

Molecular Solid State Chemistry:

intracrystalline: activation with $h\nu$ or Δ

intercrystalline: molecular crystals are contacted by gases or solids; milling/grinding increases surface and contact number but does **not** activate molecules

Mechanochemistry = mechanical bond-breaking

Only when milling, shearing, cutting, grating, forging, drilling, polishing, pulling, impacting directly **breaks chemical bonds**. Only this is mechanical activation (not the chemical follow-up reactions)

Denying such distinction is harmful and messy

Sorry, there are problems with misconceptions

„Topochemistry“ of 1964 was a **serious drawback for molecular solid-state chemistry**: denial of basic physics in textbooks also by referees!

Topochemical hypothesis: minimal atomic und molecular movements in crystals ($d < 4.2 \text{ \AA}$)

Elementary nanomechanics: „topochemical reactions“ would create local pressure in the GPa range if the molecular shape is altered that would not be released

Multiple experimental evidence is ignored. Of course everything can be simulated with ≥ 3 free parameters if data do not fit

Disprovings with experimental results are from:

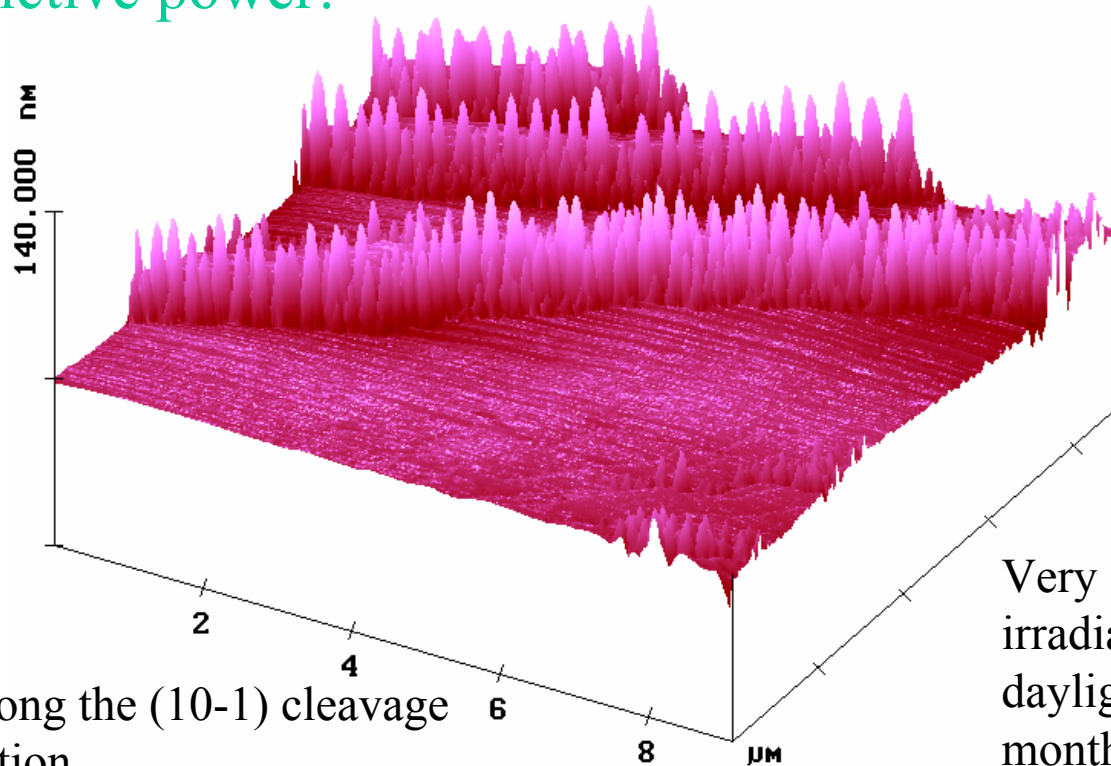
AFM and SNOM: Molecules migrate anisotropically long distances up to the μm -range and beyond the surface (that is release of local stress)

Chemistry: Without cleavage planes or channels: no reaction (valid predictions)

Nanomechanics: We also get anisotropic migrations in crystals by GPa stress

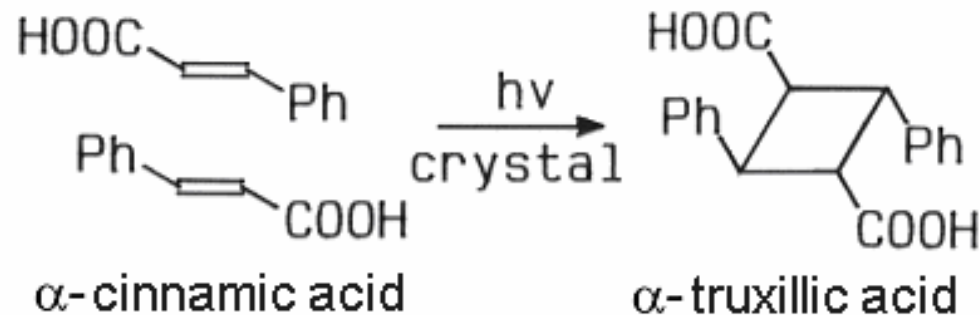
AFM: Anisotropic molecular migrations also with the standard of „topochemistry“, so what? **Answer: Topochemistry is a misconception, without predictive power!**

α -Cinnamic acid
(010)

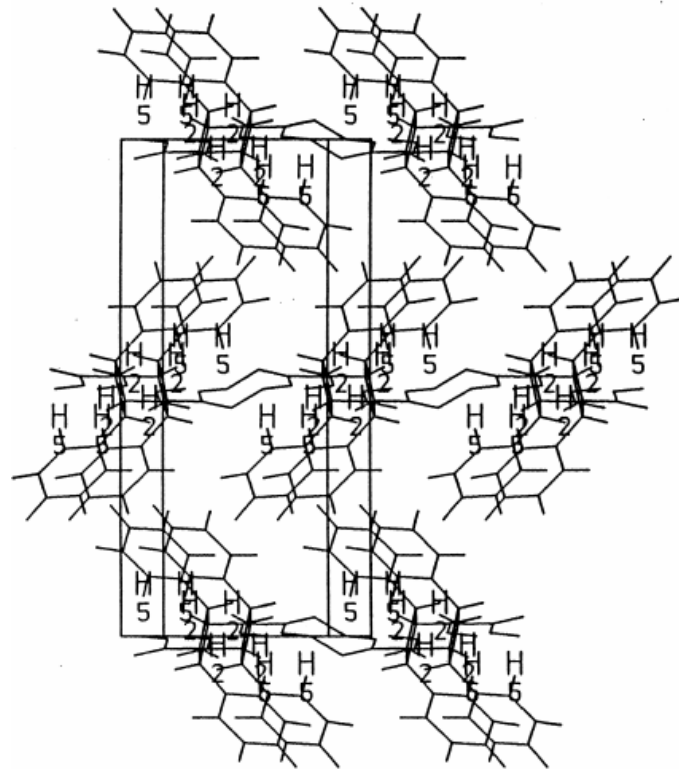


Features along the (10-1) cleavage plane direction

Very slow super-tail irradiation with filtered daylight on (010) after 6 months and 30% conversion



