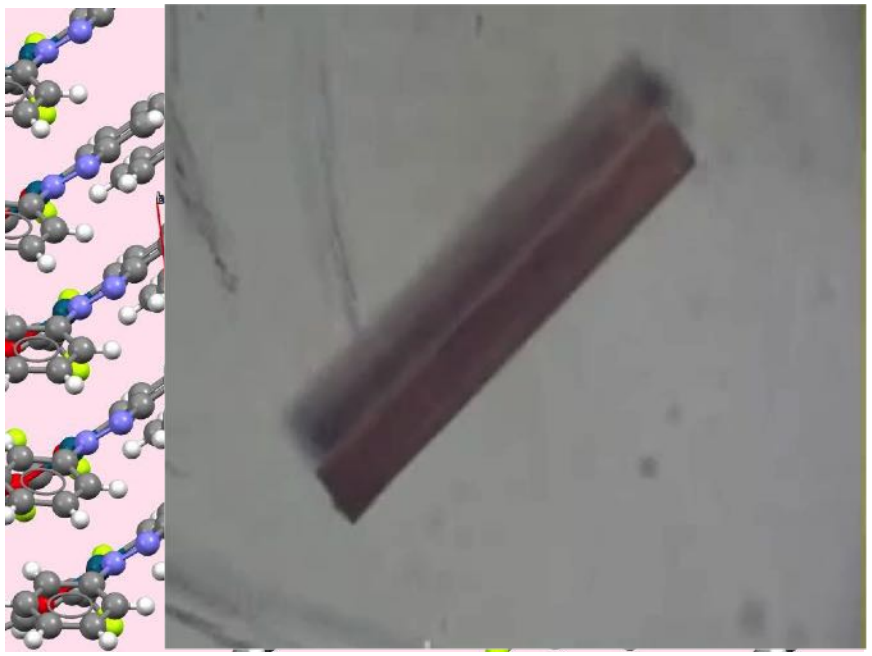
High speed recording of the habit plane progression (10 000 fps)



Three classes of thermosalient materials

Class I

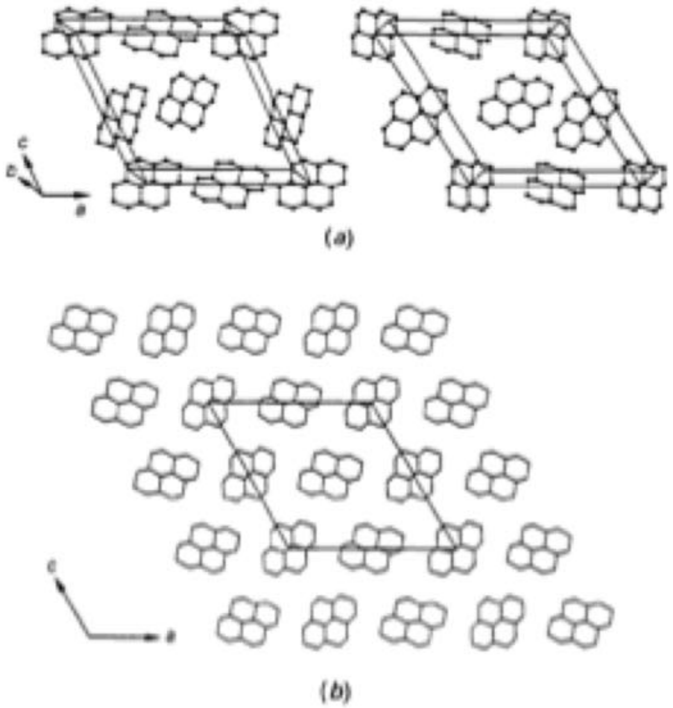
- no strong hydrogen bonds
- arranged in layers of stacked molecules

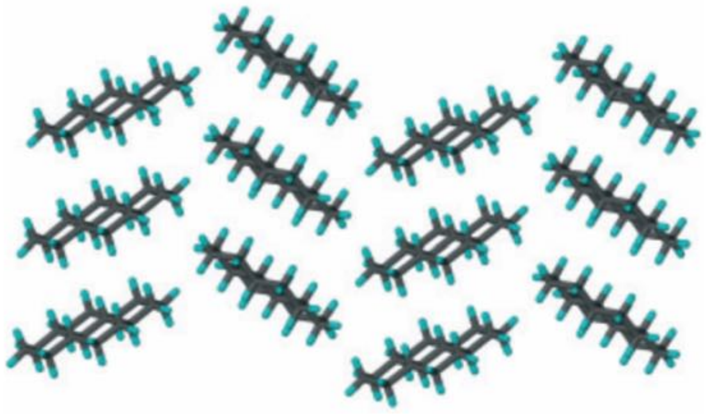


(Phenylazophenyl)palladiumhexaflouroacetylacetonate

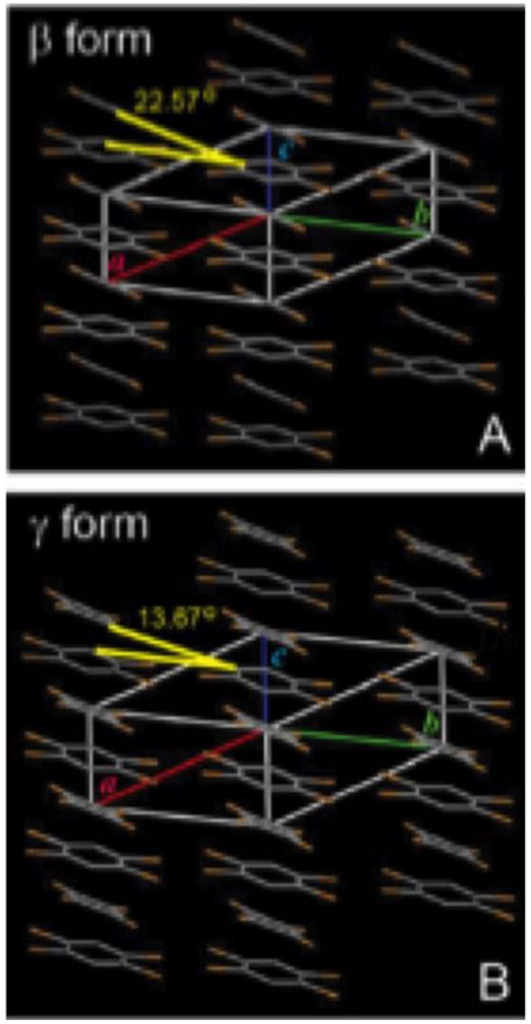
- upon heating up to 90(±10)°C yellow crystals undergo sudden discontinuous expansion of about 10% along needle axis
- no detectable change in the width of the crystal
- when heated on only one face, they jump off the stage
- on further heating they change their color to red
- molecules form stacks along ***c***-axis

trans,trans,anti,trans,trans-perhydropyrene



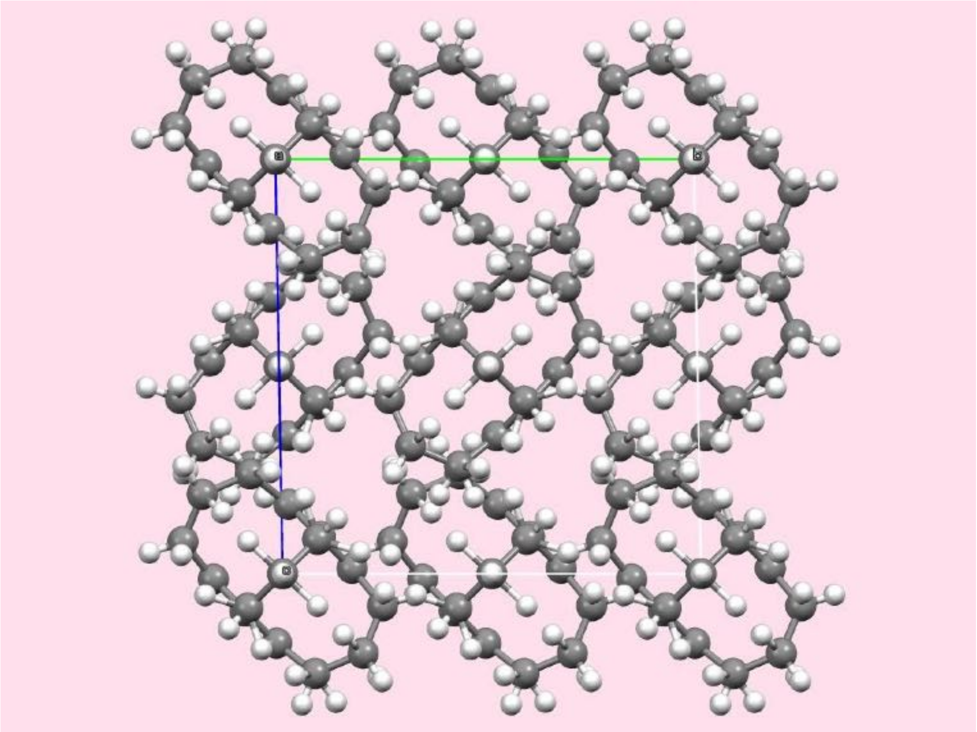


- when heated above 71.5°C, or cooled below 65.5°C, colorless needle-shaped crystals exhibit strong movements and hop about 6 cm high
- room temperature phase has a corrugated sheet like structure
- high temperature phase could not be determined due to fast sublimation



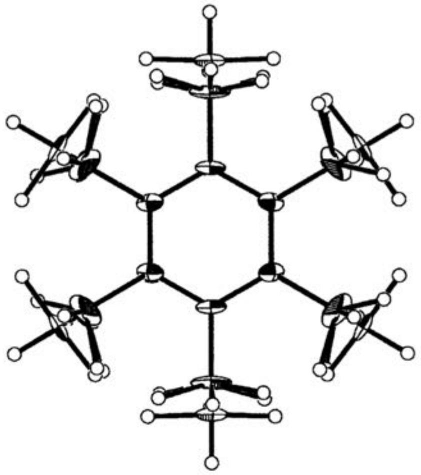
1,2,

- upon heating
transition from
to heights sev
- they are know
- heating of one
- phase transiti
rings from 22.
sheets

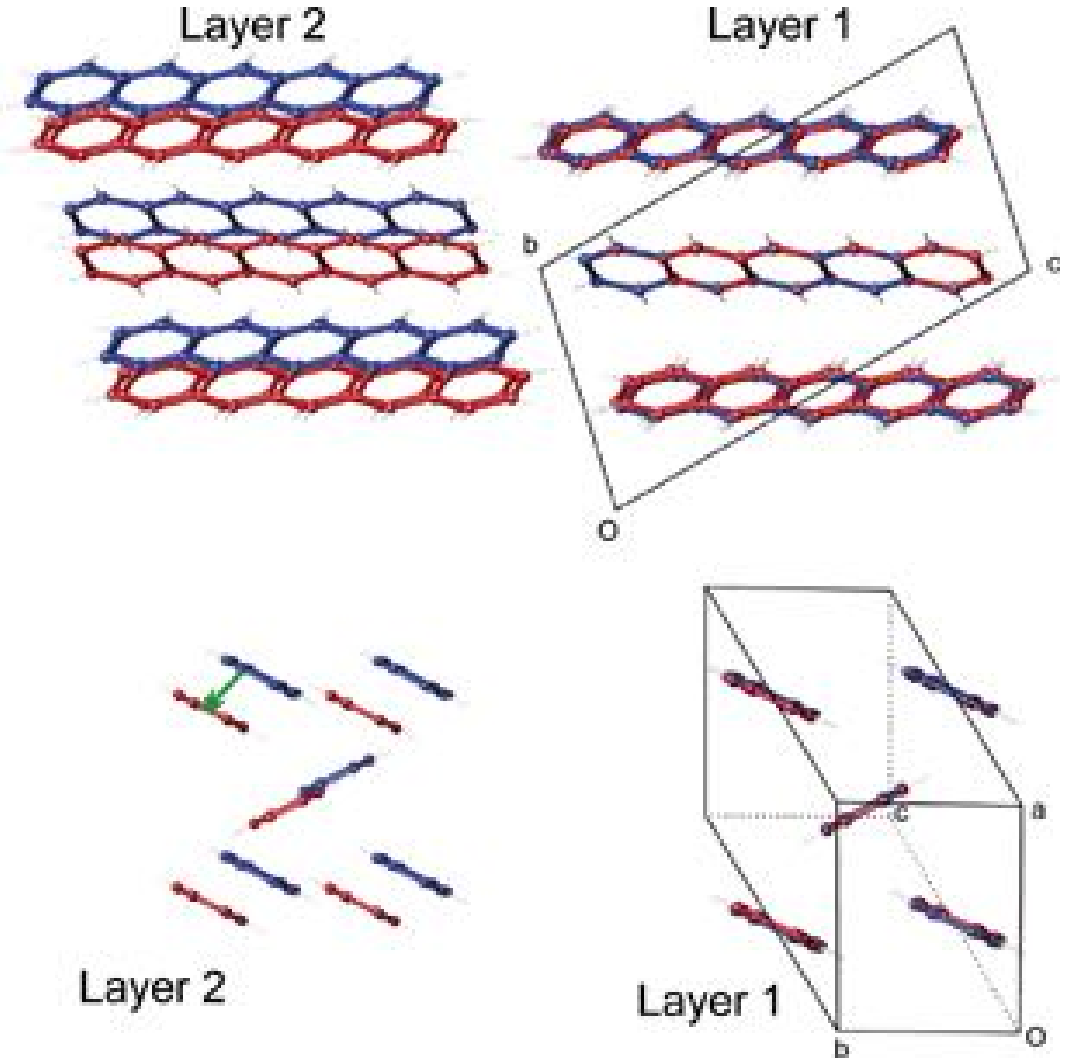


[3₆]-superphane

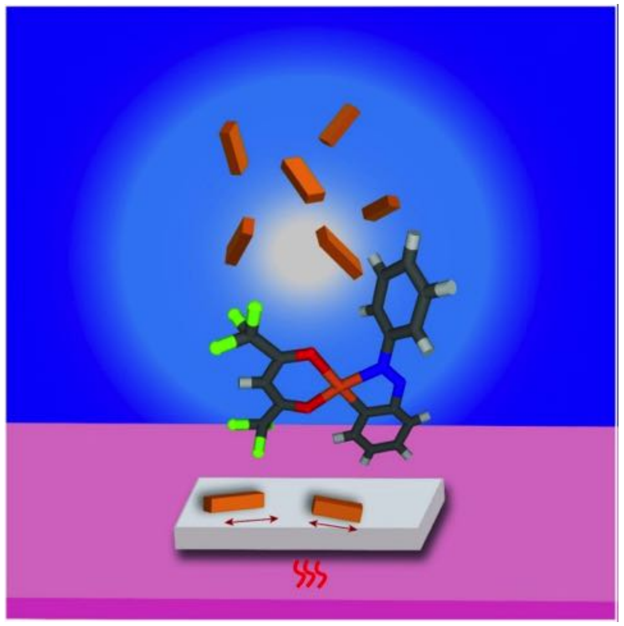
- also shows jumping behavior but the mechanism is still poorly understood

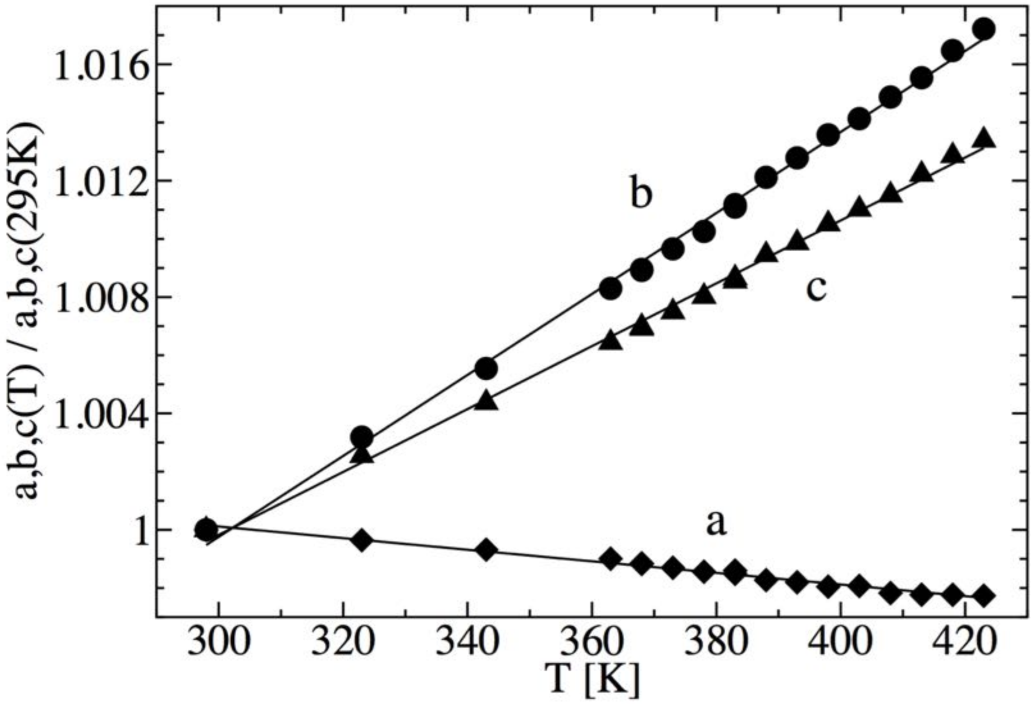


Pentacene



- low temperature phase, pentacene-LT, stable < 190°C
- how temperature phase, pentacene-HT, stable > 190°C
- high temperature data collection is hampered by cracking and sublimation at higher temperature
- crystal structure is composed of similar herringbone layers of molecules





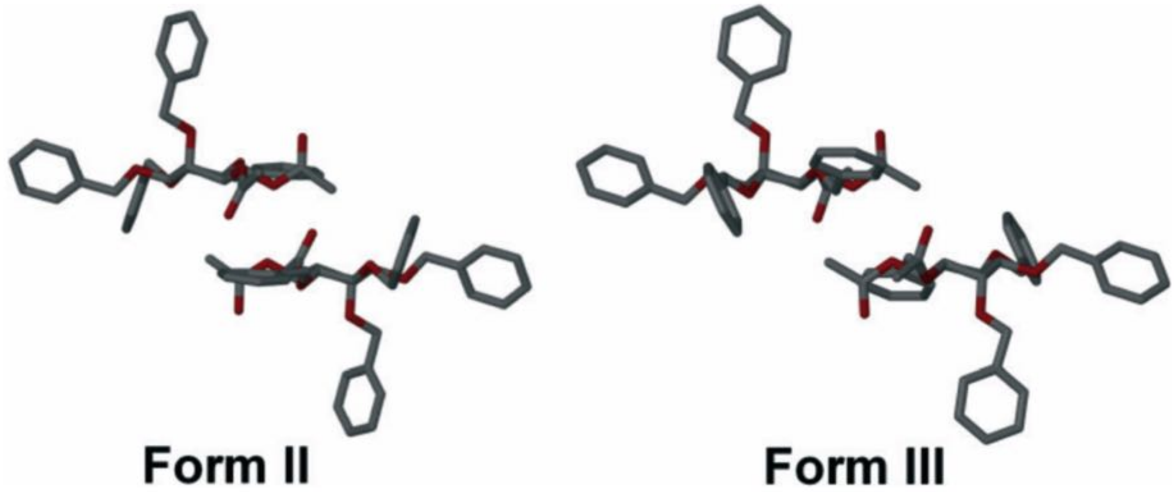
Negative thermal expansion!