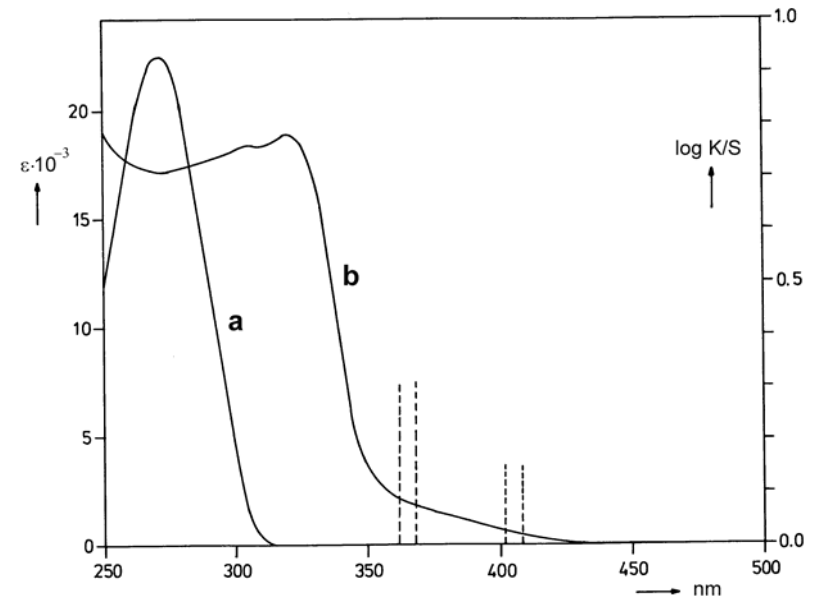
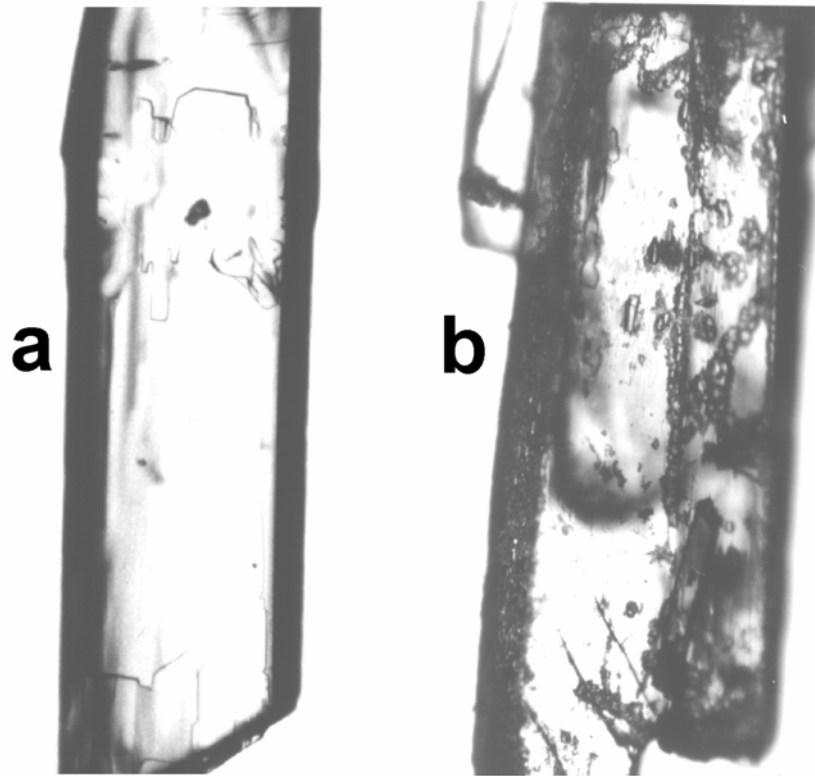
A report claimed X-ray data of truxillic acid for a 100% transformed single crystal of α -cinnamic acid; data at the right hand side are the original data



..#1	..#2	..AT1	..AT2	..G1	..G2	..R1	..R2	..DIST	..QUOT
13	15	H2	H5	1	1	1.200	1.200	2.033	.85
32	34	H2	H5	1	1	1.200	1.200	2.033	.85
51	53	H2	H5	2	2	1.200	1.200	2.033	.85
70	72	H2	H5	2	2	1.200	1.200	2.033	.85
89	91	H2	H5	3	3	1.200	1.200	2.033	.85
108	110	H2	H5	3	3	1.200	1.200	2.033	.85
127	129	H2	H5	4	4	1.200	1.200	2.033	.85
146	148	H2	H5	4	4	1.200	1.200	2.033	.85
165	167	H2	H5	1	1	1.200	1.200	2.033	.85
184	186	H2	H5	1	1	1.200	1.200	2.033	.85
203	205	H2	H5	1	1	1.200	1.200	2.033	.85
222	224	H2	H5	1	1	1.200	1.200	2.033	.85
241	243	H2	H5	1	1	1.200	1.200	2.033	.85
260	262	H2	H5	1	1	1.200	1.200	2.033	.85
279	281	H2	H5	2	2	1.200	1.200	2.033	.85
298	300	H2	H5	2	2	1.200	1.200	2.033	.85
317	319	H2	H5	2	2	1.200	1.200	2.033	.85
336	338	H2	H5	2	2	1.200	1.200	2.033	.85
355	357	H2	H5	3	3	1.200	1.200	2.033	.85
374	376	H2	H5	3	3	1.200	1.200	2.033	.85
393	395	H2	H5	3	3	1.200	1.200	2.033	.85
412	414	H2	H5	3	3	1.200	1.200	2.033	.85
431	433	H2	H5	3	3	1.200	1.200	2.033	.85
450	452	H2	H5	3	3	1.200	1.200	2.033	.85
469	471	H2	H5	4	4	1.200	1.200	2.033	.85
488	490	H2	H5	4	4	1.200	1.200	2.033	.85
507	509	H2	H5	4	4	1.200	1.200	2.033	.85
526	528	H2	H5	4	4	1.200	1.200	2.033	.85

Challenges: he carboxylic dimer structures are not planar, without any reason. All invoked examples for non-planar carboxylic dimers are sterically enforced. Irradiated crystals disintegrate above 30% at the reported irradiation procedure. The authors publish only photos from the initial, never of the final crystal. AFM/SNOM, microscopic, and nanoindent results are not appreciated or tried to falsificate

α -Cinnamic acid crystals after 6 months under argon, from same batch on (010)

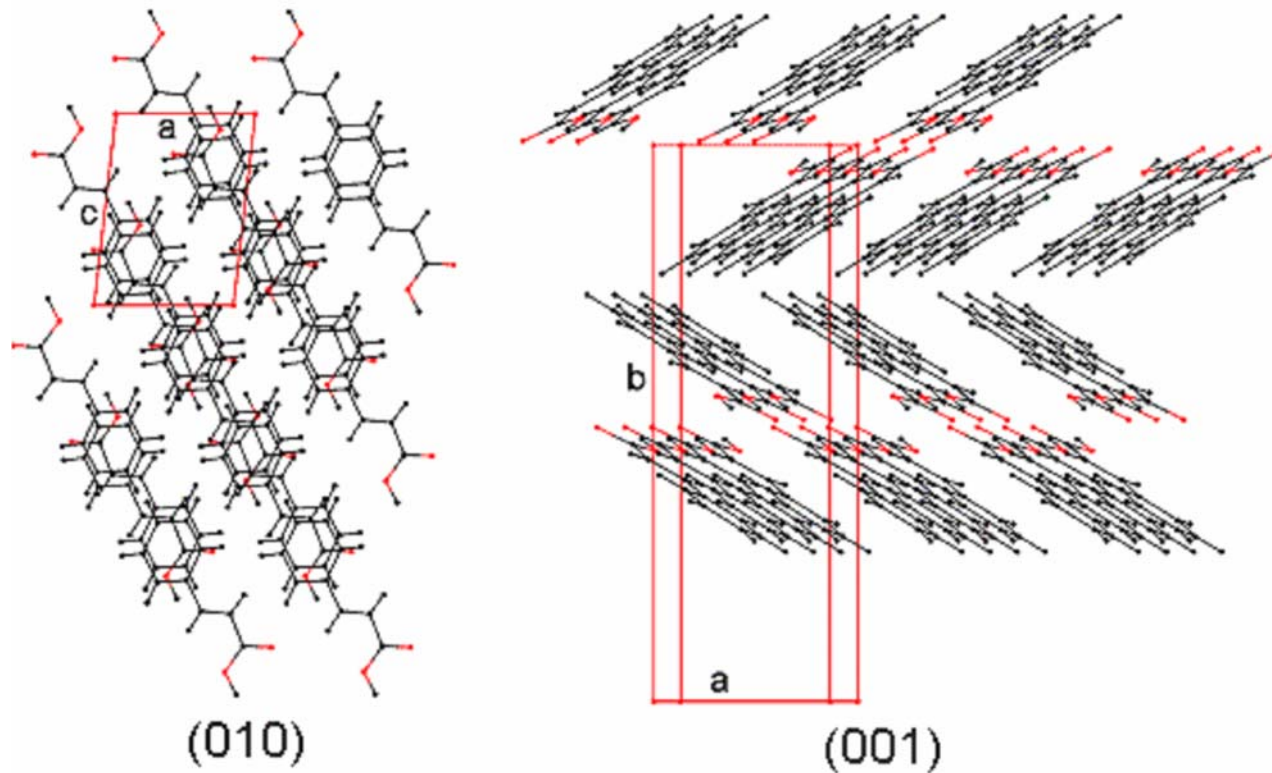


Absorption tails of α -cinnamic acid (a) in methanol, (b) crystalline powder

(a): kept in the dark; (b): kept in daylight filtered by two window and a Pyrex glasses; microscope at x 200; crystal thickness: 40-60 μm

There was all time for relaxation, but at 30% conversion of crystal (b) we see cracks along the (10-1) cleavage plane direction, crystallites on (010) and particularly crystallites on the side faces

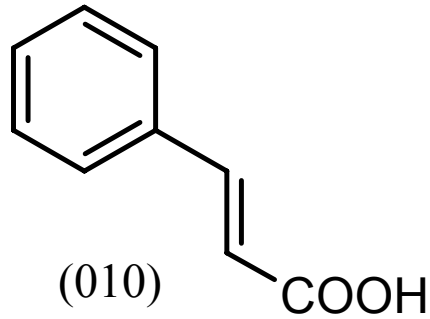
Cleavage planes of α -cinnamic acid for migration



Cleavage plane: (10-1) (010)

Clear prediction: these crystals are reactive be it photochemical or gas-solid and solid-solid, because product molecules initiate anisotropic migration within the cleavage planes rather than producing stress 6

Anisotropic molecular migrations by mechanical interaction

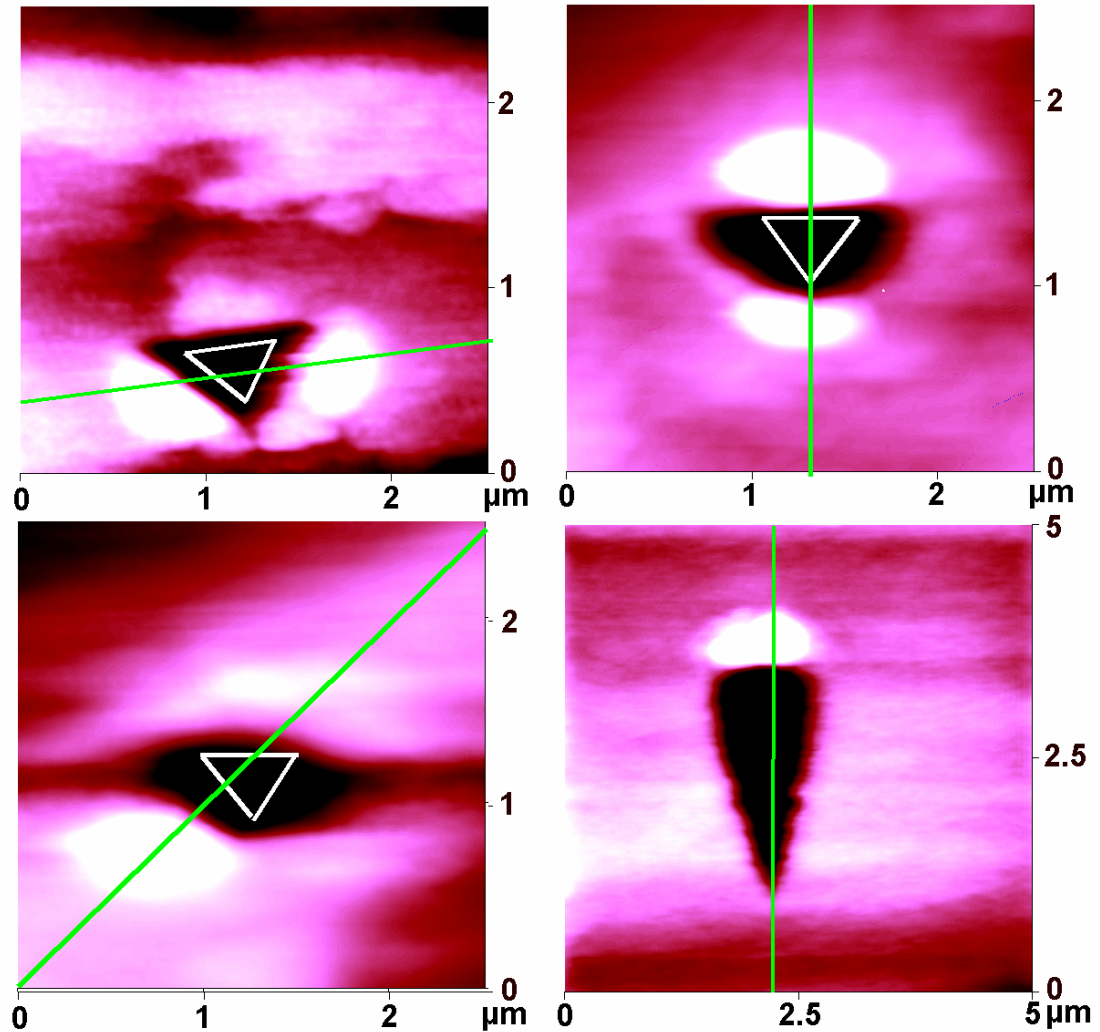


H : 200-250 MPa

E_r : 6-8 GPa

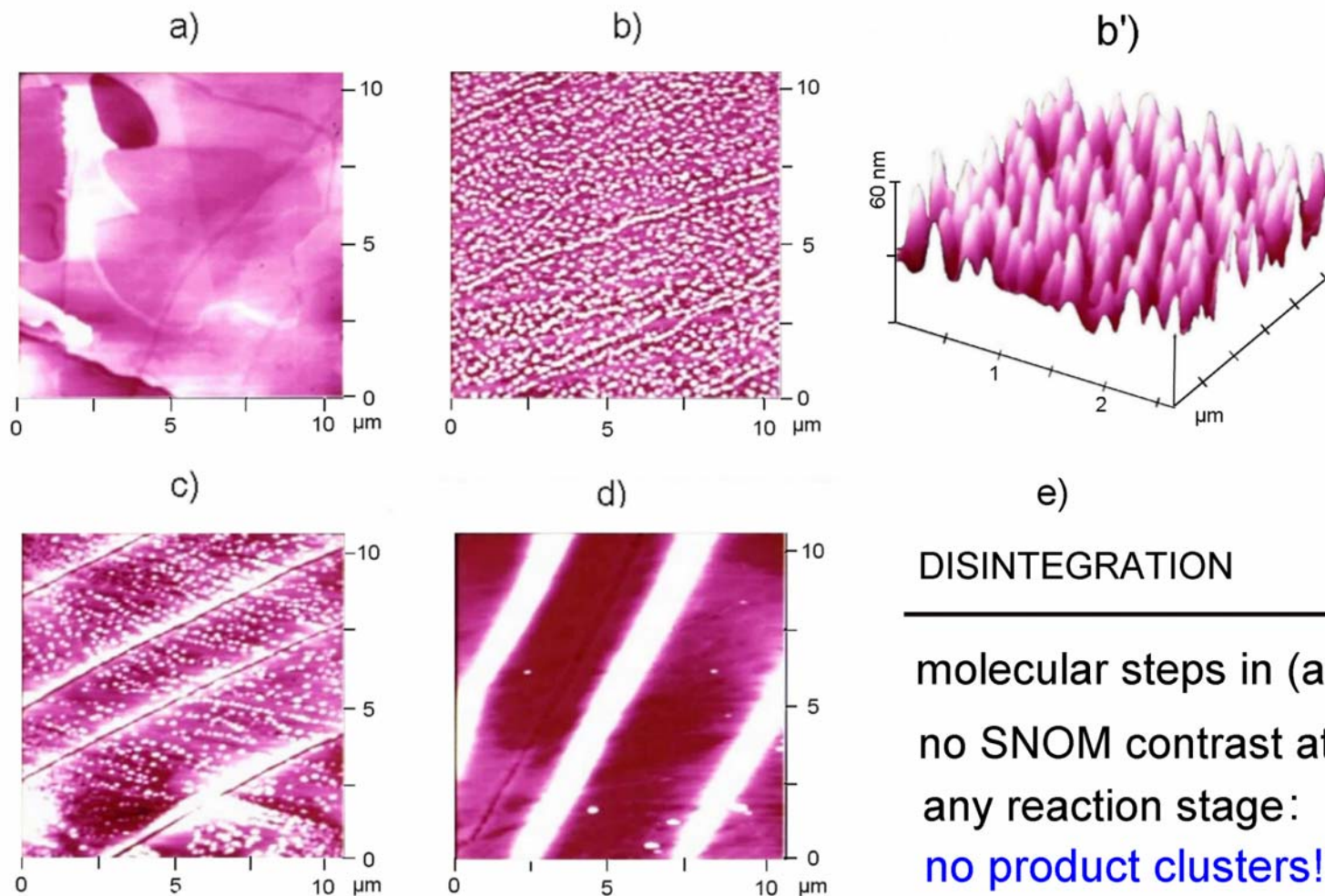
McBride (1986) derived a stress of 2 GPa in the photodecomposition of diacyl-peroxids at 20K (0.05% conversion) „confined in cavity with 10% radial expansion below 30K“