Three classes of thermosalient materials

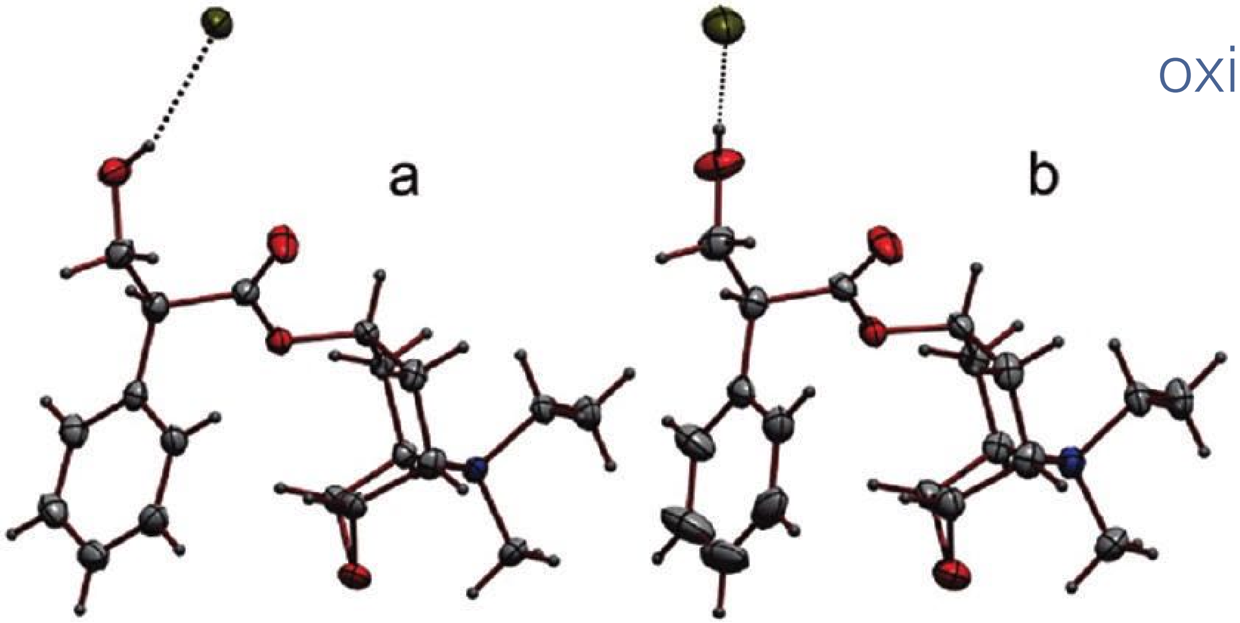
Class II

- any functional groups capable of forming strong hydrogen bonds are sterically hindered
- strong intermolecular interactions are not possible

(±)-3,4-di-*O*-acetyl-1,2,5,6-tetra-*O*-benzyl-***myo***-inositol

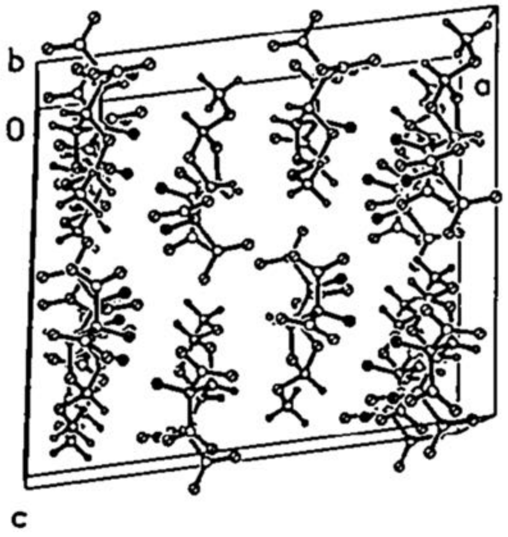


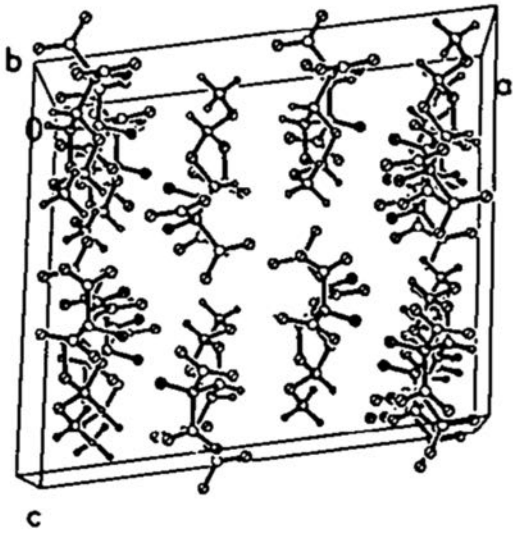
- in 1987. reported two thermosalient phases
- later reported three phases plus two glassy materials
- phase transition around 70°C is especially vigorous
- needle-like crystals jump several cm to air
- progression of the transition front can be observed
- needle length changes cca. 10%
- slight difference in crystal structure is attributed to flexibility of phenyl rings



oxitropium bromide

- anticholinergic medicine
- phase transition takes place around 45°C
- *b* axis increases by 11% and *c* axis decreases by 7%
- both phases have similar molecular conformations





4,5-Bis(flourodinitromethyl)-2-methoxy-1,3-dioxolane

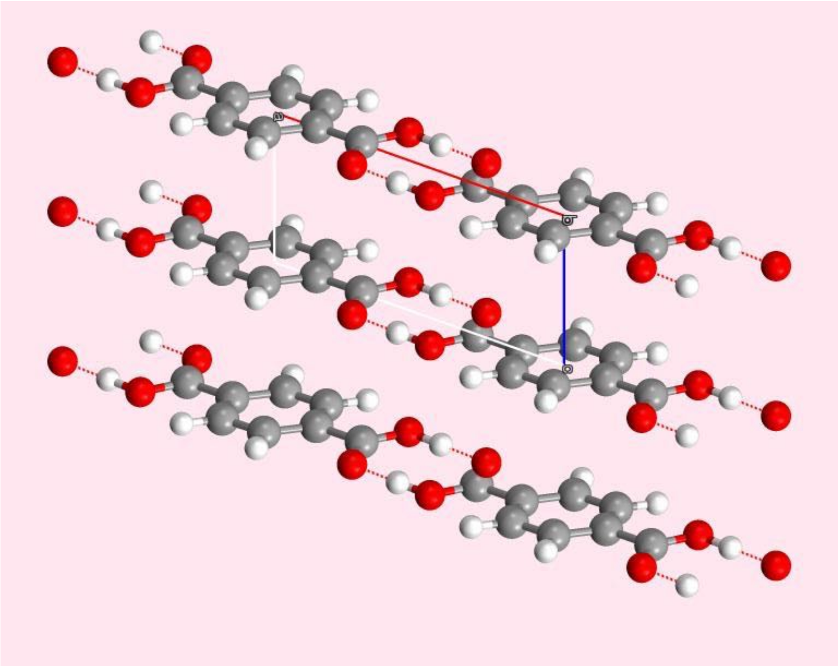
- thermosalient effect is mentioned in literature
- it was not explained in detail
- high temperature phase is unknown

Three classes of thermosalient materials

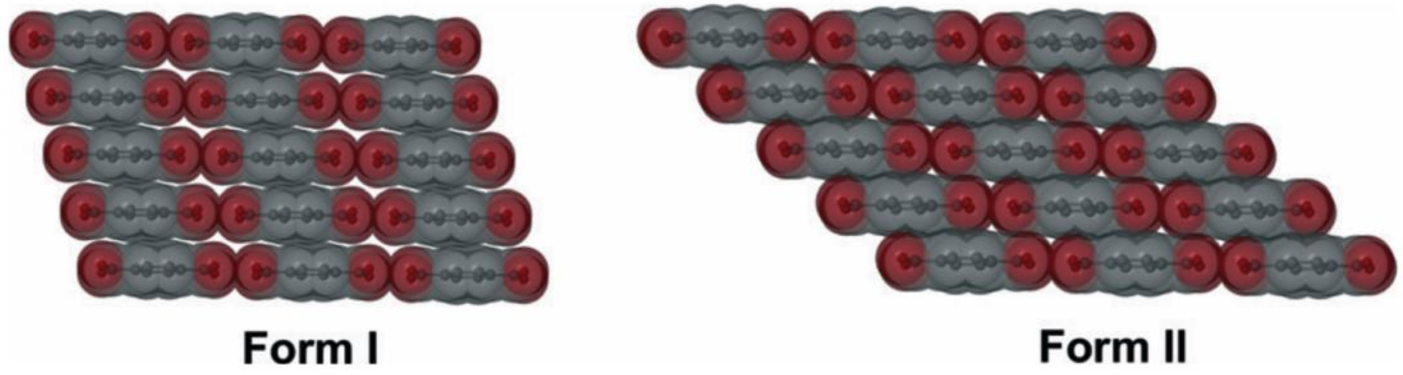
Class III

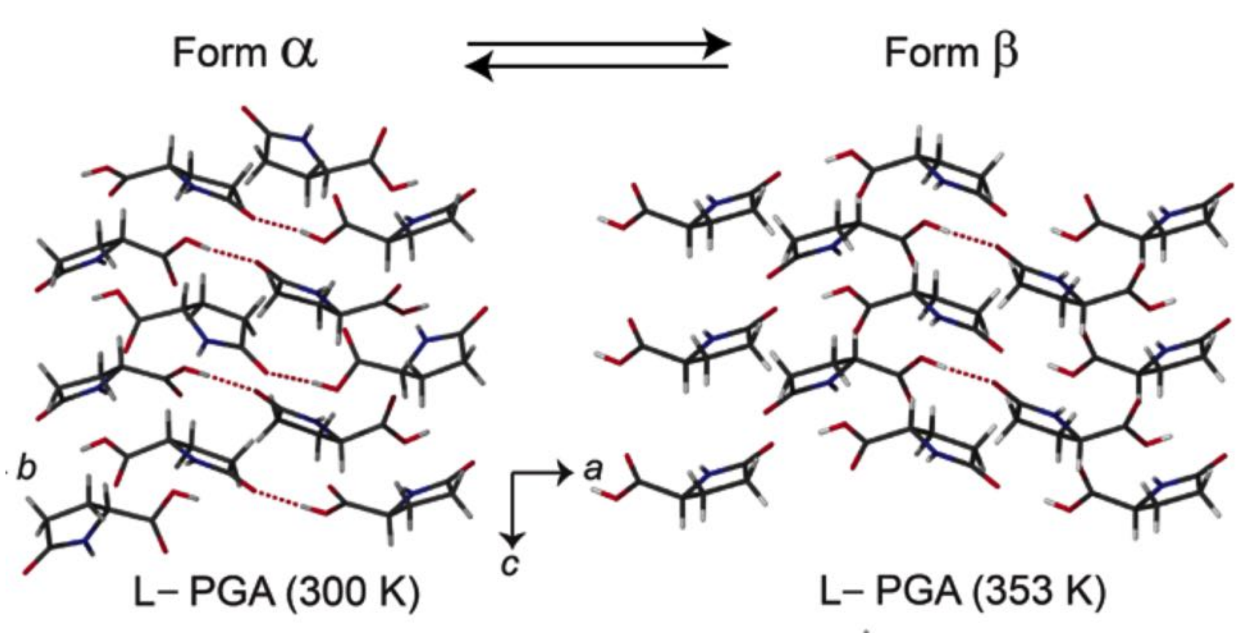
- molecules contain functional groups that are capable of forming strong intermolecular interactions which may lead to infinite hydrogen bonded tapes or chains

terephtalic acid



- trimorphic system
- when crystals of form II are heated in the range 75-100°C they undergo morphological change from rhombic to rectangular (I)
- during this reshaping some of the crystals jump
- this change is reversible on cooling to 30°C - hysteresis
- but the crystals need to be pinched with a metal point to regain rhombic shape
- *a* and *c* axis compress by 20% and 25%, resp., and *b* axis increases by 20%
- crystal structures consist of infinite chains of carboxylic acid dimers





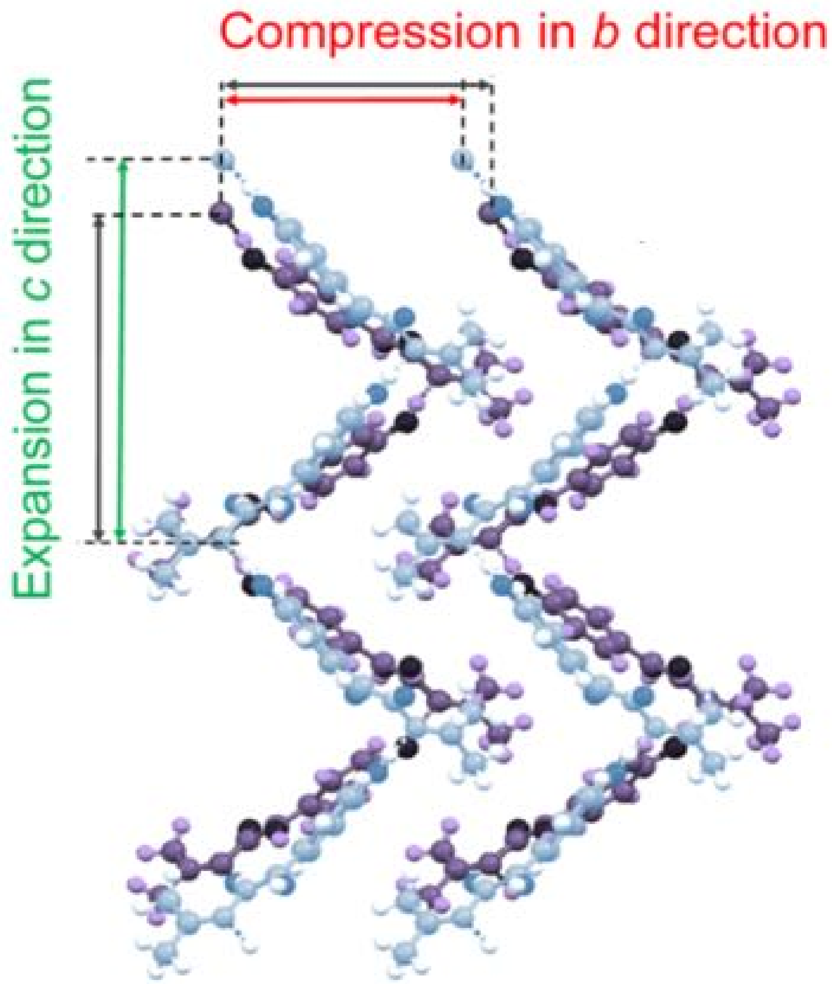
L-pyroglutamic acid

- appears in three forms; α’, α, β
- both phase transitions are thermosalient
- LT: -120ºC, HT: 55ºC
- biaxial negative thermal expansion

$$\alpha_a = -55\times10^{-6}\,\mathrm{K}^{-1}, \alpha_c = -3.6\times10^{-6}\,\mathrm{K}^{-1}$$

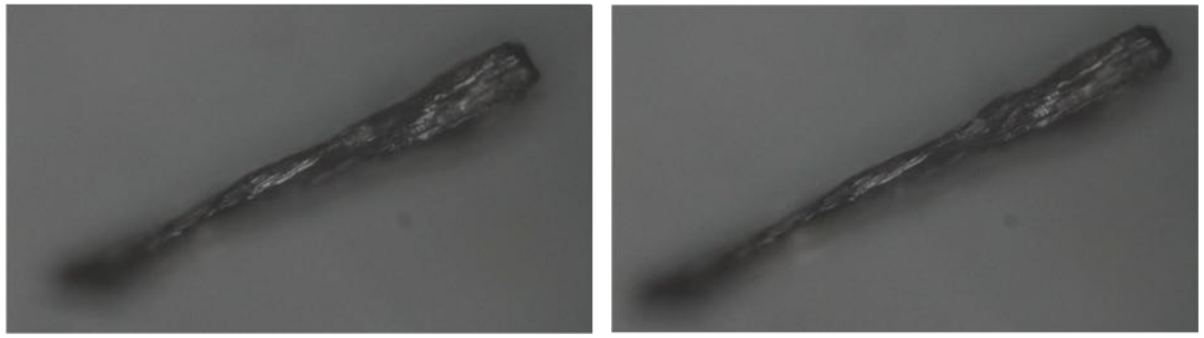
- extremely large positive uniaxial thermal expansion

$$\alpha_b = 303\times10^{-6}\,\mathrm{K}^{-1}$$



N’-2-propylidene-4-hydroxy-benzohydrazide

- appears in three forms; I, II, III
- all three forms crystallize in the polar space group *Pna*2$_1$
- phase transition I→II is not reversebile; it is thermosalient
- phase transition II III is reversible; it was reported non-thermosalient
- ***a*** and ***b*** axis expand by 8% and 12%, ***c*** compresses by 14%
- crystals jump up to 1 m
- the explanation given in the literature is via the mechanism of the sudden compression of the polar axis

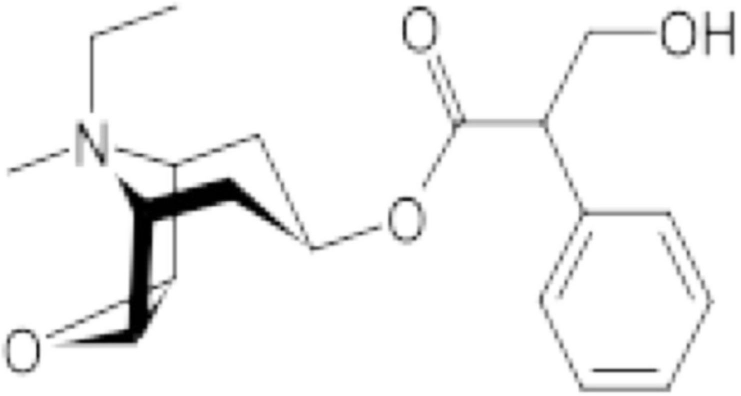


Oxitropium bromide

Introduction

Zamir, S.; Bernstein, J.; Greenwood, D. J. *Mol. Cryst. Liq. Cryst.* **1994**, *242*, 193-200.

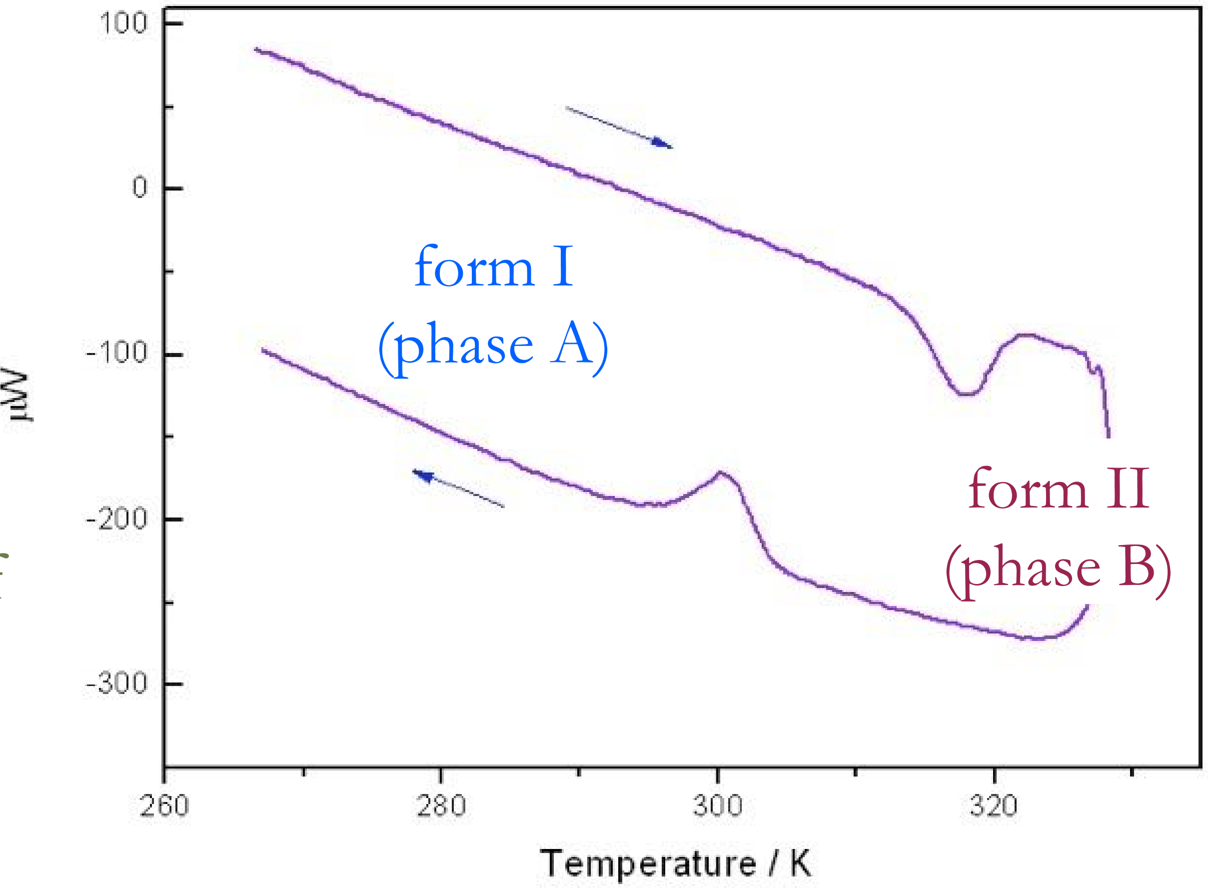
- oxitropium bromide (OXTB):
  pharmaceutical compound used as an anticholinergic drug in treatment of respiratory disorders (e.g. asthma, chronic bronchitis)



- upon heating → endothermic transition
  - form I to form II at 330.95 K
  - highly anisotropic expansion of the cell
  - *b* axis: +11%; *c* axis: - 7%
  - + 4% overall volume
  - form II to form I at 308.15 K
  - melting point is in the range 475.15-478.15 K