Nanoindentation and nanoscratching
 α -*trans*-cinnamic acid: migrations along cleavage plane direction on (010)



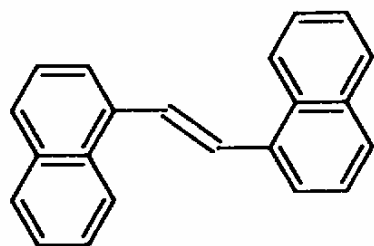
Green line gives direction of cleavage planes under (010) at crystal orientation

Development of the tail photolyses (365 nm) of α -cinnamic acid (010): solid-state mechanism by molecular scale AFM

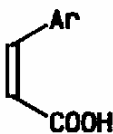


a) fresh; b) phase rebuilding; c) and d) phase transformation; e) disintegration at 30% conversion, no further AFM at that stage; Z-scale 10 nm in (a); 100 nm in (b-d).

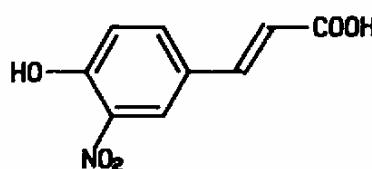
Further failures of topochemistry



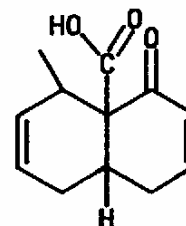
($d=4.06\text{\AA}$)
no dimer



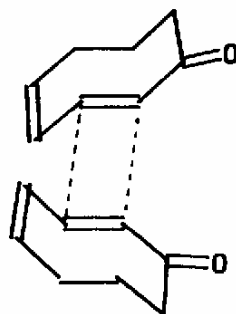
($d < 4\text{\AA}$)
no dimer



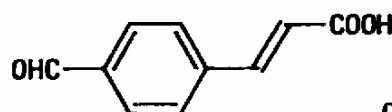
($d=3.78\text{\AA}$)
no dimer



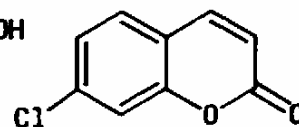
($d=3.79\text{\AA}$)
no dimer



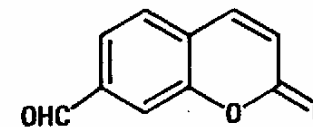
enclathrated
($d=9.780$ and 8.927\AA)
reactive



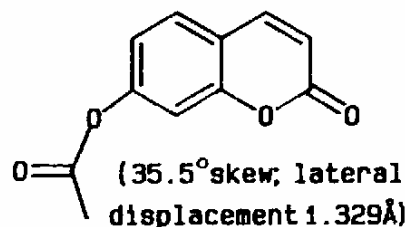
($d=4.825\text{\AA}$)
reactive



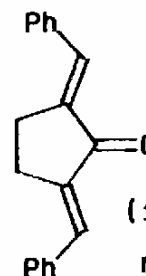
($d=4.45\text{\AA}$)
reactive



(65° skew)
reactive



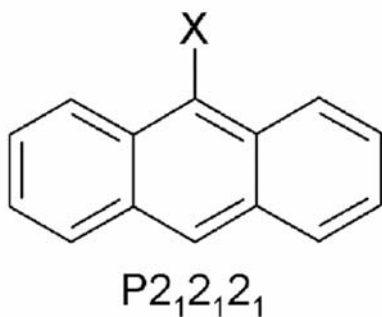
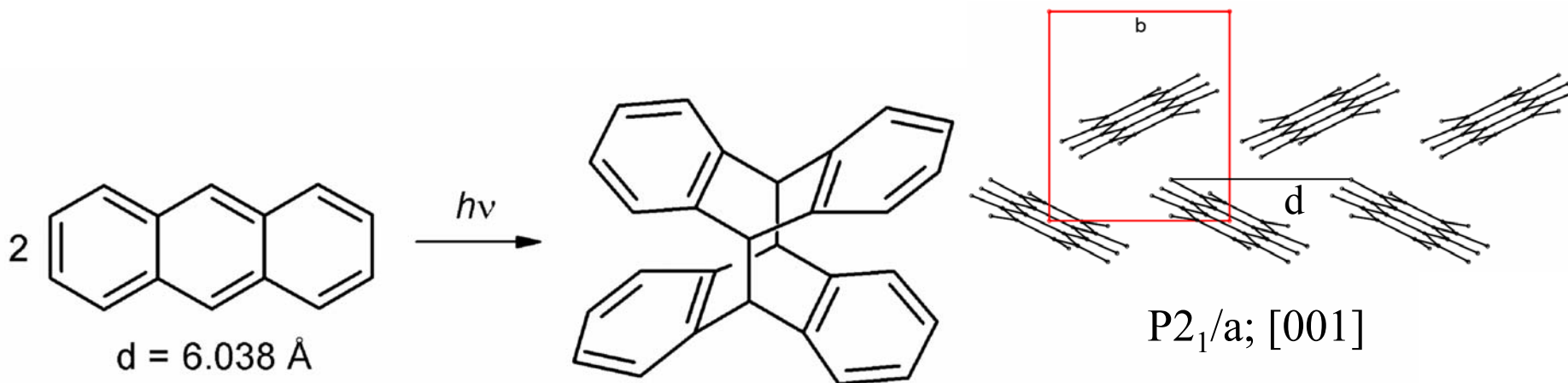
(35.5° skew; lateral displacement 1.329\AA)
reactive



(131° skew)
reactive

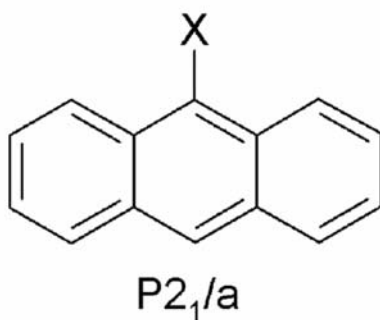
The 4.2\AA criterion does not withstand scrutiny; anisotropic far-reaching molecular migrations must be possible for pressure release

Anthracenes photodimerization: failure of topochemistry



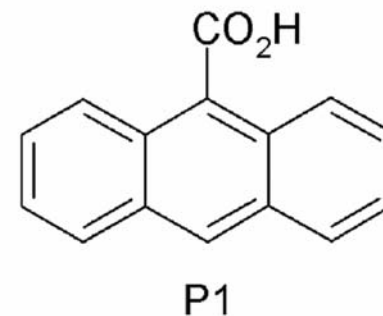
- a:** X = CHO: $d = 3.93$
- b:** X = CN: $d = 4.29$
- c:** X = Cl: $d = 4.0$