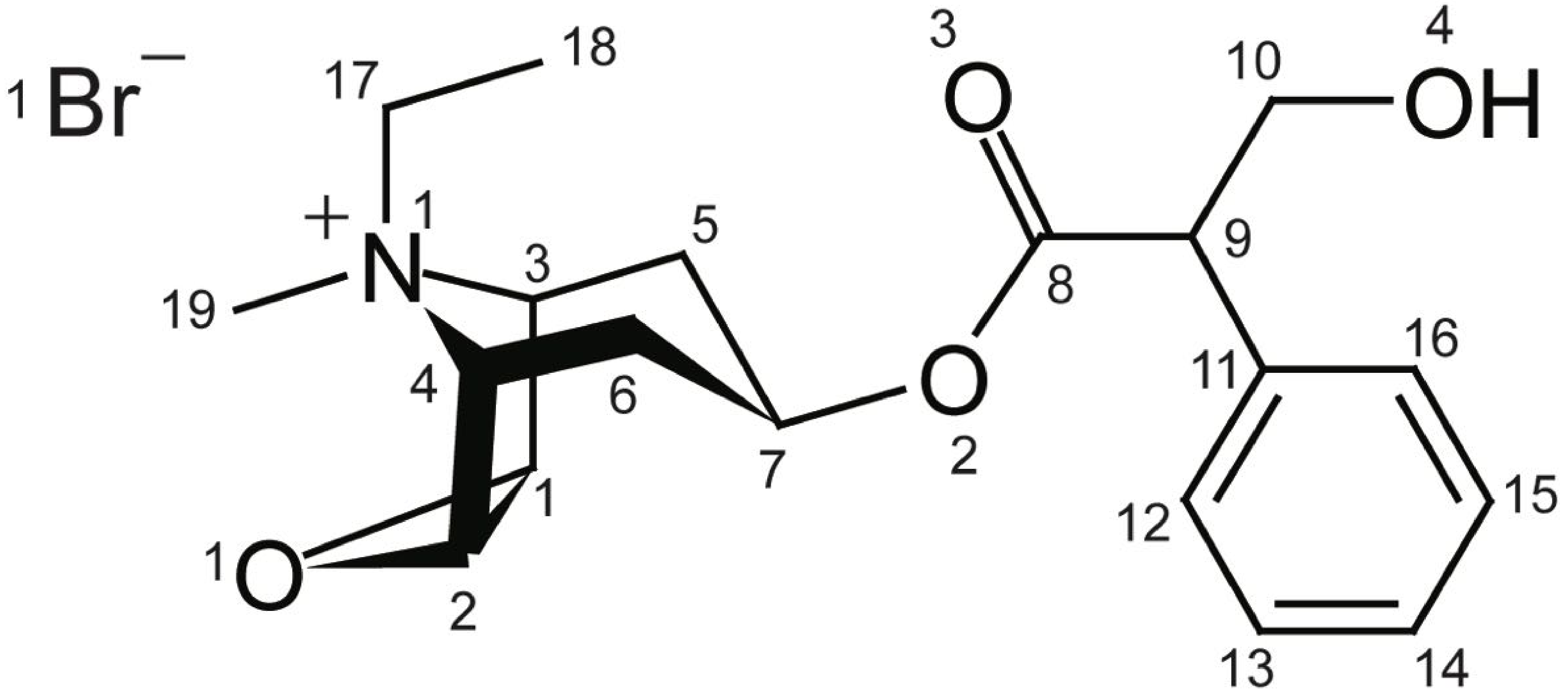
- the two forms were characterized by means of infrared spectroscopy, differential scanning calorimetry and powder X-ray diffraction

DSC curve of OXTB



Oxitropium bromide

Introduction



Zamir, S.; Bernstein, J.; Greenwood, D. J. *Mol. Cryst. Liq. Cryst.* **1994**, *242*, 193-200.

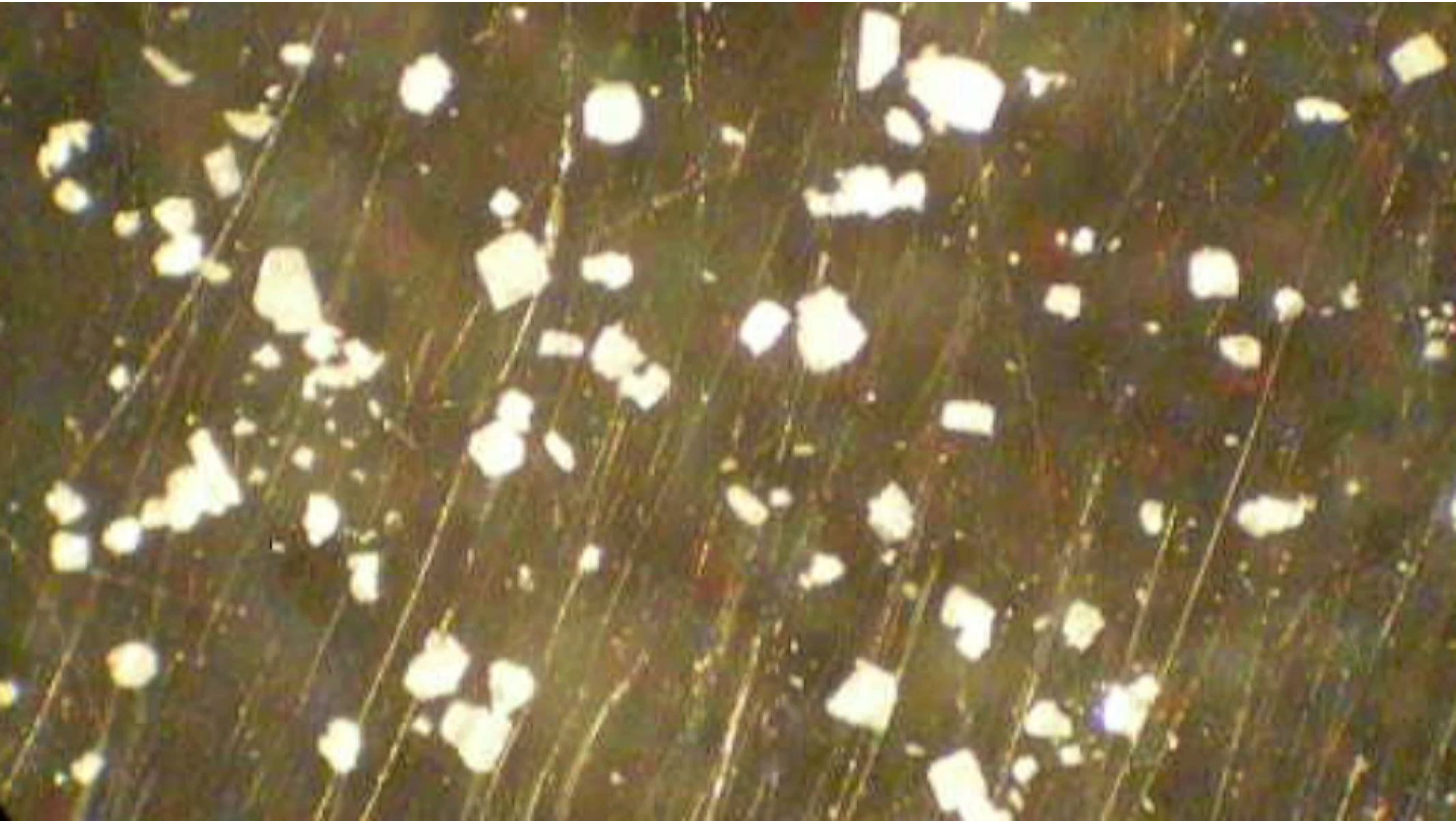
What was resolved?

- the crystal structure of the LT form I has been determined
- powder XRD pattern of the HT form II has been recorded

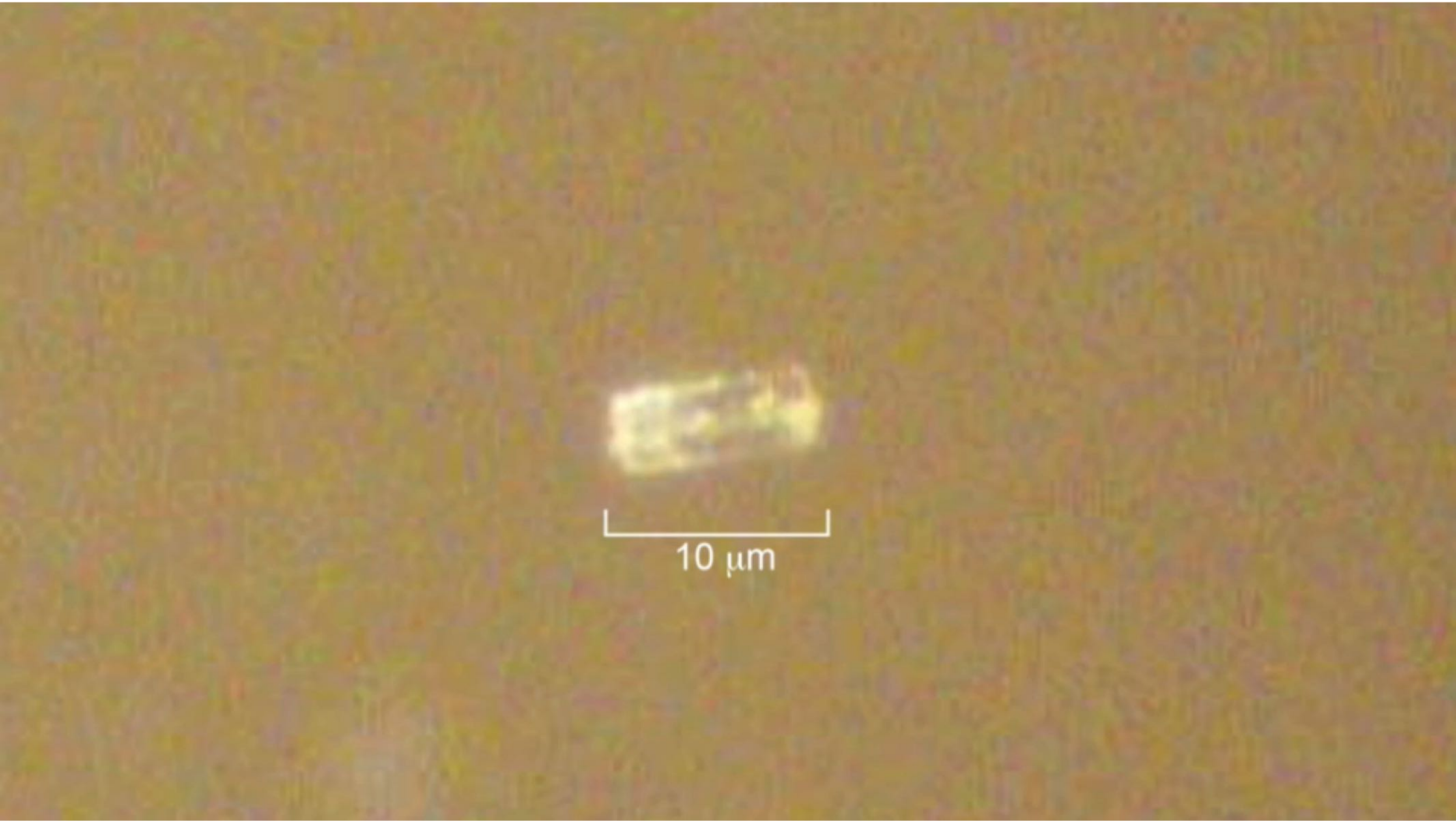
What remained unresolved?

- crystal structure of the HT phase II has **not** been determined
- mechanism underlying the thermosalient effect in this compound has not been explained

Oxitropium bromide during heating



Oxitropium bromide during heating



Oxitropium bromide

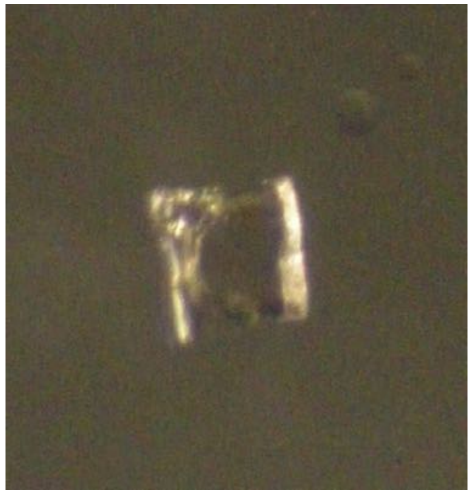
Experimental

Polymorph screening:

- oxitropium bromide was commercially supplied (original sample)
- oxitropium bromide was dissolved in: acetone, ACN, $CHCl_3$, DCM, EtOH, EtOAc, *i*-PrOH, MeOH, THF, H_2O and several combinations of these solvents.
- successful recrystallizations :

Phase A	Phase A	Phase B
blocky crystals	prismatic crystals	prismatic crystals
DCM, ACN/DCM	MeOH/DCM	acetone, $CHCl_3$

a = 7.3927 Å
b = 10.1512 Å
c = 24.6291 Å



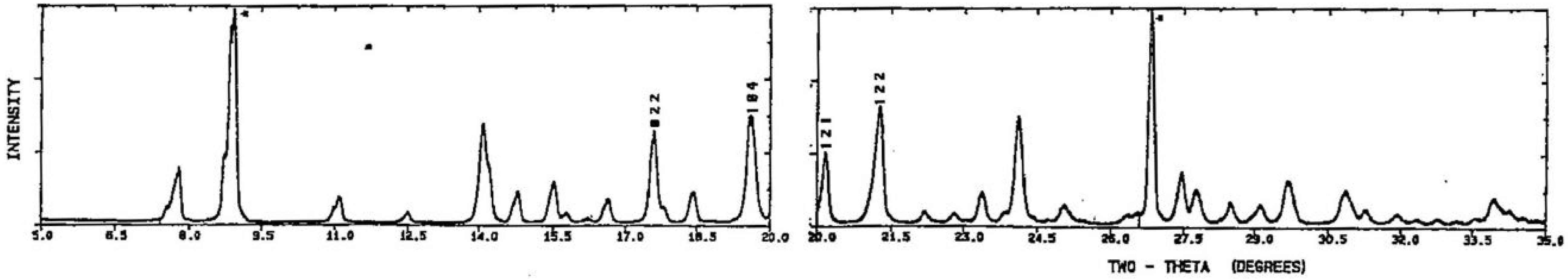
a = 7.4514 Å
b = 11.2179 Å
c = 22.8043 Å

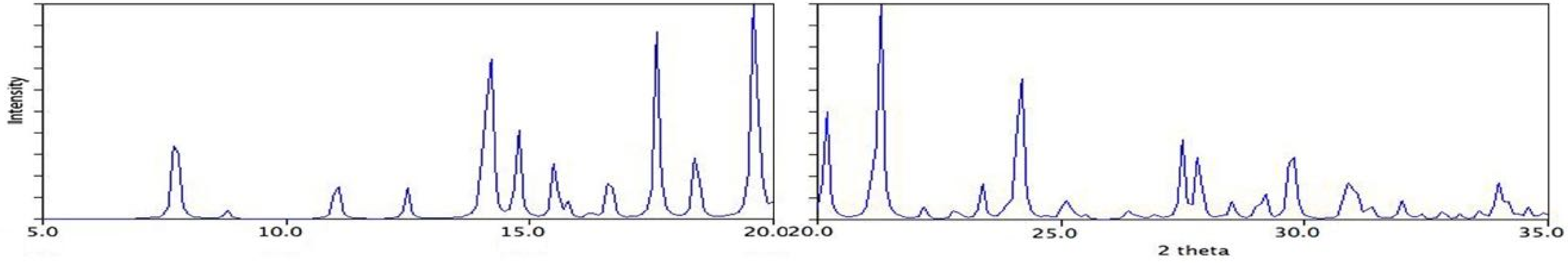
Oxitropium bromide

Experimental

PXRD pattern of the HT phase (form II)

Zamir, S.; Bernstein, J.; Greenwood, D. J. *Mol. Cryst. Liq. Cryst.* **1994**, *242*, 193-200.





PXRD pattern calculated from our single-crystal data (form B)

Perfect match!

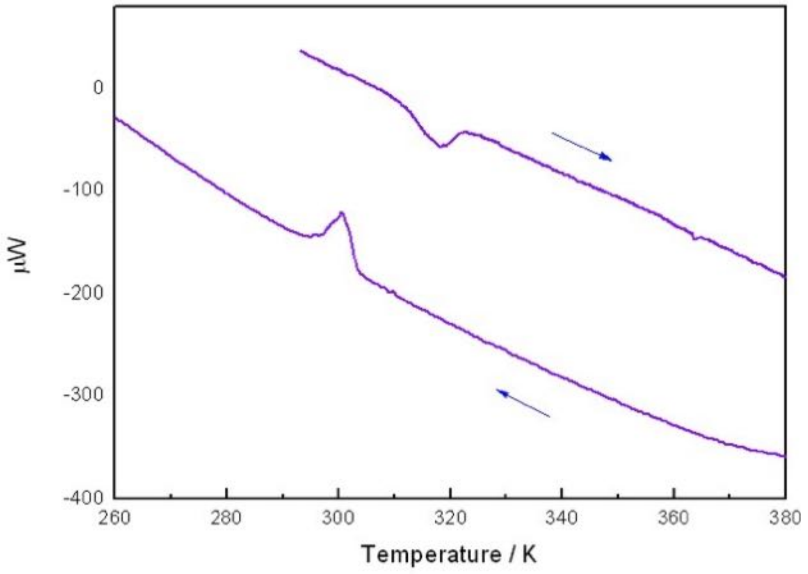
Oxitropium bromide

DSC

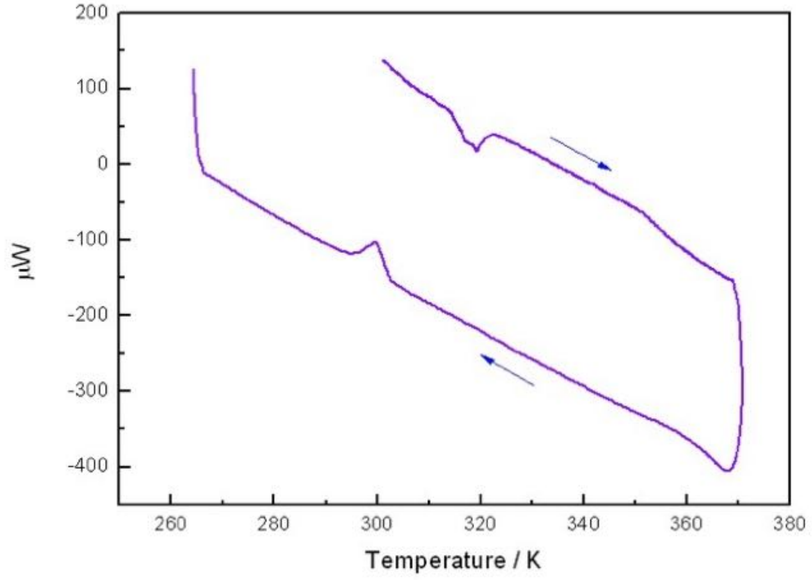
Thermal methods (differential scanning calorimetry):

The DSC curves were recorded for:

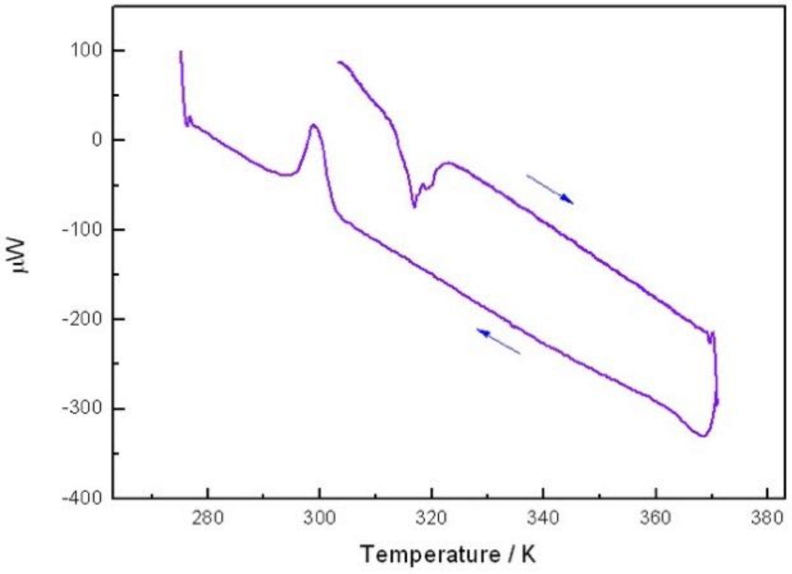
1. phase A (prismatic)



2. phase A (blocky)



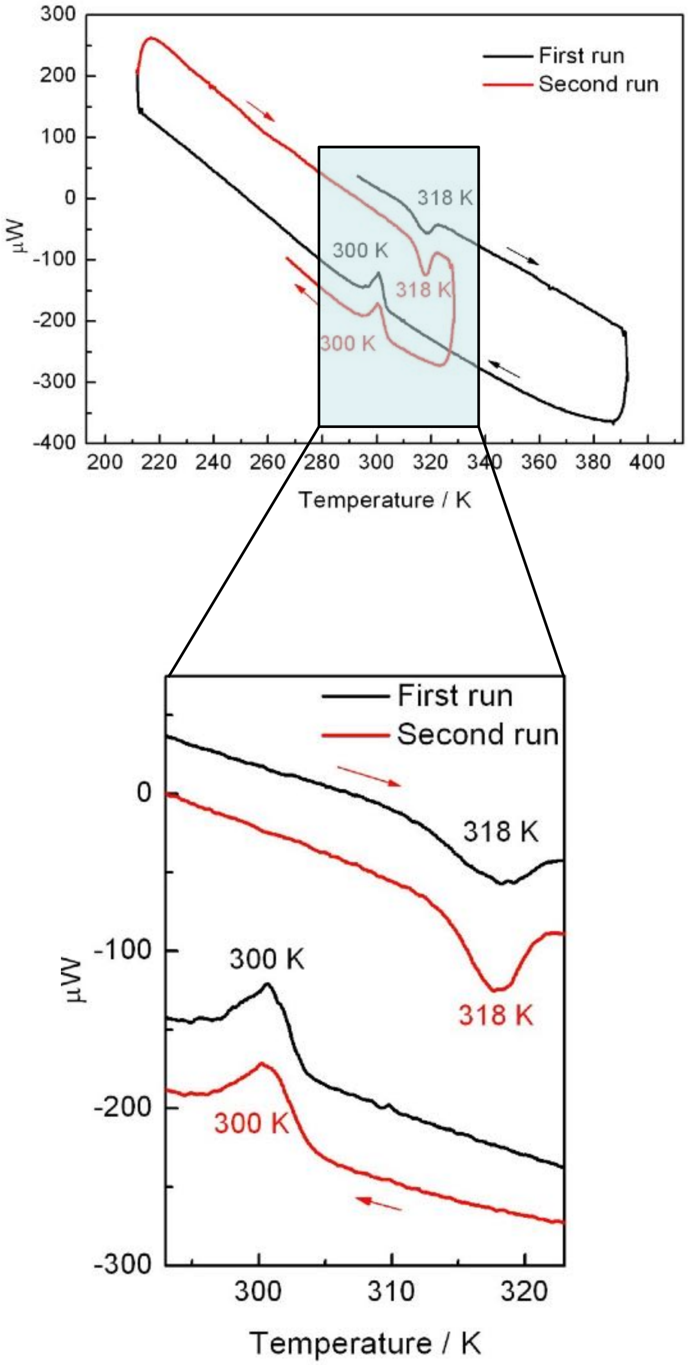
3. original sample
(phase A)



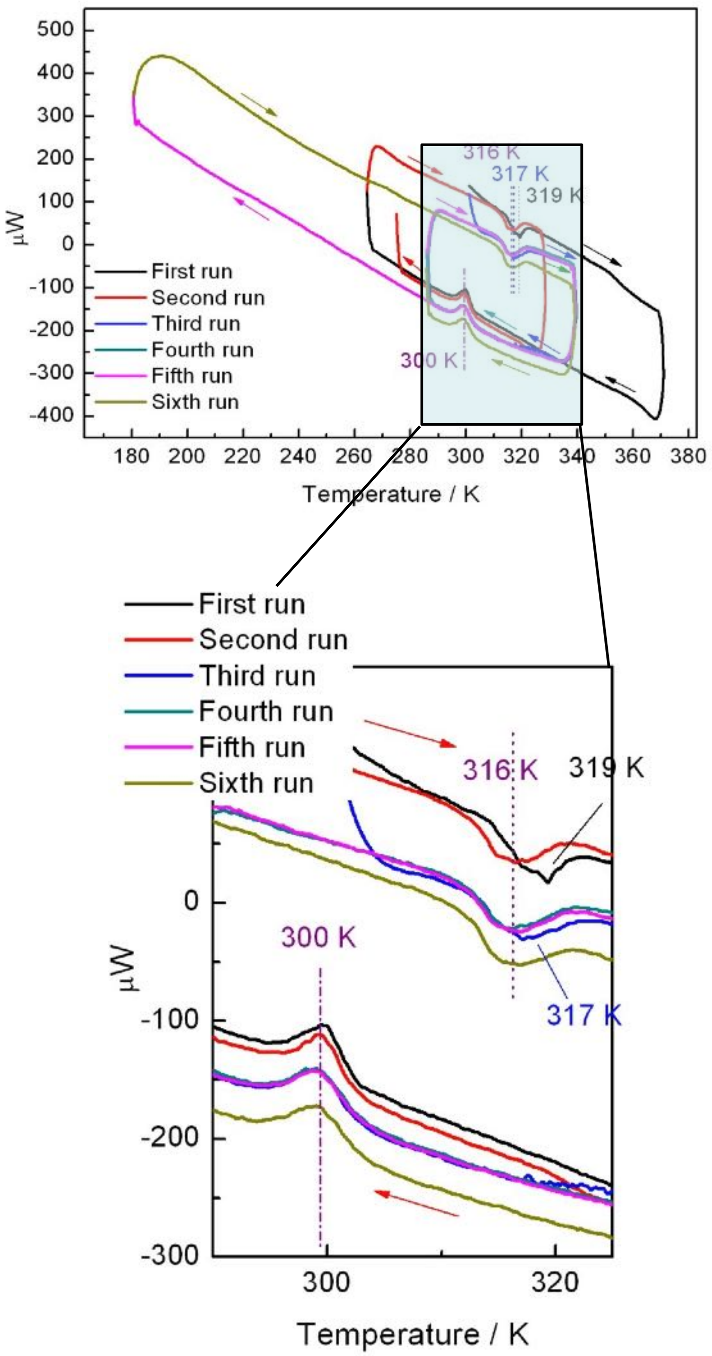
Oxitropium bromide

DSC

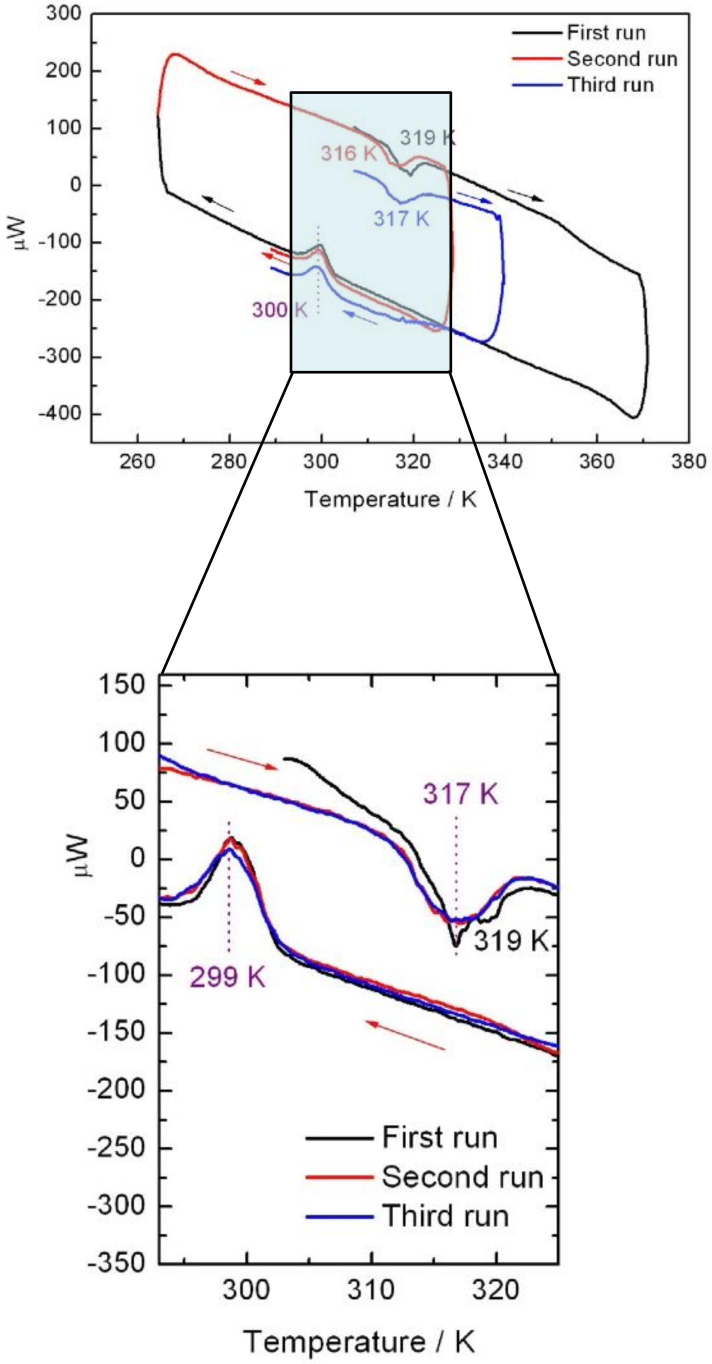
Phase A
(prismatic)



Phase A
(blocky)



Phase A
(original)

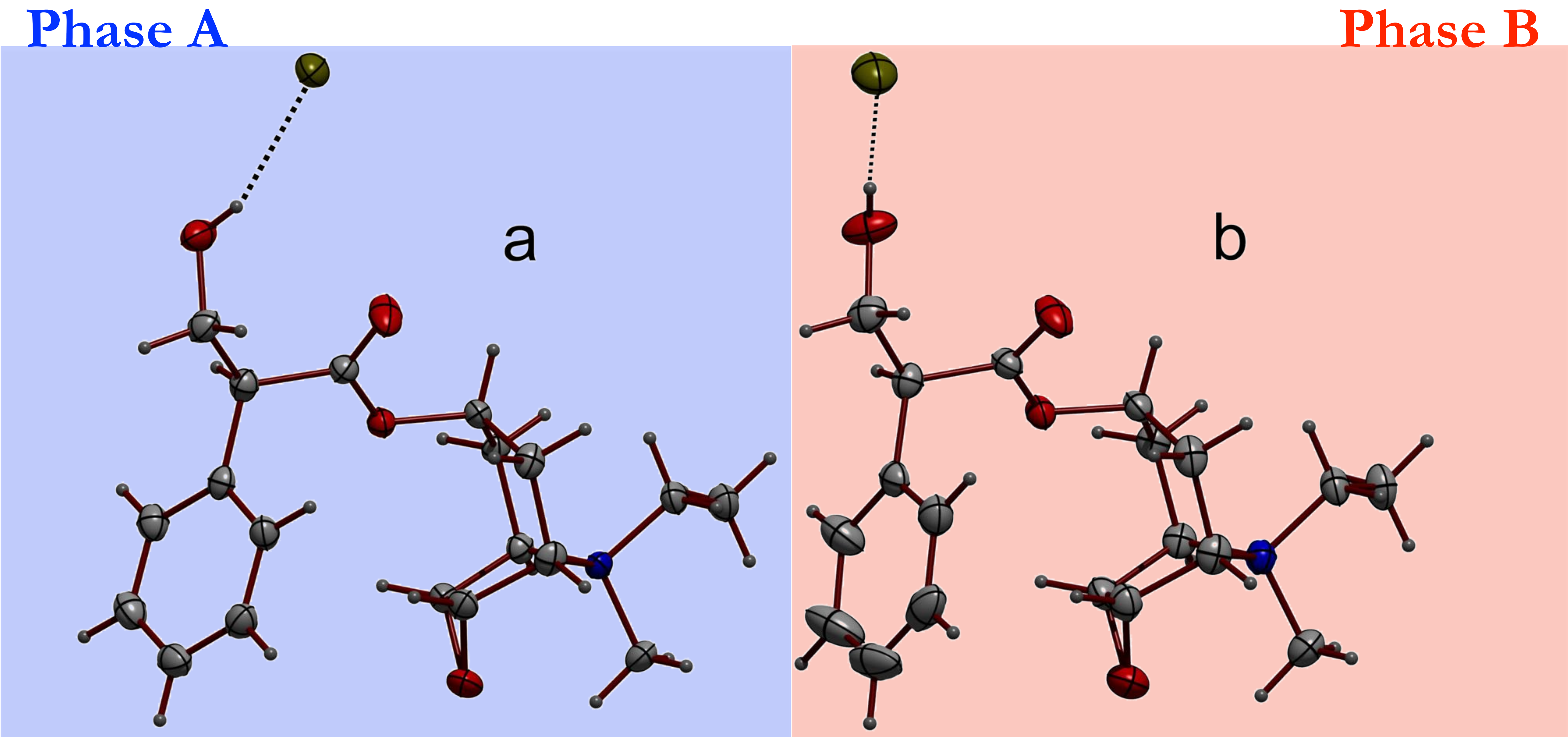


Oxitropium bromide

XRD

Molecular structures of phases A and B

- both obtained from recrystallization and stable at RT



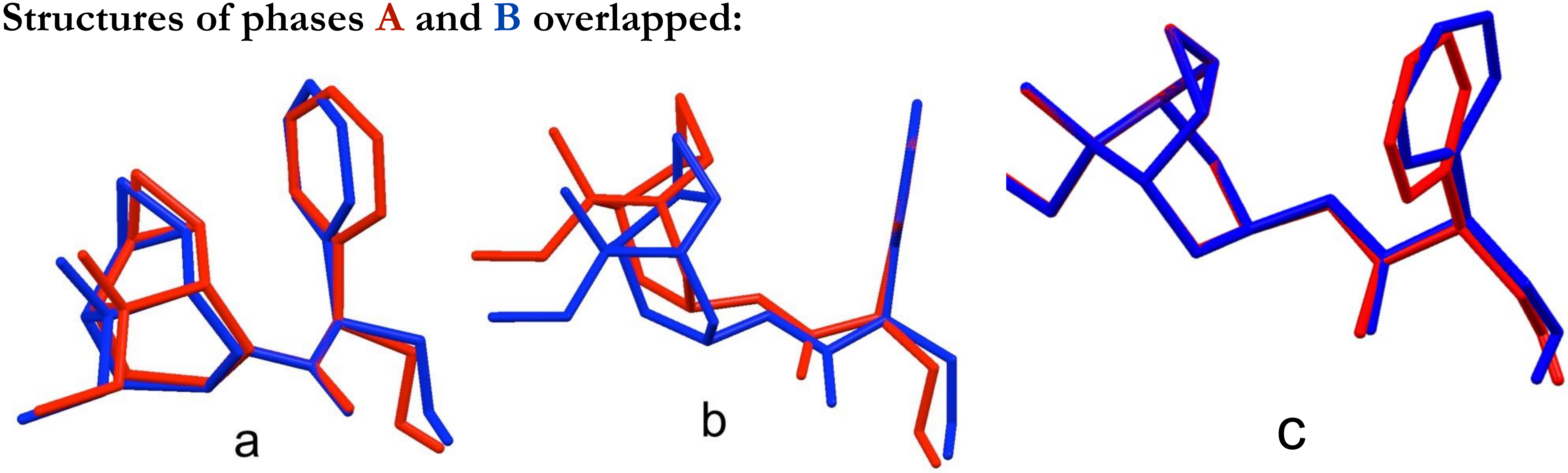
(blocky and prismatic are identical!)

Orthorhombic, space group $P2_12_12_1$

Oxitropium bromide

XRD

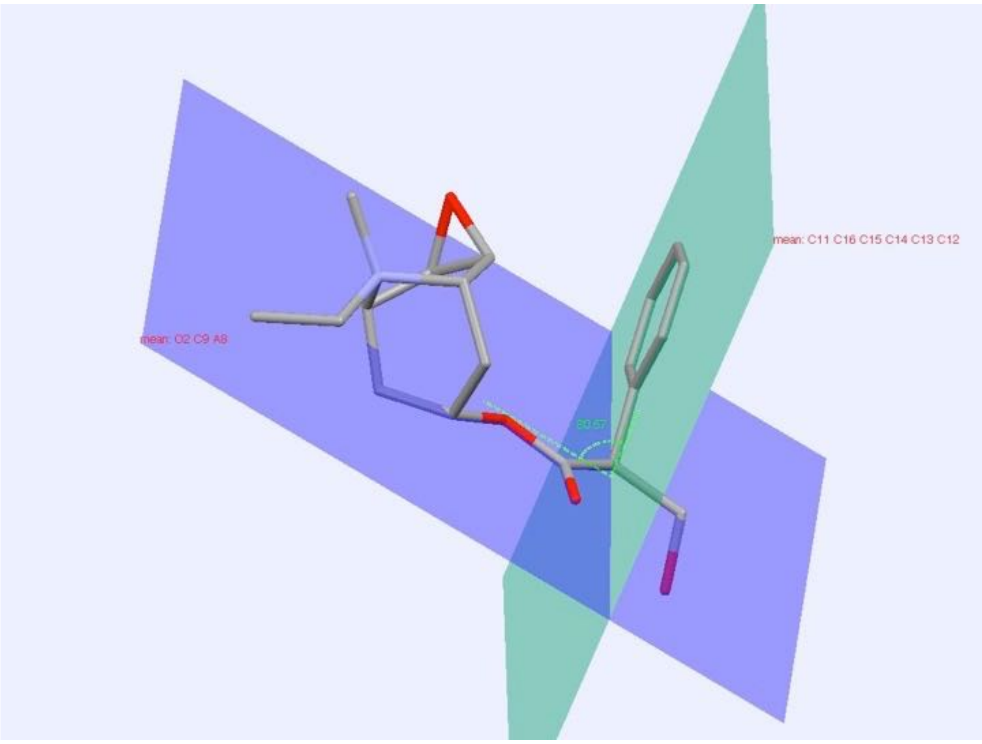
Structures of phases A and B overlapped:



at the three bridging atoms **at the phenyl ring** **at the tricyclic moiety**

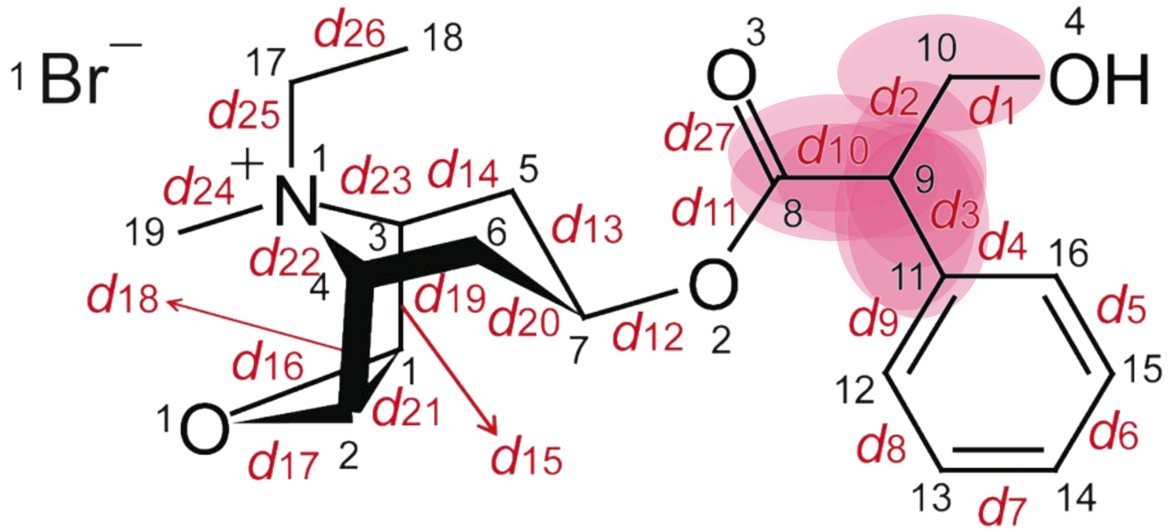
phase A φ ≈ 80º

phase B φ ≈ 89º



Oxitropium bromide

XRD



Largest differences in distances between molecular structure A and B

Distance	Phase A (Å)	Phase B (Å)	Relative difference (%)
d_9	1.393(4)	1.379(6)	1.01
d_7	1.374(5)	1.34(9)	2.47
d_5	1.379(4)	1.395(7)	1.16
d_{26}	1.515(4)	1.498(5)	1.12
d_{19}	1.532(3)	1.513(5)	1.24
d_{10}	1.517(4)	1.496(5)	1.38

Largest differences in angles between molecular structure A and B

Angle	Phase A (°)	Phase B (°)	Difference (°)
d_3-d_2	111.3(2)	114.1(3)	2.8
d_6-d_7	119.4(3)	120.7(5)	1.3
d_{10}-d_3	112.5(2)	109.0(3)	3.5
d_1-d_2	112.7(2)	108.4(3)	4.3