packing: head to head
product: head to tail



- a:** X = CO₂Me: $d = 4.15$
- b:** X = Br: $d = 4.1$

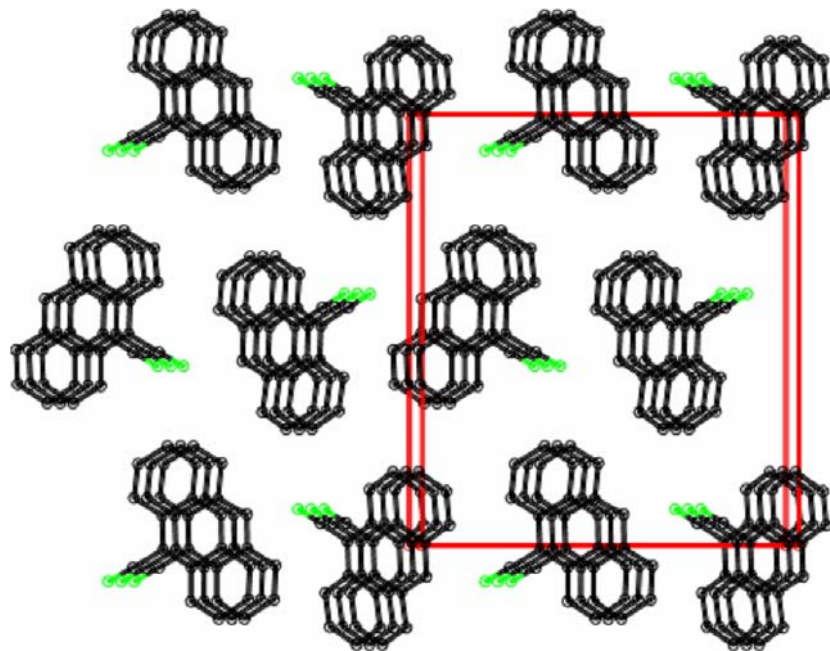
packing: head to head
unreactive



$d = 3.88$

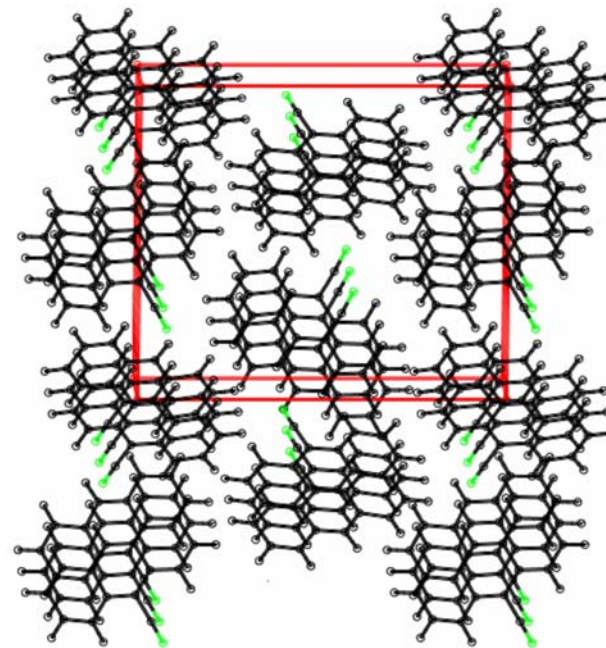
packing: head to head
unreactive

Solution of the 9-cyanoanthracene „anomaly“



(001) slightly around y

$P2_12_12_1$



(011)

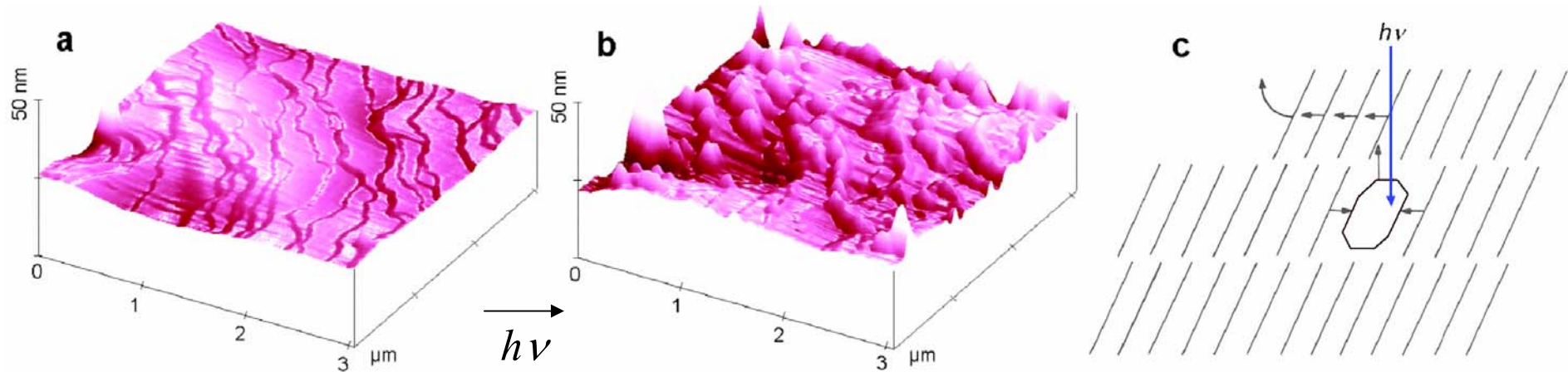
Mechanism for head-to-tail dimerization: head-head is thermoreversible (decay after formation).

Molecules cannot rotate around the long axis of the ring system.

(011) has the central molecule surrounded from all sides; the only possibility is **rotation around center of the rings by 180°** for creating the suitable head-to tail orientation.

Migration along the (poor) cleavage plane is helped by channels, and the predisturbed lattice. This provides the observed stable head to tail photoproduct

Anthracene: the excuse of „defect sites reaction“ challenged with AFM and SNOM



AFM does **not** support energy transport to defect sites and reaction only there!

(a) is a fresh anthracene (001) face with molecular steps (1-5)

(b) after short irradiation molecules exit along these steps

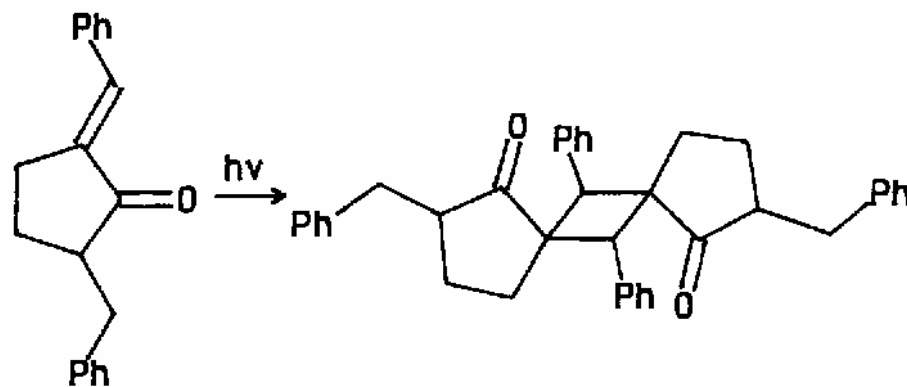
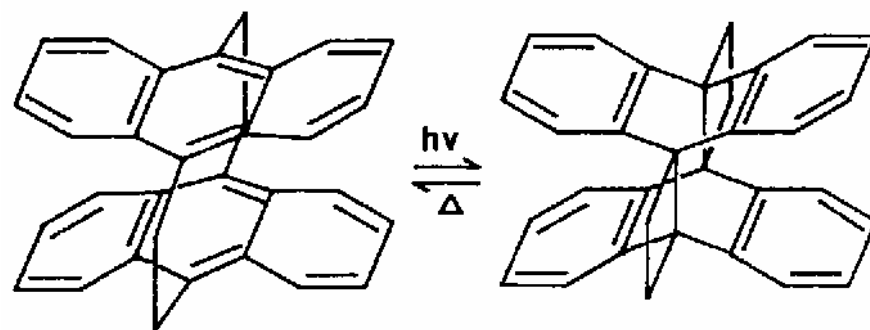
(c) sketches why there is molecular migration

SNOM gives no chemical contrast in the optical image. Thus, there is **no accumulation** of dimer at the exit sites and the whole surface exhibits the same conversion.

Most of the claimed „topotactic“ reactions do not withstand scrutiny

They must be secured at the direct molecular level of AFM that is now everywhere available and user-friendly.