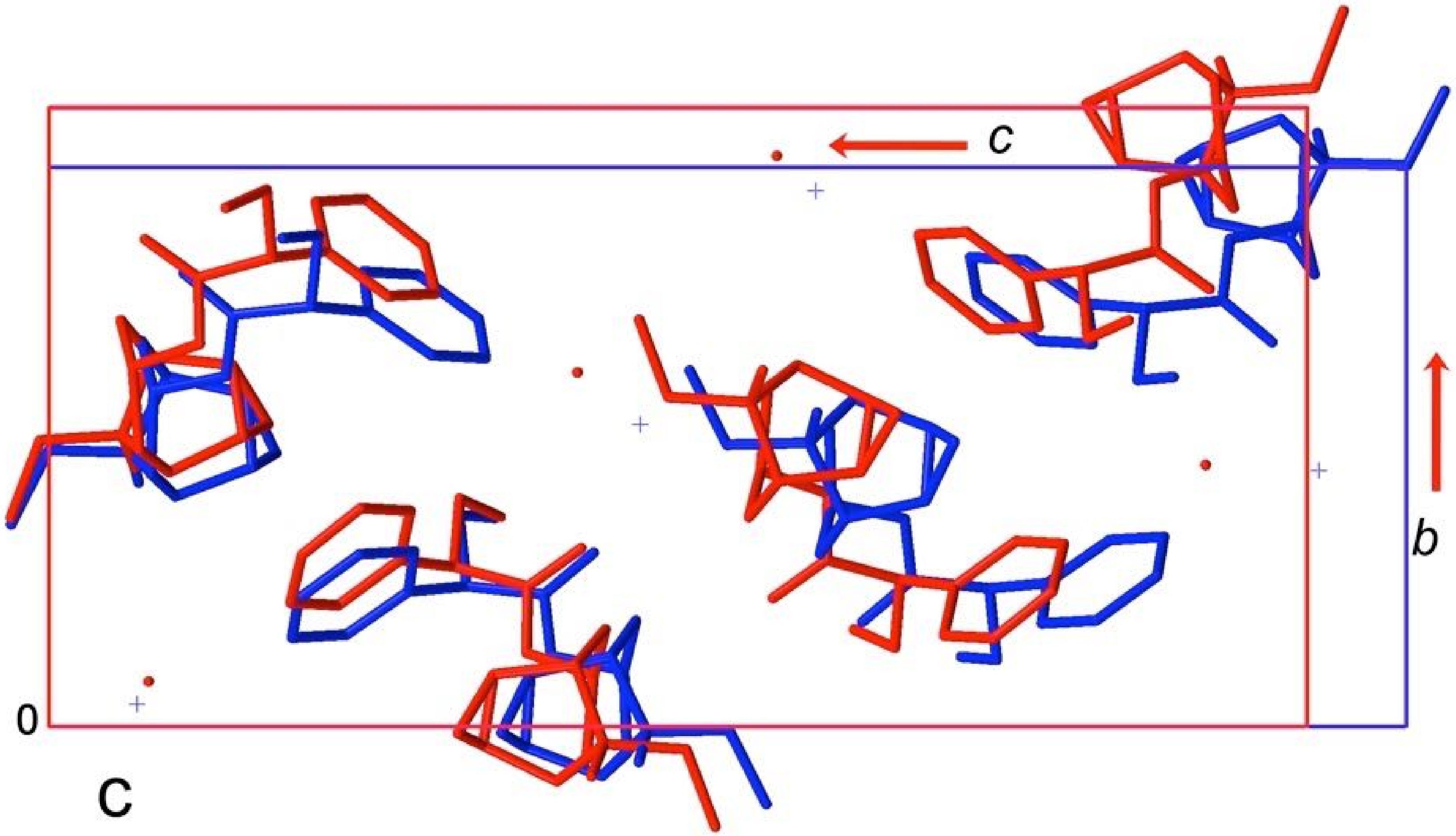
Largest differences in dihedral angles between molecular structure A and B

Dihedral angle	Phase A (°)	Phase B (°)	Difference (°)
d_2-d_3-d_9	101.20(29)	115.85(43)	14.65
d_2-d_3-d_4	75.85(32)	66.16(45)	9.69
d_3-d_2-d_1	161.05(22)	168.32(33)	7.27
d_{14}-d_{13}-d_{20}	29.42(31)	25.92(43)	3.5
d_{14}-d_{13}-d_{12}	91.08(25)	94.52(34)	3.44
d_{12}-d_{11}-d_{10}	179.05(21)	175.29(27)	3.76
d_{10}-d_3-d_9	134.38(25)	119.60(38)	14.78
d_{11}-d_{12}-d_{20}	156.88(20)	162.69(26)	5.81
d_{10}-d_2-d_1	73.21(29)	67.93(42)	5.28
d_{11}-d_{12}-d_{13}	76.89(25)	70.66(35)	6.23
d_{10}-d_3-d_4	48.76(35)	58.40(42)	9.64
d_{11}-d_{10}-d_2	177.96(22)	169.92(28)	8.04
d_{11} d_{10} d_3	52.91(29)	63.41(37)	10.5
d_{27}-d_{10}-d_2	2.89(39)	13.63(55)	16.52
d_{27}-d_{10}-d_3	127.94(31)	113.03(43)	14.91

Oxitropium bromide

XRD

Crystal packing of phases A and B



Phase A
$b = 10.1512$ Å, $c = 24.6291$ Å

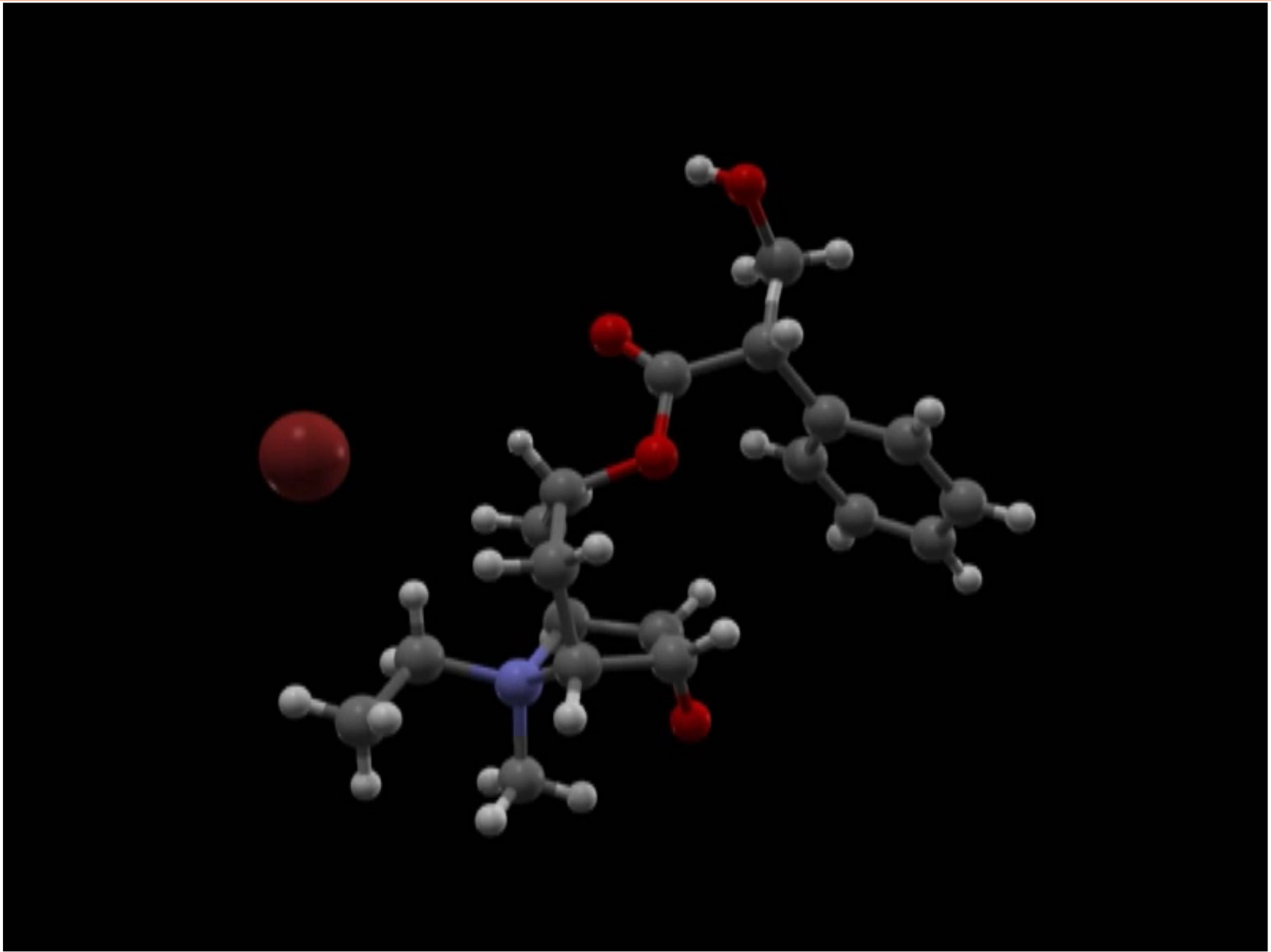
Phase B
$b = 11.2179$ Å, $c = 22.8043$ Å

-intermolecular hydrogen bonds were found in both phase A and B

Phase	D-H distance (Å) (O4-H4)	H..A distance (Å) (H4..Br1)	Angle (°)	D..A distance (Å) (O4..Br1)
A	0.82	2.491	156.68	3.260
B	0.82	2.402	178.77	3.222

Oxitropium bromide

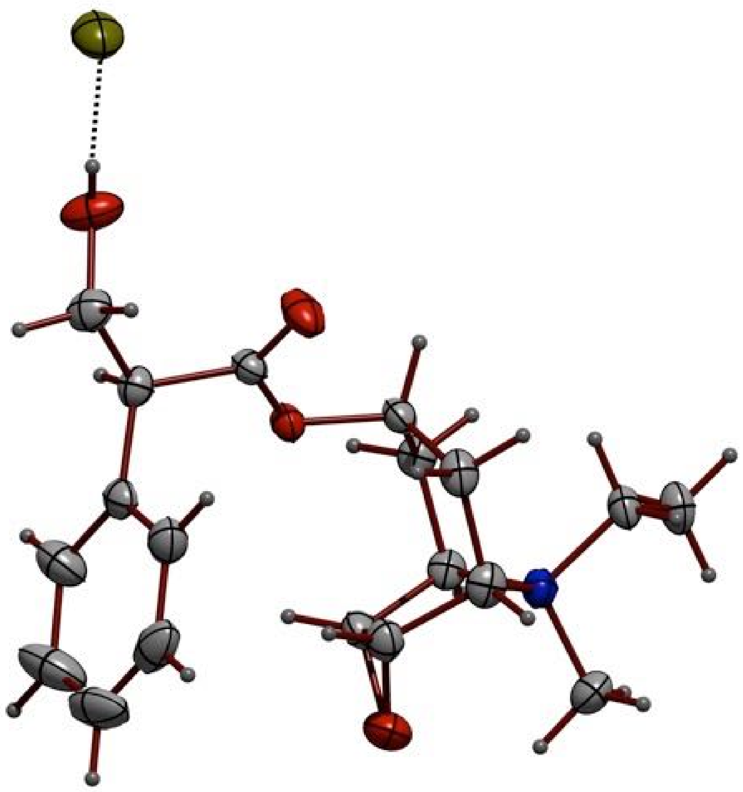
Mechanism of the phase transition



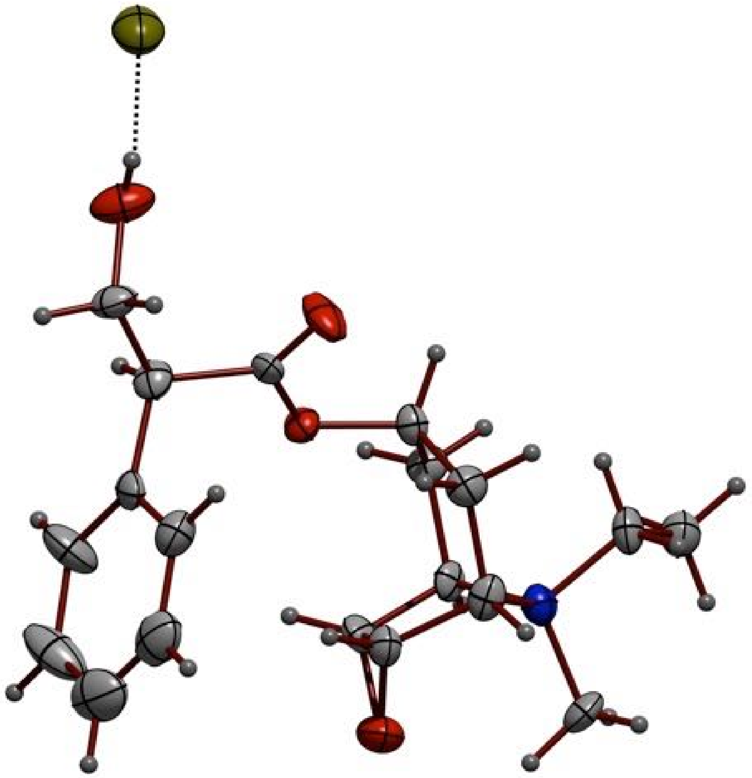
Oxitropium bromide

XRD

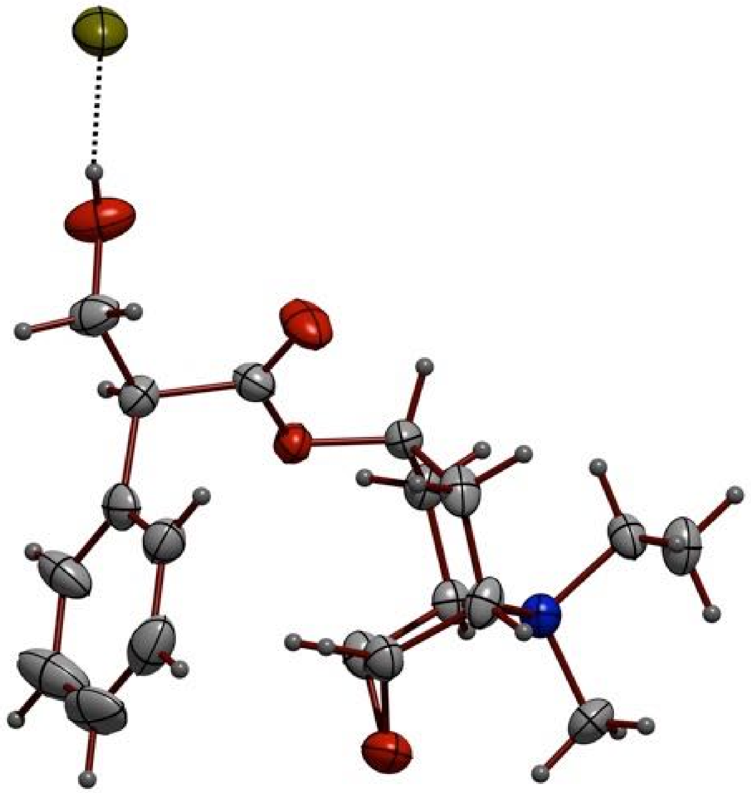
Single crystal to single crystal phase transition, induced by heating and by UV irradiation!



as-crystallized

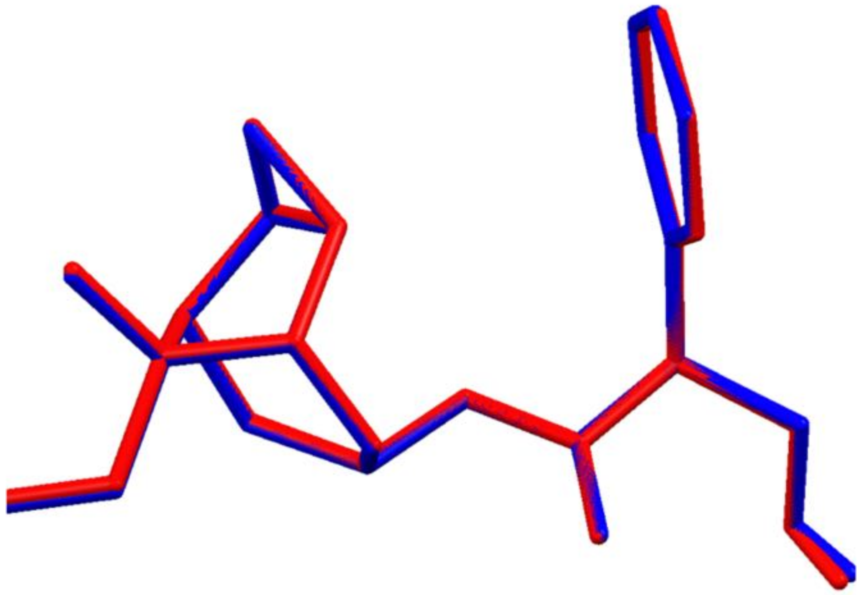


thermally induced



UV-induced

Identical to phase B obtained by recrystallization!



UV irradiated

heat induced

overlapped at the three bridging atoms

Oxitropium bromide
FTIR and ^{1}H NMR

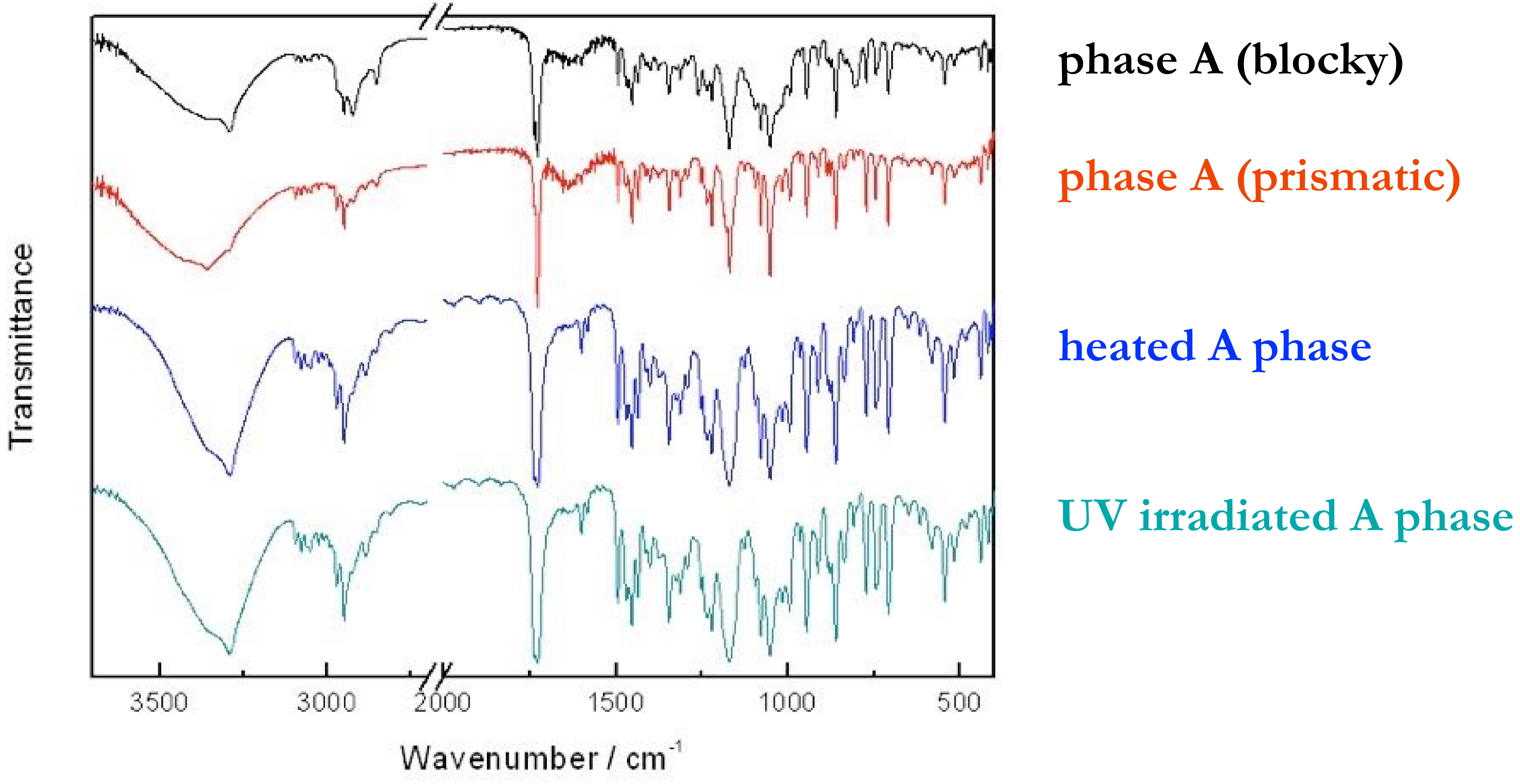
FTIR spectra revealed:

- clear differences in spectra of the OXTB-A and OXTB-B phases
- spectra of the blocky and prismatic crystals of OXTB-A were identical, and the spectra of the heated and UV irradiated crystals corresponded to those of OXTB-B phase
- dependence of the spectrum of the OXTB-A phase on grinding (with or without presence of KBr)
- carbonyl stretching band (1726 cm^{-1}) disappearing while a new band appearing (1735 cm^{-1})
- this indicates a probable mechanically induced phase transition OXTB-A → OXTB-B
- spectrum of the UV irradiated samples depended on the presence of KBr
- ^{1}H NMR analysis showed that the UV irradiation of OXTB mixed with KBr causes significant irreversible changes of hte NMR spectrum of the data
- in the presence of KBr, OXTB underwent a UV-induced reaction at the bistricyclic moiety, probably opening of the epoxide ring

Oxitropium bromide

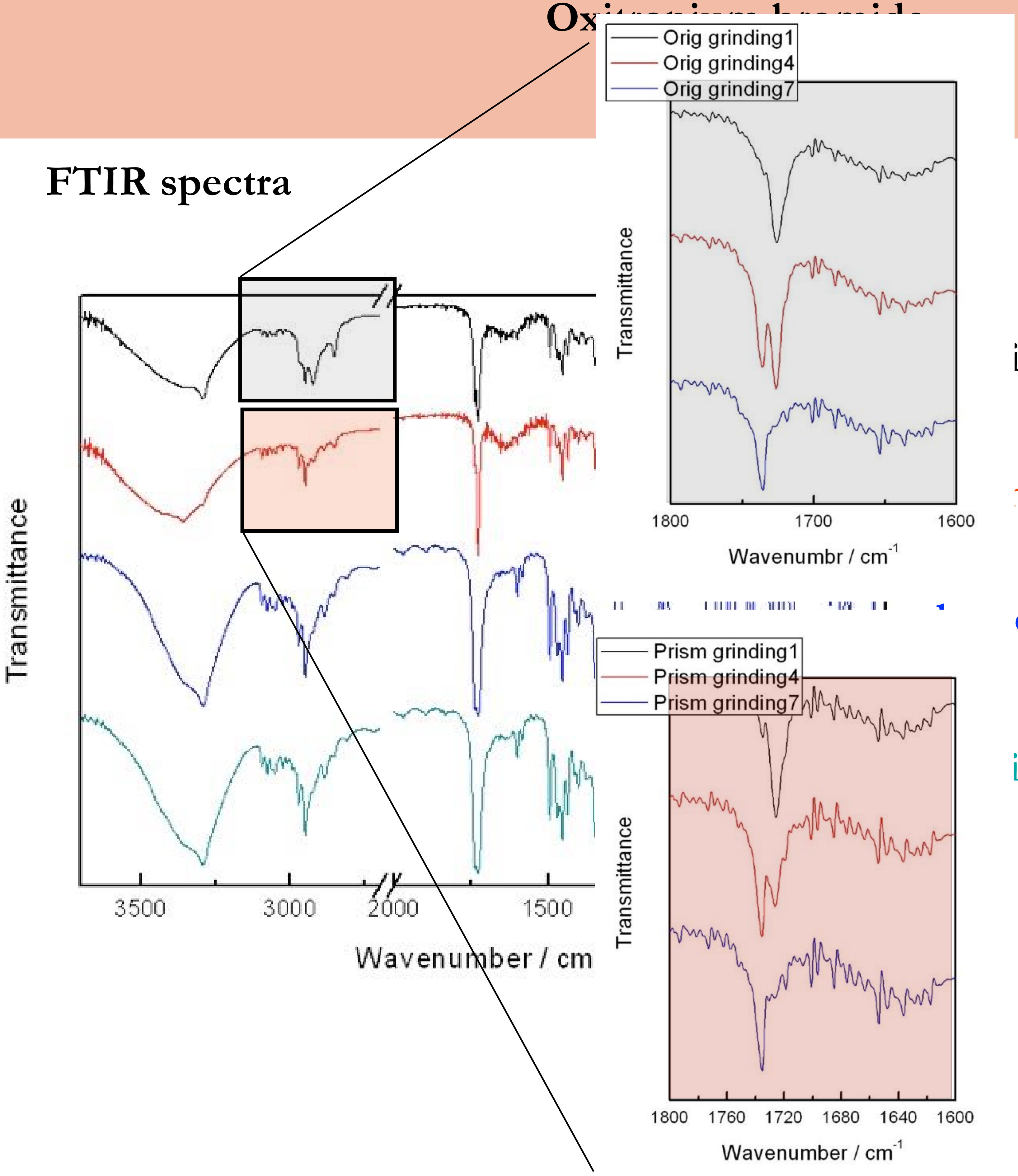
FTIR

FTIR spectra



Oxitropium bromide

FTIR spectra



inal sample

matic A phase

ed original sample

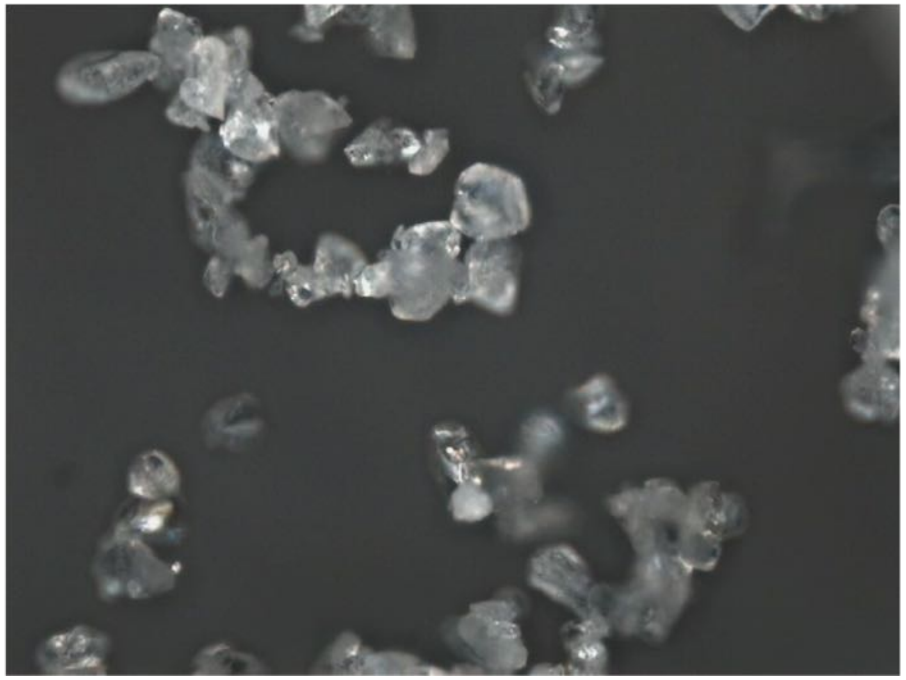
irradiated original sample

N’-2-propylidene-4-hydroxybenzohydrazide

*Centore et al., CrystEngComm, 2012, **14**, 2645*
*Naumov et al., Scientific Reports, 2016, **6**, 29610*

$$\begin{tikzcd}
\mathrm{I} \arrow[r, "147^\circ\mathrm{C}"] & \mathrm{II} \arrow[r, "238^\circ\mathrm{C}"] \arrow[d, shift right] & \mathrm{liquid} \\
 & \mathrm{III} \arrow[u, shift right, "88^\circ\mathrm{C}"'] &
\end{tikzcd}$$

- three polymorphic forms
- same polar space group $Pna2_1$
- phase transitions are topotactic

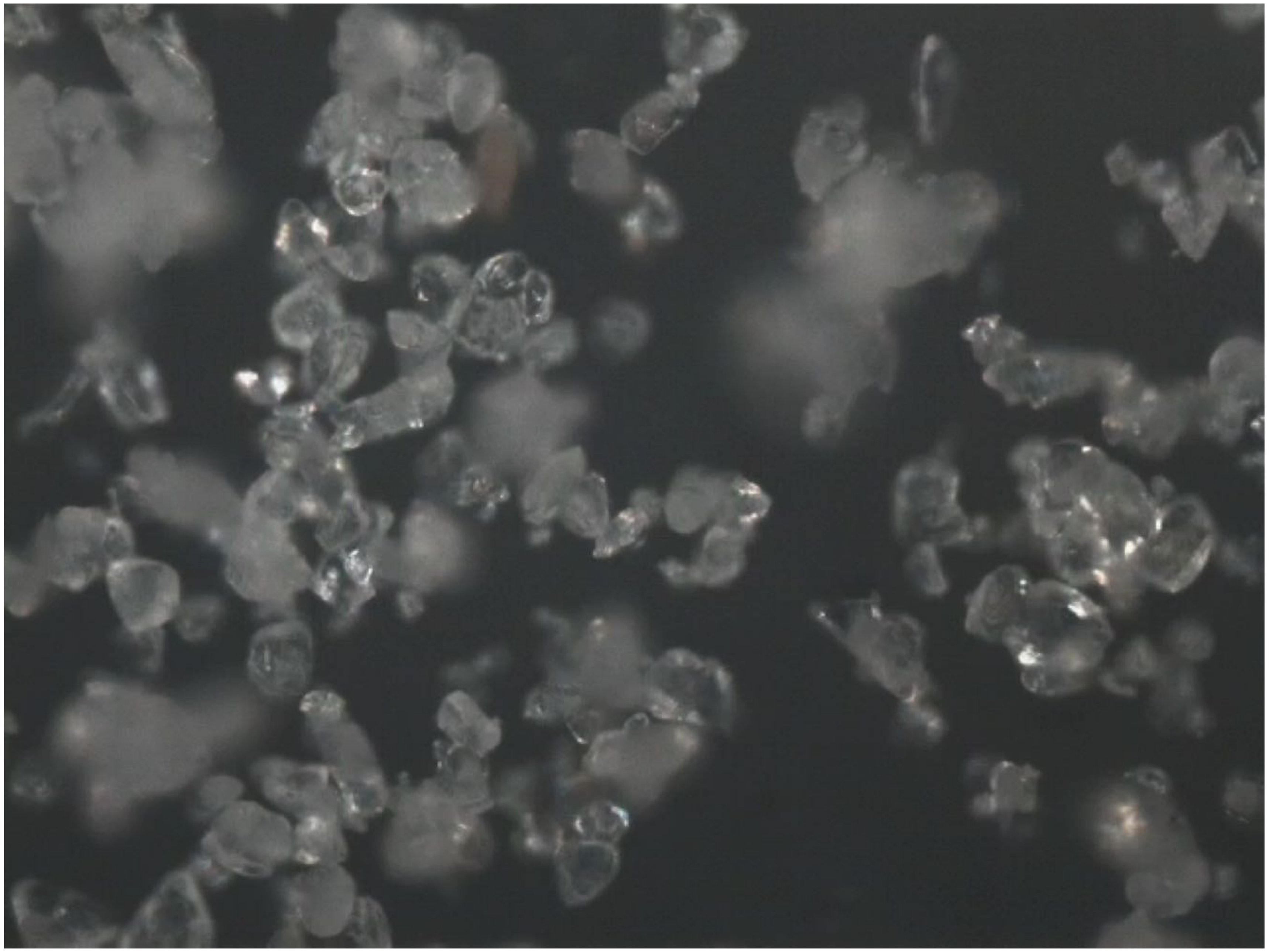


Reported: transition I → II (thermosalient)
- crystals undergo rotations and flips after which are violently shattered

transition II ↔ III (non-thermosalient)
- smooth, with no jumping or shattering of the crystals

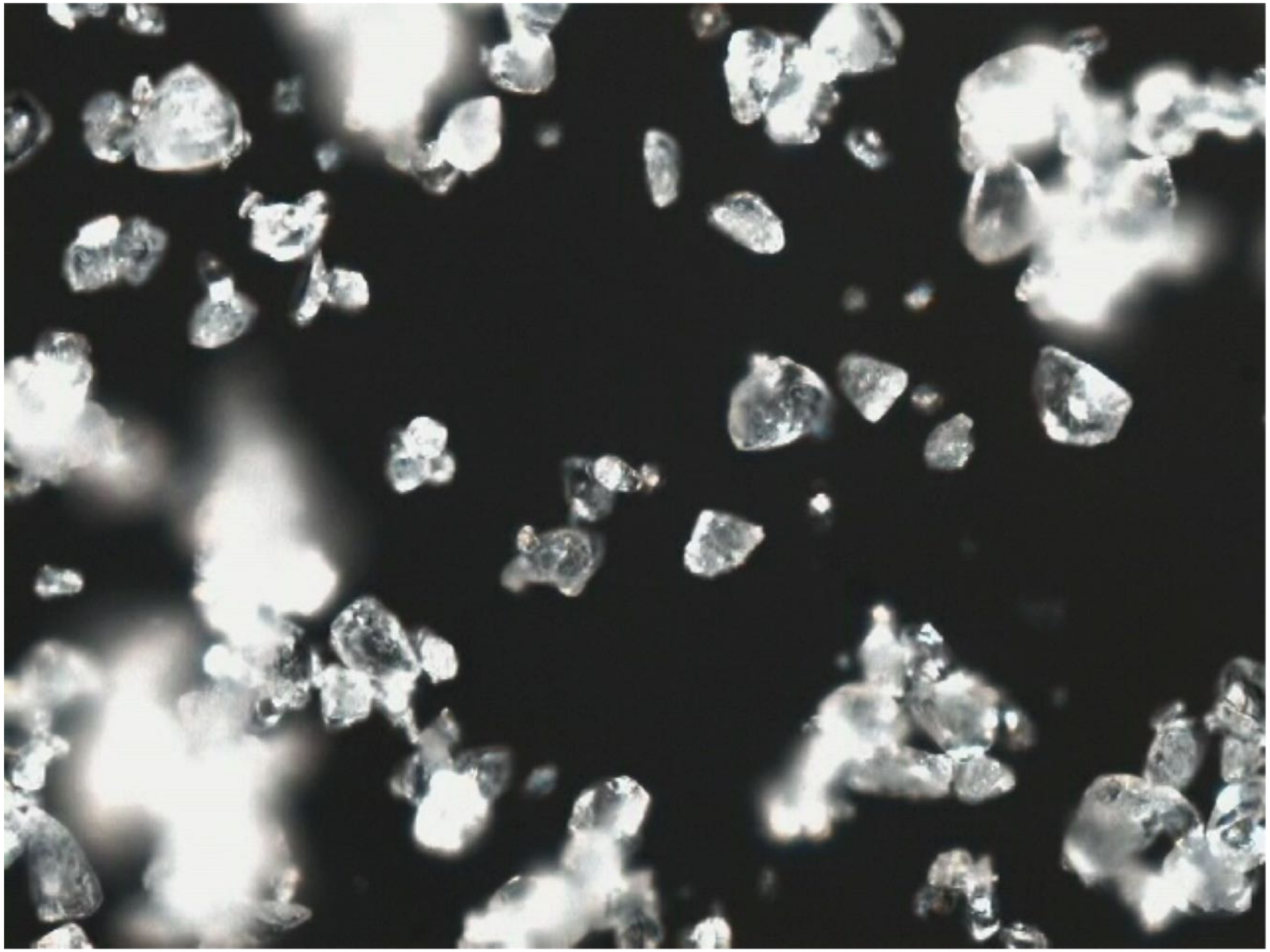
Phase transition II - III

cooling rate: 30 K/min

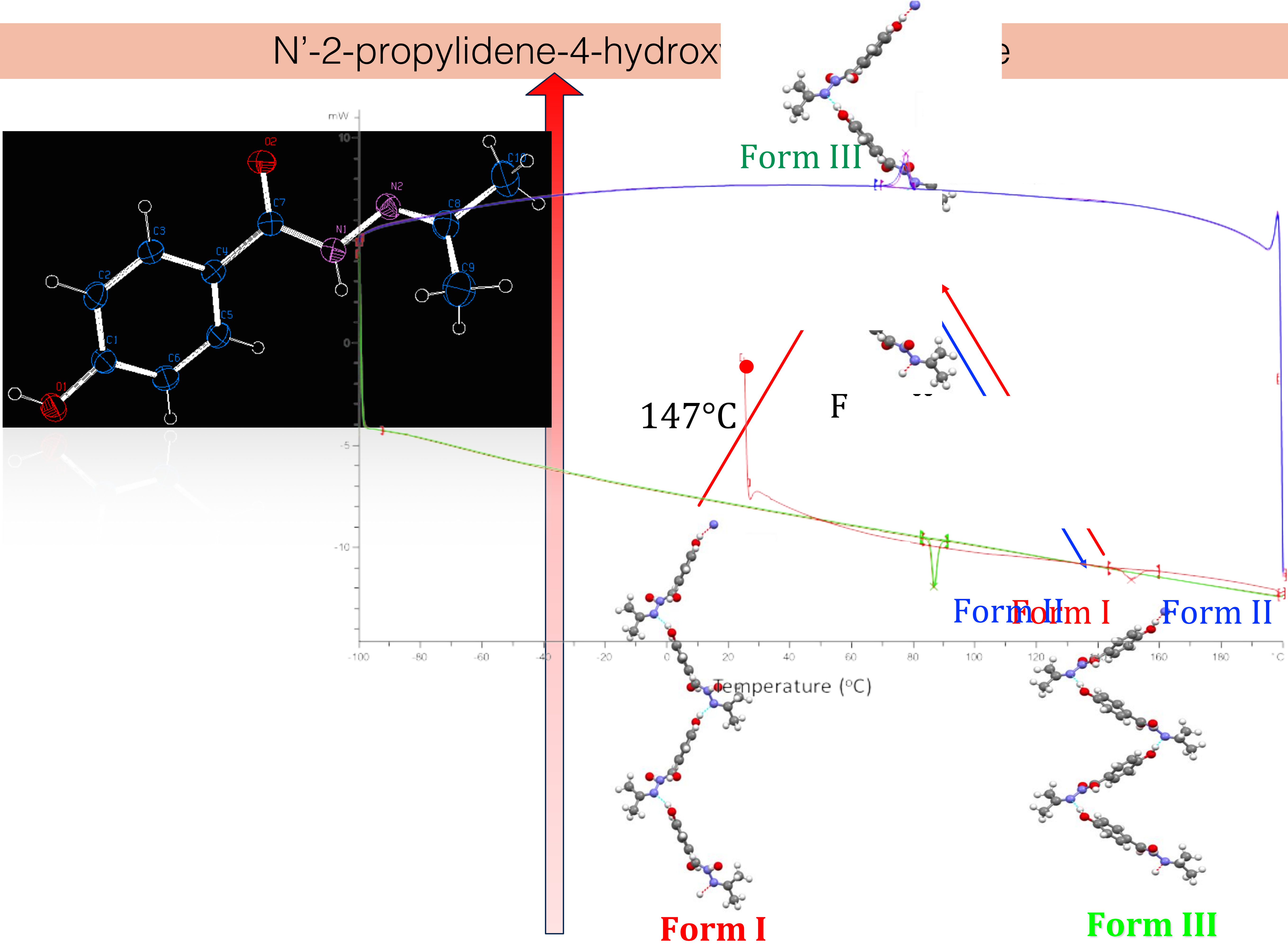


Phase transition III - II

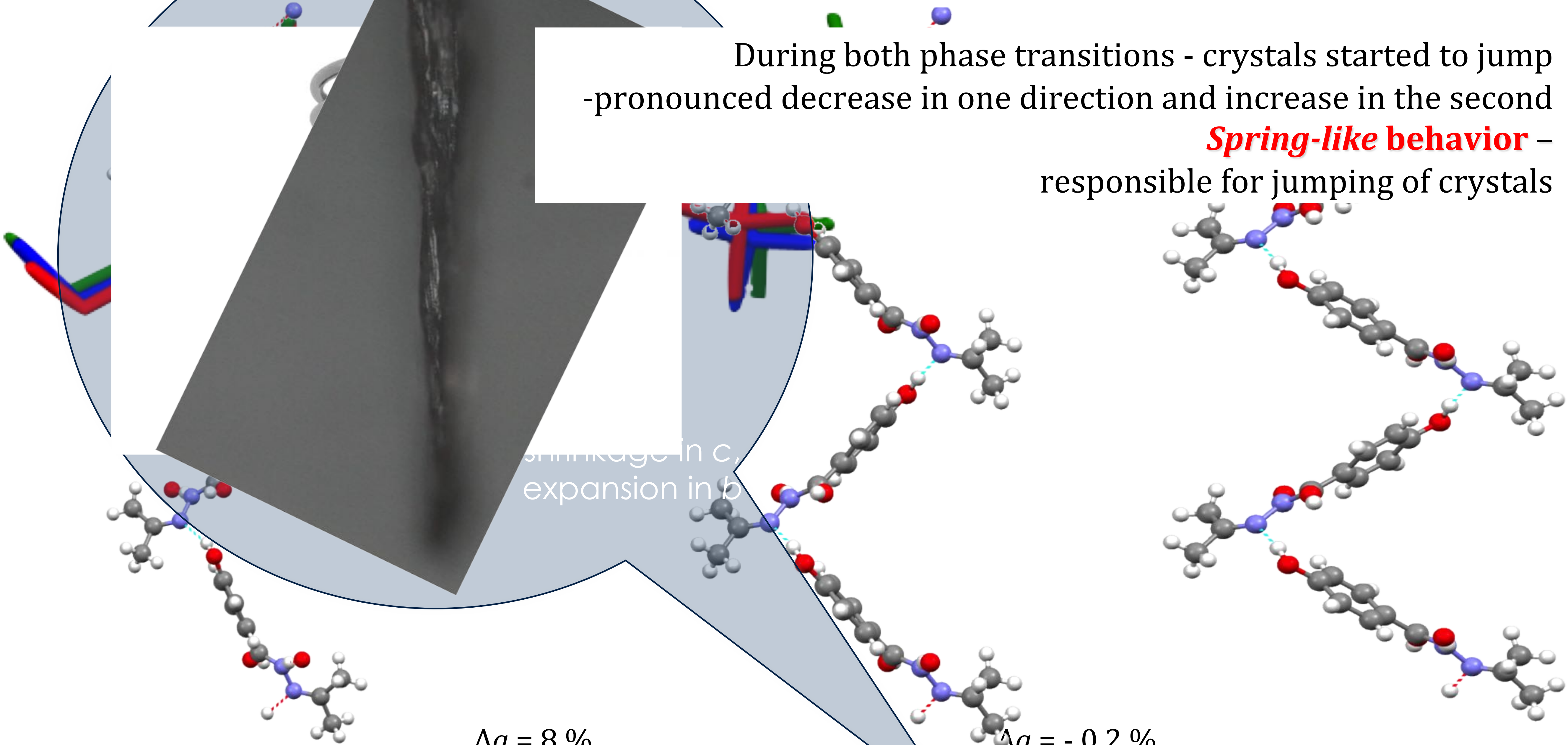
heating rate: 30 K/min



N’-2-propylidene-4-hydrox e



N’- pylidene-4-hydroxybenzohydrazide



During both phase transitions - crystals started to jump
-pronounced decrease in one direction and increase in the second
Spring-like **behavior** –
responsible for jumping of crystals