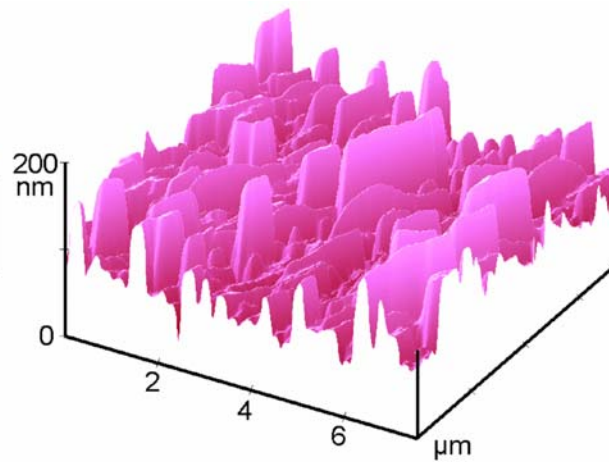
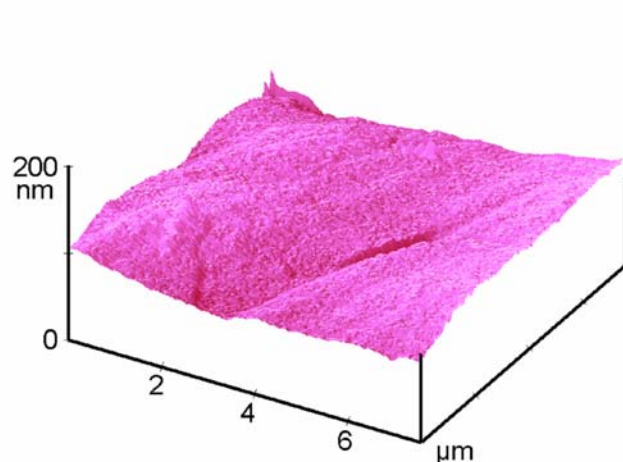
These two photoreactions are genuinely topotactic, because AFM excludes surface changes with molecular precision:



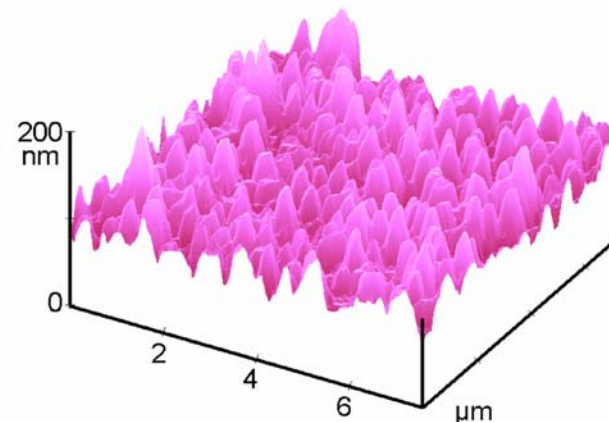
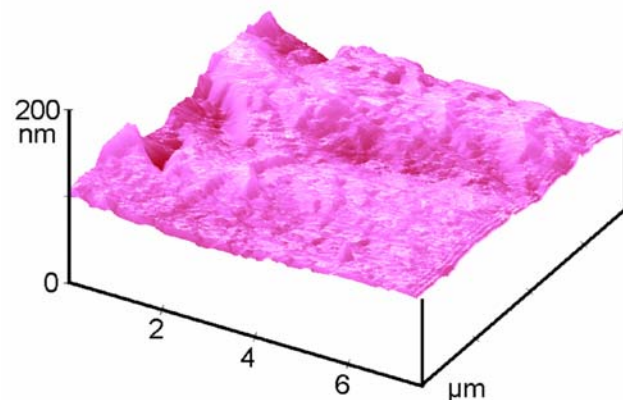
Strict face selectivity for anisotropic migrations

9-Chloroanthracene, [4+4]-photodimerization on the AFM (1992)

main-face
cleavage plane
cutting there

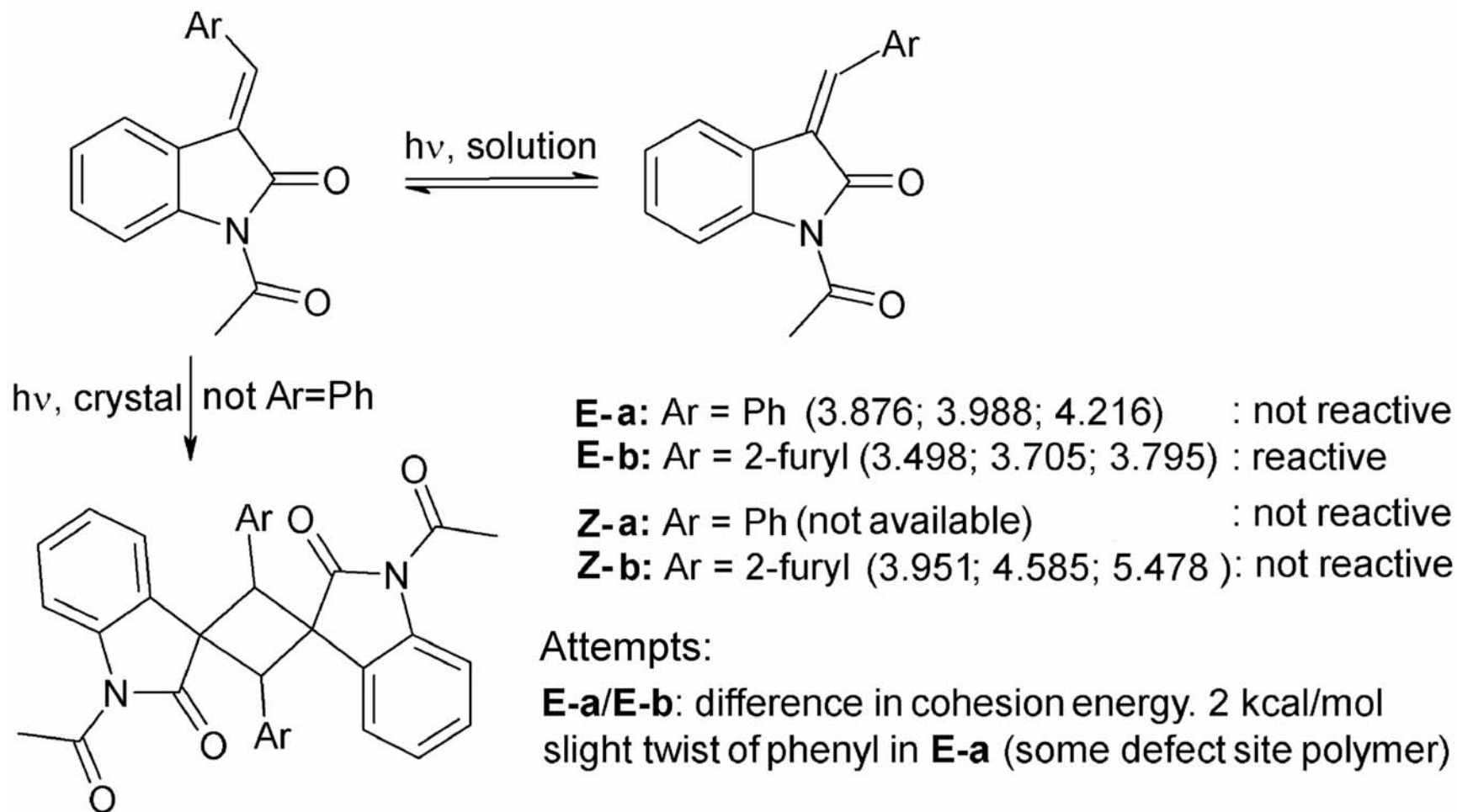


long side-face
flat layers



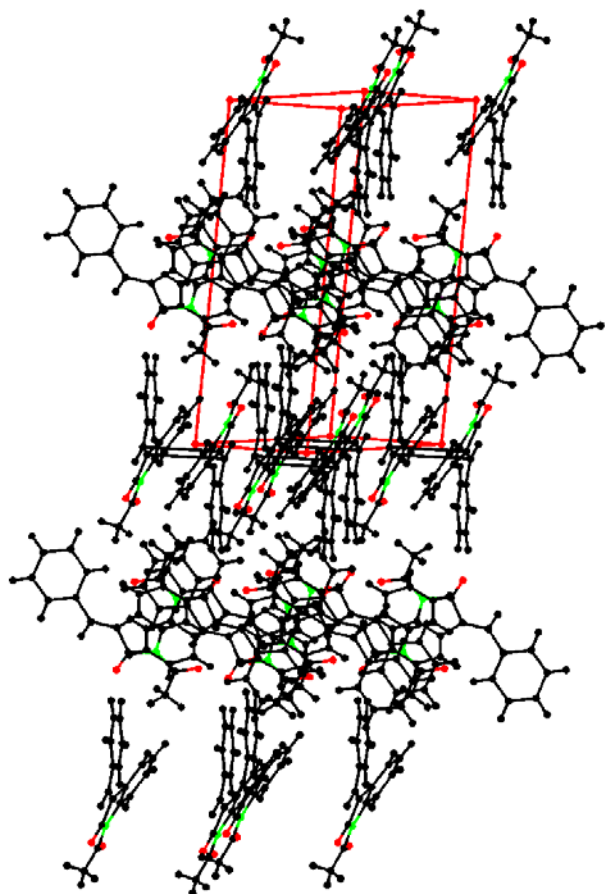
*Luty and Eckhard (JACS 1995) accepted pressure but apparently not the then very abundant experimental anisotropic migrations: their attempt to formulate „reaction cavities“ with „elastic multipoles“ was thus superficial and obsolete (cannot save „topochemistry“).*¹⁴