Form I
$a = 9.1764(3)$ Å
$b = 7.2214(2)$ Å
$c = 15.5834(5)$ Å
$V = 1032.66$ $Å^3$

$\Delta a = 8$ %
$\Delta b = 12$ %
$\Delta c = -13$ %

Form II
$a = 9.952(2)$ Å
$b = 8.115(2)$ Å
$c = 13.508(3)$ Å
$V = 1090.91$ $Å^3$

$\Delta a = -0.2$ %
$\Delta b = 12$ %
$\Delta c = -13$ %

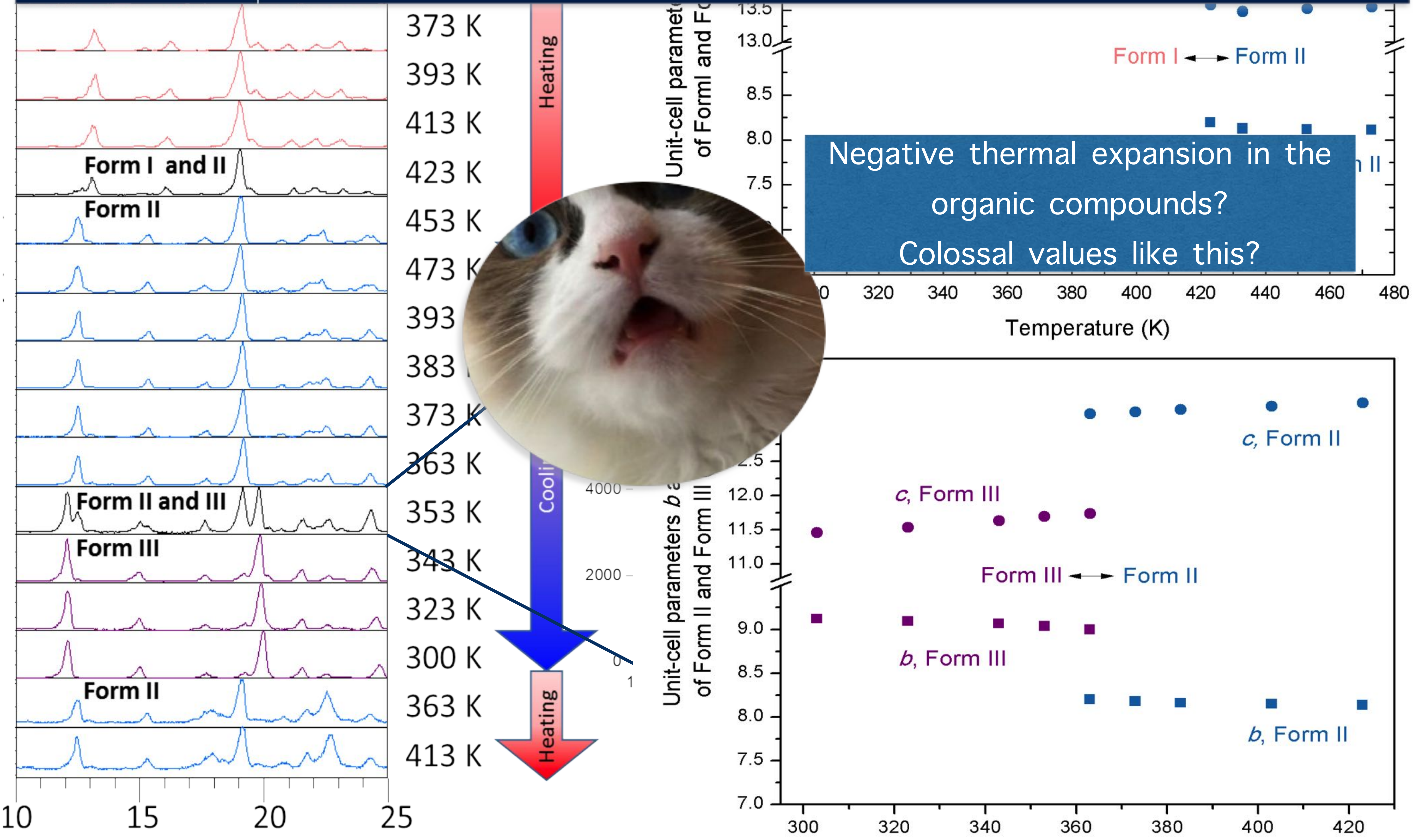
Form III
$a = 9.932(2)$ Å
$b = 9.120(3)$ Å
$c = 11.701(2)$ Å
$V = 1059.8$ $Å^3$

Main difference between crystal forms – anisotropic change of unit cell dimensions.

What happens before the actual phase transition ?

zig-zag chains formed *via* H-bonds

	T (K)	α (10⁻⁶ K⁻¹)		
		$\bar{\alpha}_a$	$\bar{\alpha}_b$	$\bar{\alpha}_c$
Form I	303-423	230	230	-280
Form II	423-363	28	-130	186
Form III	363-303	60	-220	360

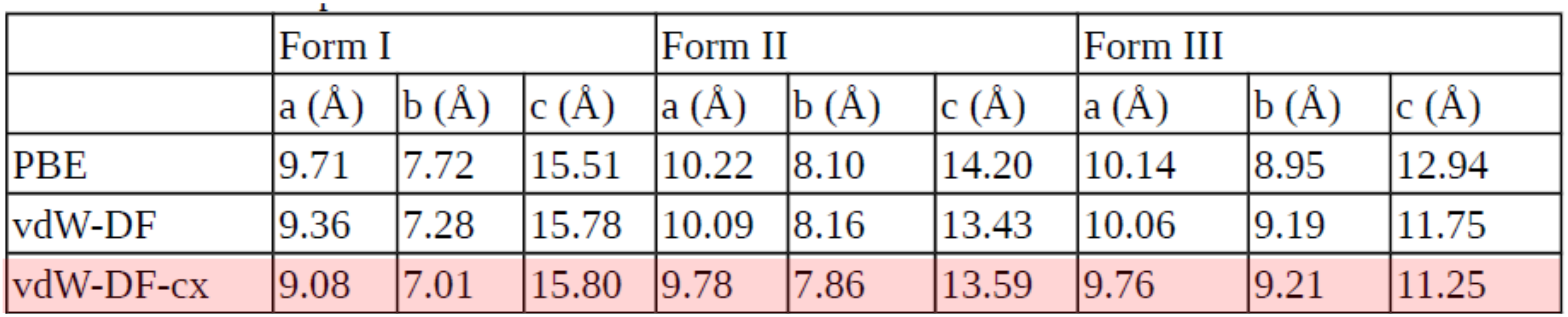


Negative thermal expansion in the organic compounds?

Colossal values like this?

DFT aiming at elucidation of TS phenomena

- First attempt to elucidate phase transitions in thermosalient system by DFT
- Large unit cells usually prohibit the use of high-level quantum chemistry calculations **- with the recent progress in development of DFT with the van der Waals (vdW) interactions** - good accuracy and predictability in modeling of molecular crystals has become accessible
- plane-wave basis set code in **Quantum Espresso** and **van der Waals density functional with consistant exchange (vdW-DF-cx)**



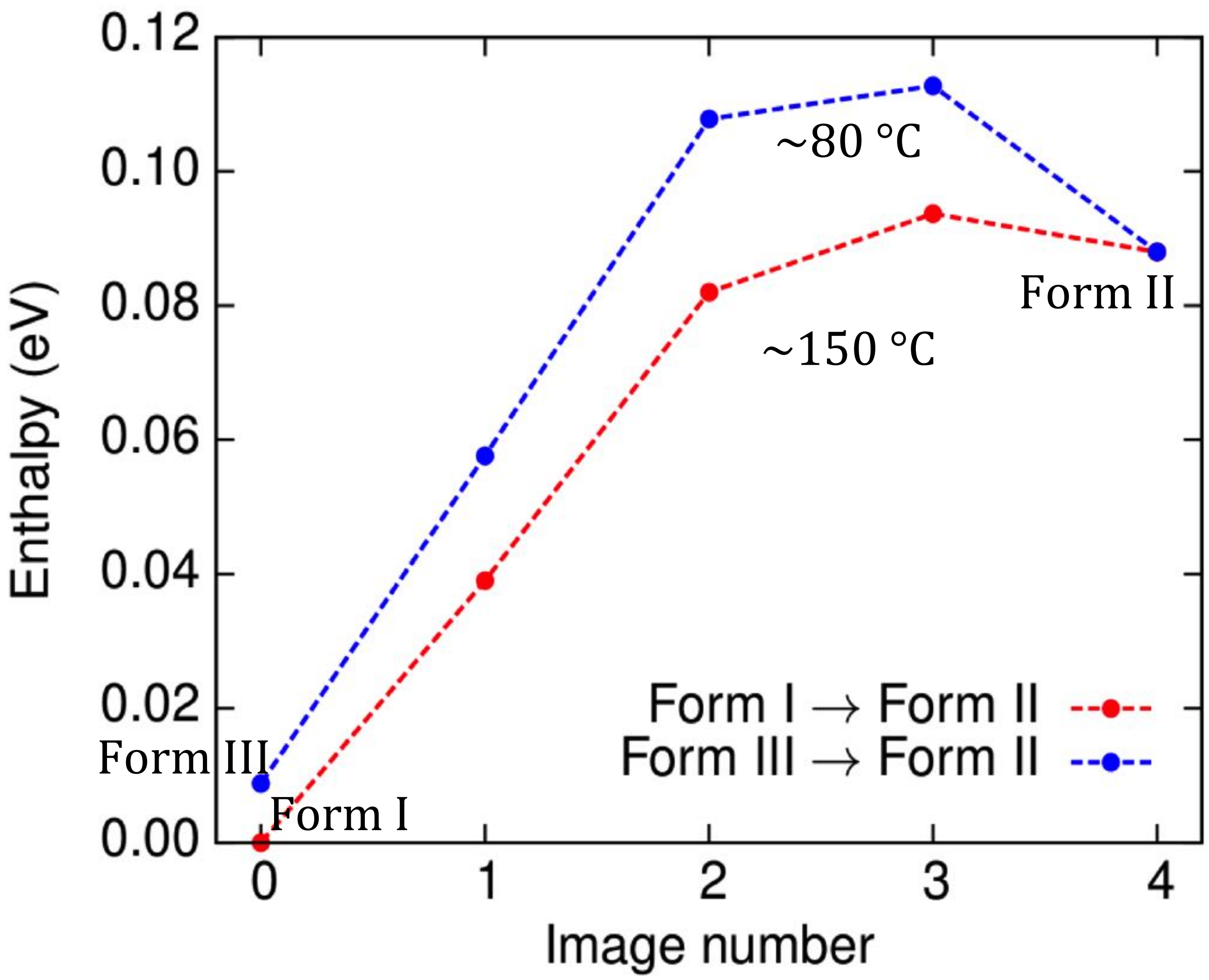
	Form I			Form II			Form III		
	a (Å)	b (Å)	c (Å)	a (Å)	b (Å)	c (Å)	a (Å)	b (Å)	c (Å)
PBE	9.71	7.72	15.51	10.22	8.10	14.20	10.14	8.95	12.94
vdW-DF	9.36	7.28	15.78	10.09	8.16	13.43	10.06	9.19	11.75
vdW-DF-cx	9.08	7.01	15.80	9.78	7.86	13.59	9.76	9.21	11.25

Exp. 9.09 7.04 15.88 9.80 7.93 13.61 9.78 9.19 11.21

- good agreement of calculated and experimentally determined lattice constants (better than with original vdw-DF and commonly used PBE functional)

- minimum energy transition path between the crystal forms - **climbing image solid state nudged elastic band (CI-SSNEB)**
- phonon calculations - **density functional perturbation theory (DFPT)**
- interatomic force constants were calculated 3x3x3 q-point mesh.
- interpolated on a 13x13x13 q-point mesh to obtain DOS and vibrational part of free energy
- plane wave basis set cutoff is 680 eV for phonon calculations and 820 eV for stress calculations.
- atoms were relaxed until total energy change was <$10e^{-5}$ eV and all forces < $5e^{-4}$ eV/A

Energy transition paths from LT forms (I and III) to HT form (II)

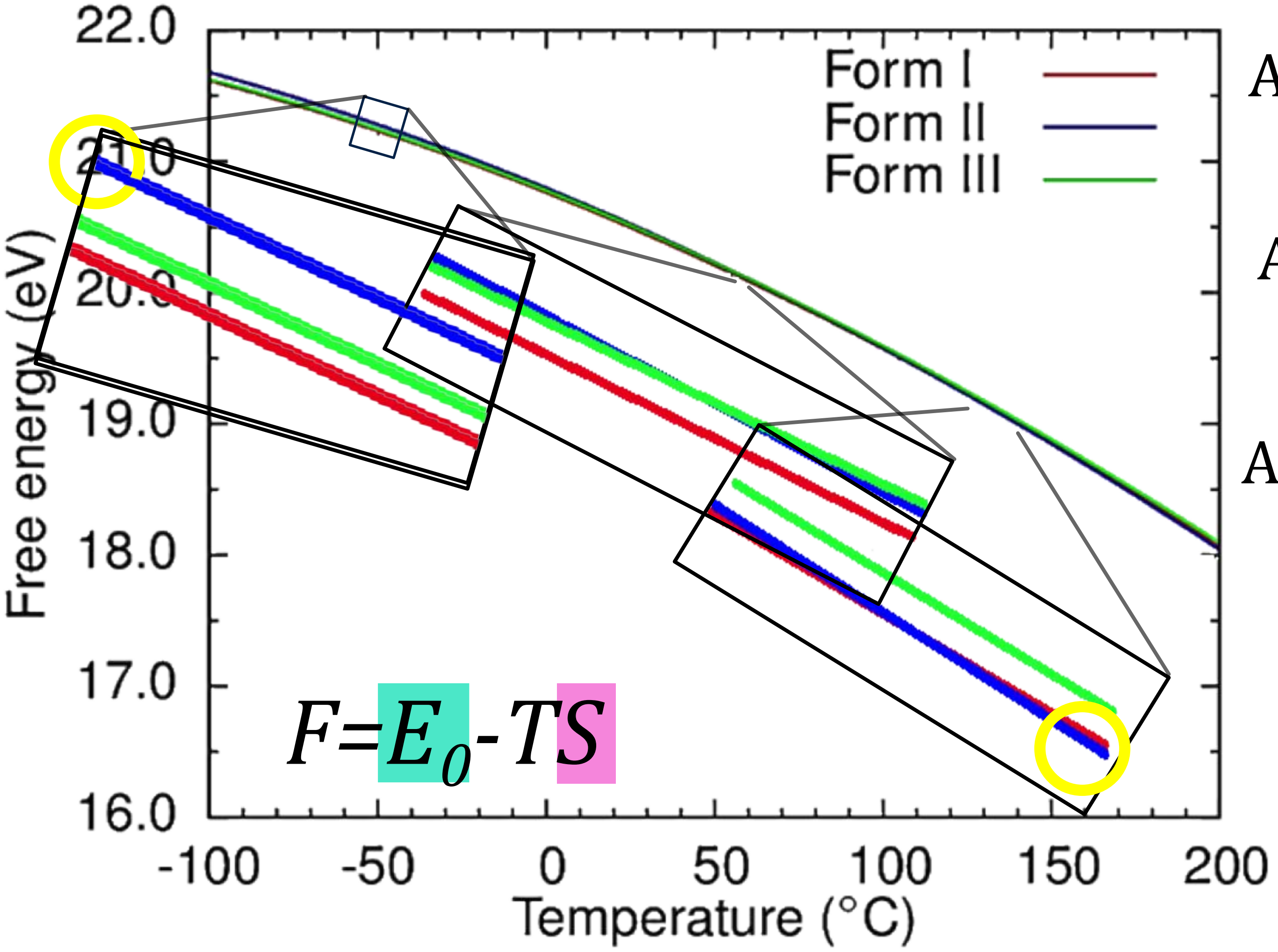


- At T=0 Form I has the lowest enthalpy (slightly lower than Form III)
- Form II has noticeably higher enthalpy (~0.09 eV).
- Energy paths from both low temperature forms, Form I and Form III, feature a **transition barrier** to Form II.

Problems

- Why is only phase II present at HT?
- Barrier is smaller for I→II compared to III→II – one would expect that I→II happens at lower temperature
- from experimental data we know it is just opposite – to understand phase transitions in this system one has to go beyond the model at T=0.
- Why is only II-III reversible?

Temperature dependance of Helmholtz free energy



At low T **Form I** lowest free energy
Form II highest free energy

At 66 °C **Form II** becomes stable than **Form III**
(exp: phase transition II-III at 80 °C)

At 130 °C **Form II** becomes stable than **Form I**
(exp: phase transition I-II at 150 °C)

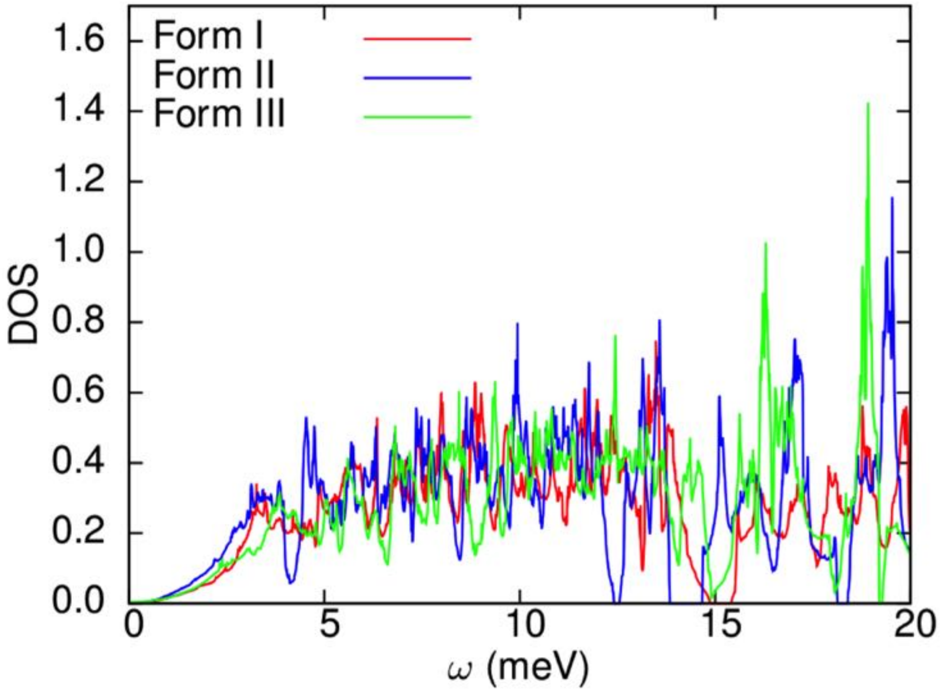
Zero point energy - determined by *high energy modes* - similar in all forms **- does not make a difference in free energy between forms** (intramolecular bonds are almost the same)

$$\frac{1}{2}\sum_{q,n}\hbar\,\omega(q,n)$$

Entropy term – determined by *low energy modes* – **Form II** has initial faster increase of DOS at **lower** energies compared to other forms - its entropy increases the fastest with the temperature.

$$k_B T\sum_{q,n}\ln[1-\exp(-\hbar\omega(q,n)/k_B T)]$$

$$\frac{dF}{d\omega}=\left(n+\frac{1}{2}\right)\hbar,\quad n=1/\left[\exp(\hbar\omega/k_B T)-1\right]$$



wilEntropy: subtraction a large number, the free energy wil eventally becomes lowest

Negative thermal expansion by the DFT

- Thermal expansion coefficient: $\alpha = C^{-1} I(T)/V$

  C^{-1} is elastic compliance matrix

  $I(T)$ is vector proportional to Grüneisen parameter.

- Grüneisen parameters (measures how does the vibrational frequencies change with changes of unit-cell) are quite cumbersome to calculate → calculated positive Grüneisen parameters

- From stress-strain relations → elastic constants C_{ij} → C matrix

  Form I (179, 26, 24, 320, 345, 524) kbar,
  Form II (200, 30, 23, 406, 300, 296) kbar,
  Form III (300, 10, 10, 579, 281, 208) kbar.

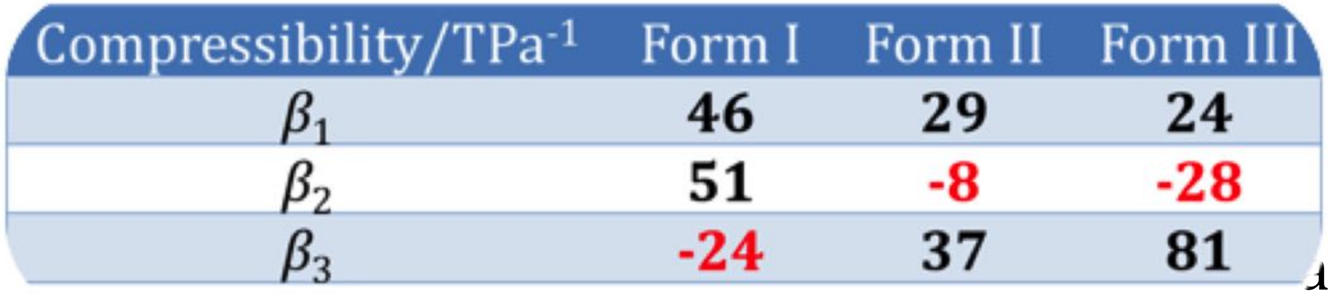
- Invert C matrix (in order to obtain elastic compliance matrix) and multiply it by any positive element vector I → obtained negative values for the thermal expansion along the *c*-axis in the case of Form I, and in the *b*-direction in the cases of Form II and Form III

- Multiply C^{-1} with unity vector – obtain the **linear compressibility coefficients $\boldsymbol{\beta}_{\mathrm{i}}$**

Compressibility/TPa^{-1}	Form I	Form II	Form III
β_1	**46**	**29**	**24**
β_2	**51**	**-8**	**-28**
β_3	**-24**	**37**	**81**

uniaxial negative thermal expansion results as a consequence of another extraordinary feature - negative linear compressibility (NLC) – one edge of the crystal will increase upon the application of pressure on it.

Negative linear compressibility materials (NLCs)



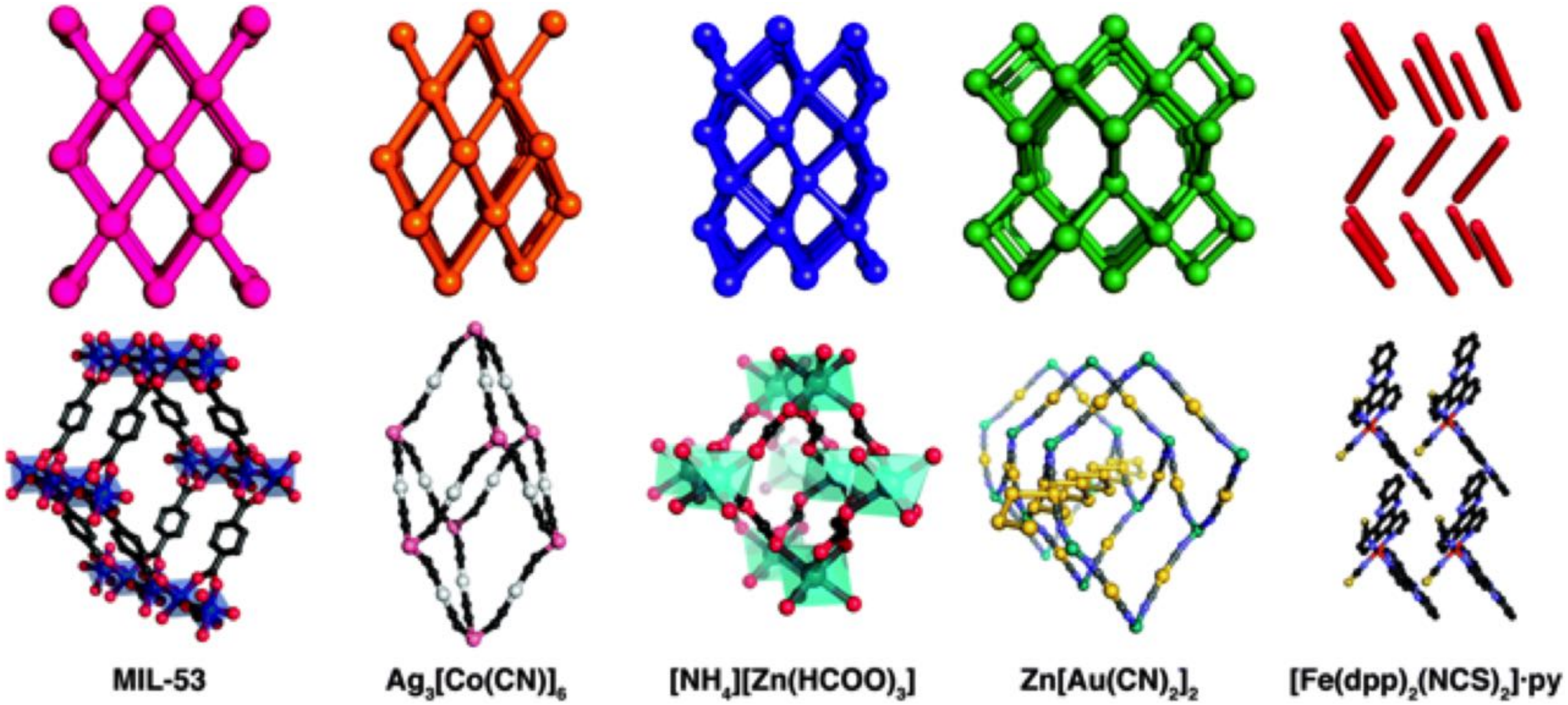
Compressibility/TPa^{-1}	Form I	Form II	Form III
β_1	46	29	24
β_2	51	-8	-28
β_3	-24	37	81

re known to show such unusual behavior.

Among all NLC materials, organic compounds are extremely rare.

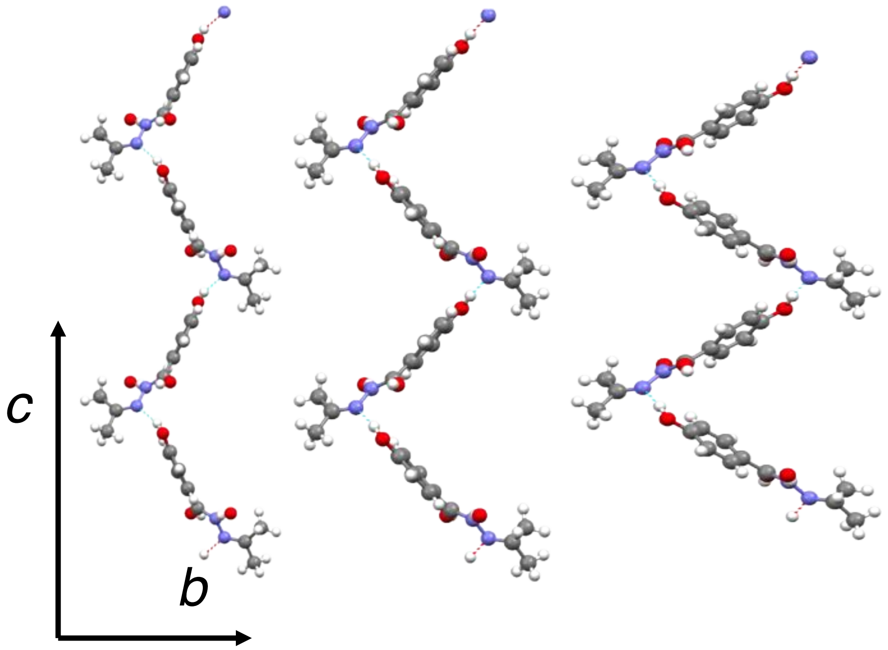
Compared to methanol monohydrate (-3.8 TPa^{-1}) our compound has one order of magnitude higher negative compressibility

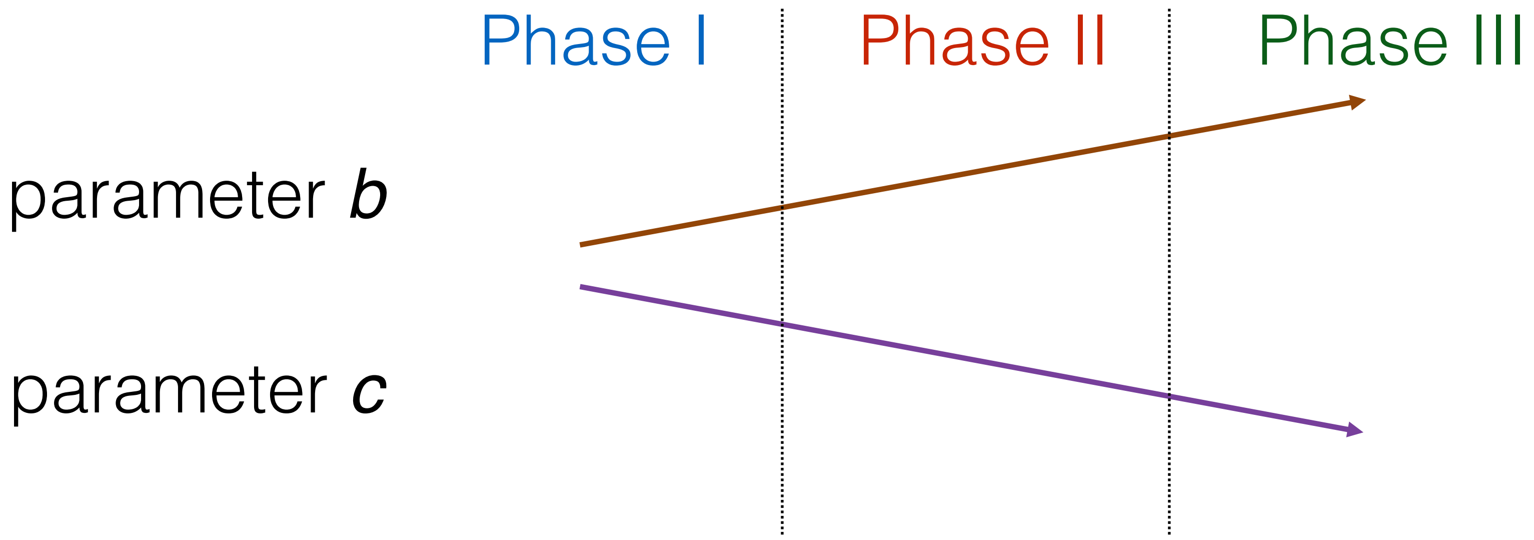
Not only that, our compound exhibits larger NLC compared to inorganic solids (metal oxides and fluoride) as well.



In fact, NLC values in N’-2-propylidene-4-hydroxybenzohydrazide are rivaled only by the ones of molecular frameworks - the class of compounds showing the most pronounced NLC.

Explanation for irreversibility of the I - II transition




Phase I | Phase II | Phase III

parameter *b*

parameter *c*

I - II proceeds in through path consistent with linear compressibility → least stress

On cooling II, transition to I is not in accordance with thermal coefficients

	α_b	α_c
Phase I	+	-
Phase II	-	+
Phase III	-	+

Rapidnes of phase transition in TS system

Thermosalient phase transitions are rapid.

„Regular" phase transition

- transformation occurs quasi-stationary
- just before the phase transition the long range correlation occurs, two phases coexist, order parameter goes to infinity, and finally, the parameter fluctuations transfer the one crystal phase to another phase.

In jumping crystals

- one thermosalient phase briskly transforms to the second one - transition is non-stationary.
- such rapidness can only be obtained by joint molecular displacements and not on one-by-one molecule basis.

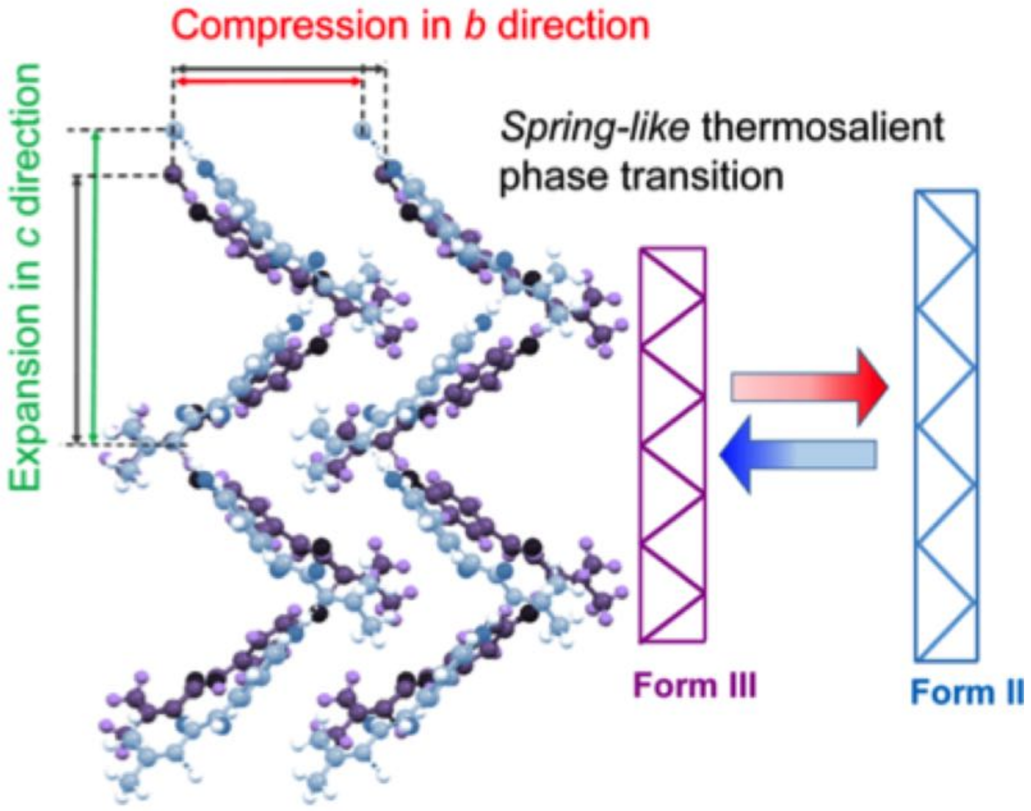
- Anwar et al. studied joint molecular displacements in molecular crystals of the amino acid DL-norleucine.
    - Transformation involving joint movements is caused by the specific phonon which frequency goes to zero at the temperature of phase transition.

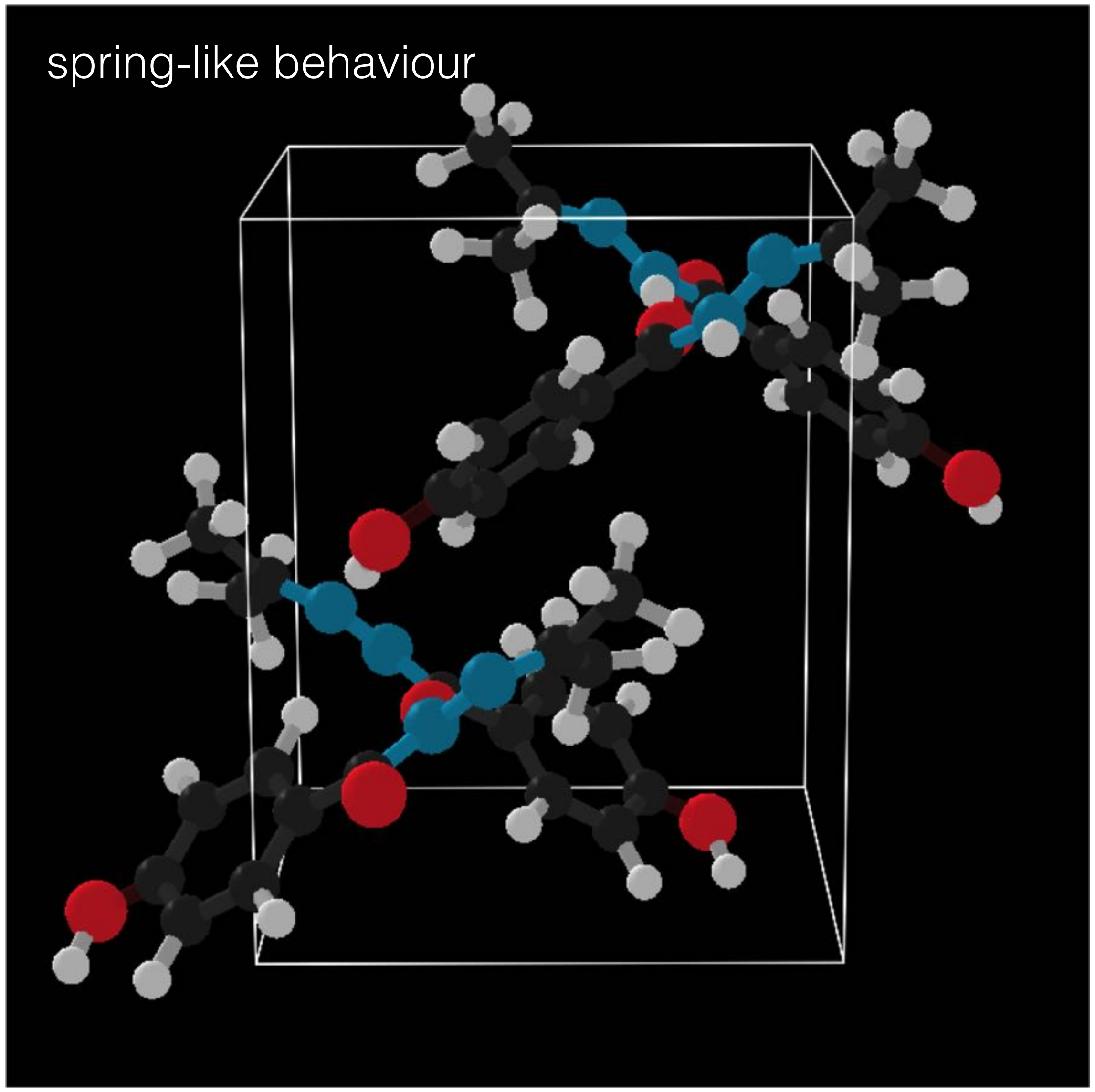
- To check this hypothesis: performed an additional phonon calculation of Form III with extrapolated lattice beyond transition temperature
    - expected to observe that specific phonon with $\omega \rightarrow 0$.
    - observed a softening of all low energy vibrations (frequency decrease up to the order of 10%) - none of the phonon frequencies seemed to go to 0

Mechanism of phase transition in TS system

- low energy phonons are playing the main role in TS transition
- slight softening of the low energy modes helps overcoming the barrier in the Gibbs potential energy → system violently collapses to the new minimum → causes a rapid response and jumping

Recall the structures: the transition between Form III and Form II - spring relaxation from tightened form to more lose one





Summary

1. Experimental methods have to be combined with theoretical calculation in order to fully elucidate thermosalient materials
2. Still not able to predict thermosalient behavior, although we established few features common to all thermosalient materials:
    - anisotropic change of the unit-cell
    - negative thermal expansion as a consequence of intrinsic elastic properites of the crystal under study
    - very fast phase transition
    - cooperative action of molecules assisted by low energy phonons