Confusion in the contemporary literature: one reaction works, three closely related reactions do not work

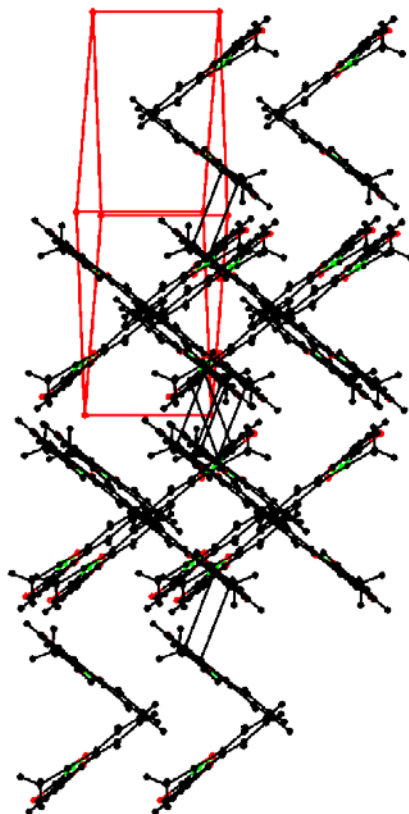


Why not consider crystal packing?

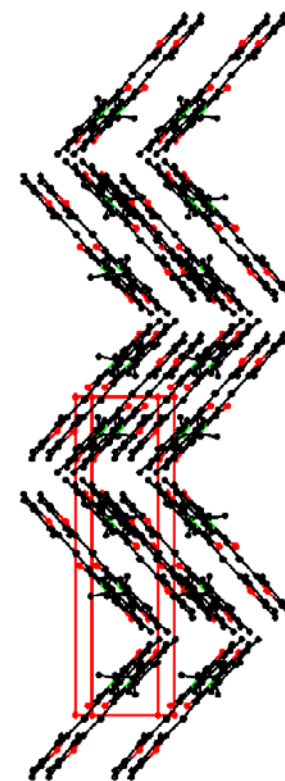
The answer: local stress in the crystal bulk must be released



E-a (110) unreactive
strongly interlocked



E-b (-102) reactive
cleavage plane



Z-b (-102) unreactive
interlocked and steep

It is observed as necessitated by the crystal packing

Elastic multipole concept for reaction cavities is useless: the crystal yields; when stress₁₆ cannot be released by far-reaching migration no reaction occurs.

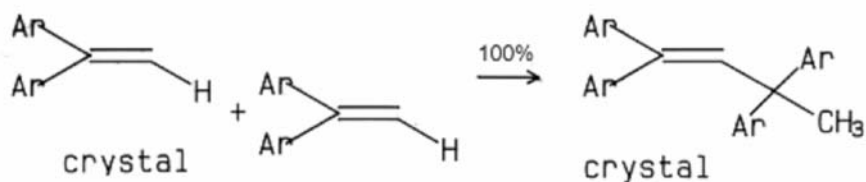
A systematic of anisotropic migrations within reacting crystals (**the molecular packing is crucial**)

positive pressure	no pressure	negative pressure
expansion	no geometric change	shrinkage
migration	no migration	migration
surface features	no surface features	surface features
very frequent	extremely few approved cases	frequent

The 4.2 Å distance and minimal movements claim of topochemists is not predictive but unreasonable; close distance may help or impede; only crystal packing is crucial and its analysis is not at all difficult (use databases)

Neglecting pressure/stress and its relief is a severe and basic error, textbooks must be rewritten

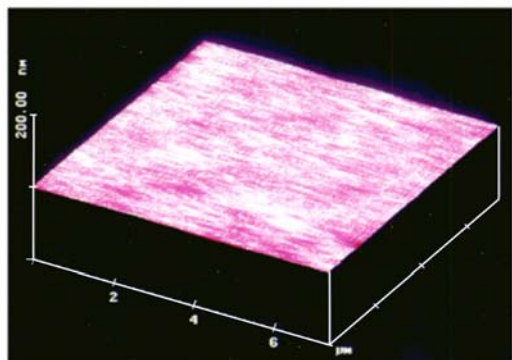
Catalytic solid-state dimerization of 1,1-bis-aryl-ethenes; AFM analysis



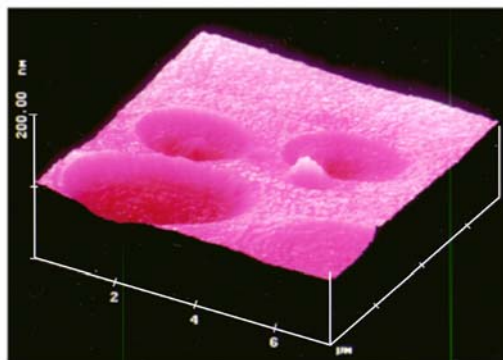
Ar = 4-H; -CH₃; -OCH₃

gaseous catalysts: HCl; HBr; BF₃; XeF₂

preparatively at -50°C to +25°C (must stay solid)

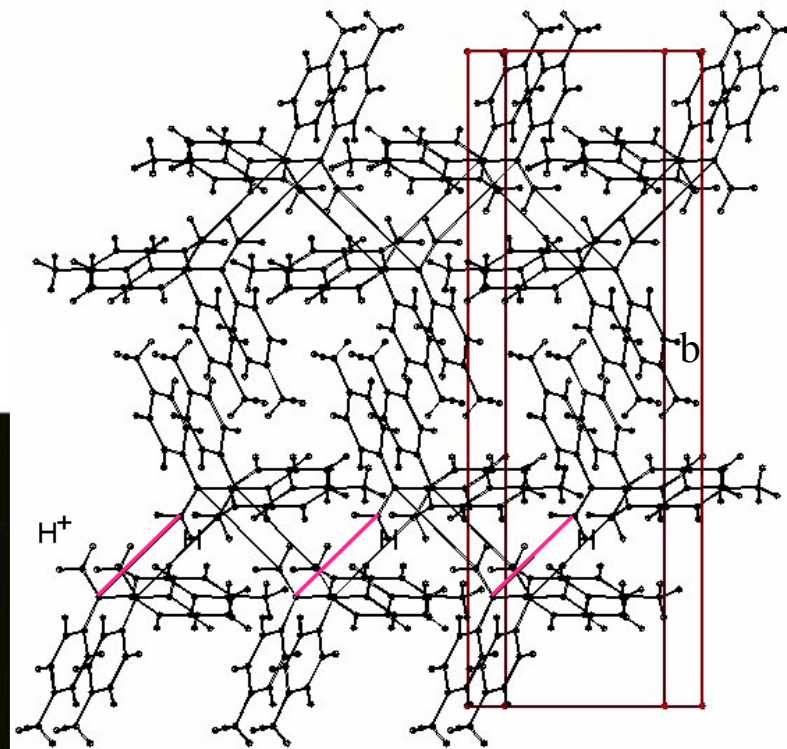


(100)-face



after treatment with gaseous HCl

Molecules after addition of HX would not be able to migrate, but they can shrink by linear h/t dimerization for migrations leaving crater



1,1-bis-*p*-tolyl-ethene

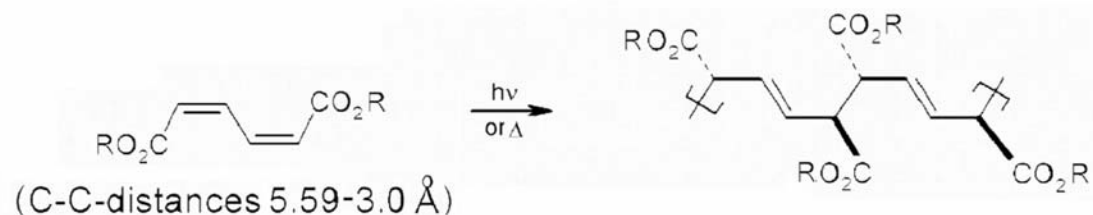
(100); $a = 6.362\text{\AA}$; $P2_1/c$

Distance for head-head dimerization with completing H-transfer is 4.402 Å (not used)

Distance for head-tail dimerization with completing H-transfer is 4.566 Å (these are all drawn)

The larger distance is quantitatively chosen! Only the extended arrangement fits into the shrinking lattice, leaving the craters; interlocking next layers must cooperate

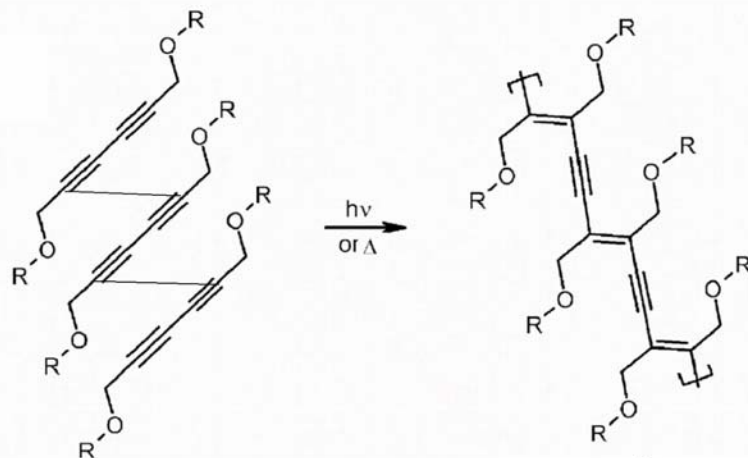
Applications for stacked polymerizations without imposed pressure



6 with C-C distance above 5.3 Å: polymer

10 with C-C distance below 4.2 Å: no polymer

< 4.2 Å distance claim is useless



distance between reacting centers < 4.2 Å in all cases,

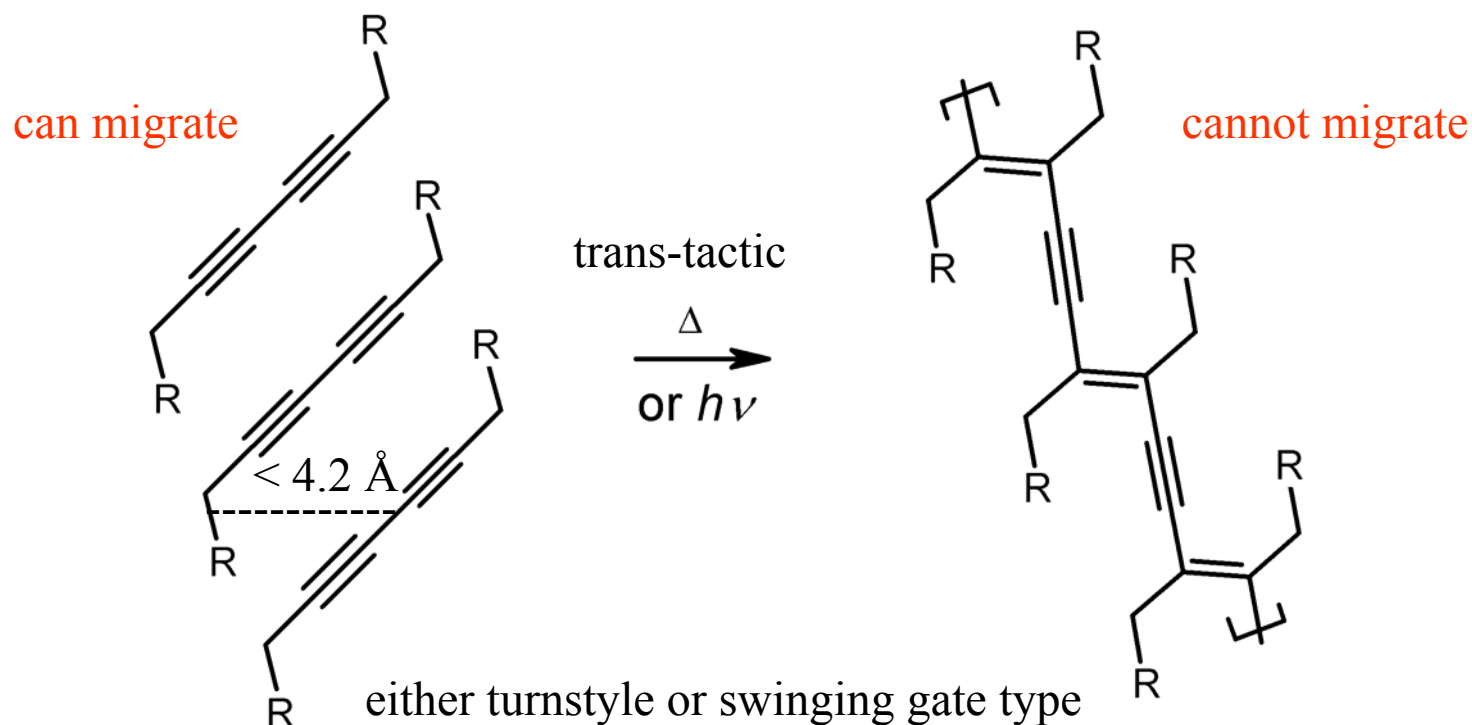
but most of them are not polymerizing

Very puzzling when denying molecular migrations

Valid prediction when appreciating molecular migrations:

Polymer must not become longer, but also not too much smaller than monomer stacking (our experimental limit is at about 6 nm after 100 polymerization steps)

Three examples out of hundreds of publications



R = 4-Pyr ... (HOOCCH₂NHCOC)₂: stack 4.93 Å; period 4.9 Å, coincidence, polymerization

R = OSO₂-4-fluorophenyl: long stack 5.80 Å, period 4.9 Å, too far migration, at best oligomer

R = CH₃: short stack 3.8 Å, period 4.9 Å, polymer would be longer, no polymerization

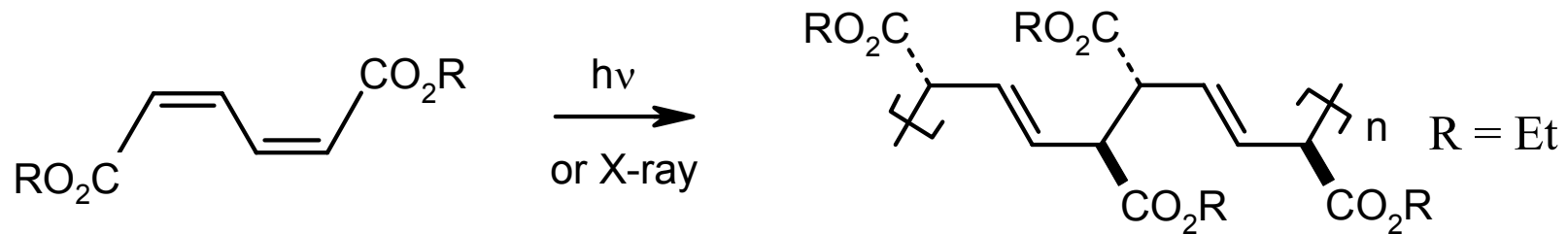
Short is detrimental! Only the migrational issue provides the correct answers

Millions of \$ of research funds could have been saved for decades by not denying

20

Beware of rare phase transition of the monomer before the polymerization!

One example out of 69 studied solid 1,3-dienes



polymorph with spacing 4.931 \AA reacts
polymorph with spacing 4.250 \AA does not react

period 4.841 \AA

Topochemists rationalization: „such diminution of the spacing by 14 % is minor but it deviates from the empirically found favorable $4.7\text{-}5.2 \text{ \AA}$ spacing”

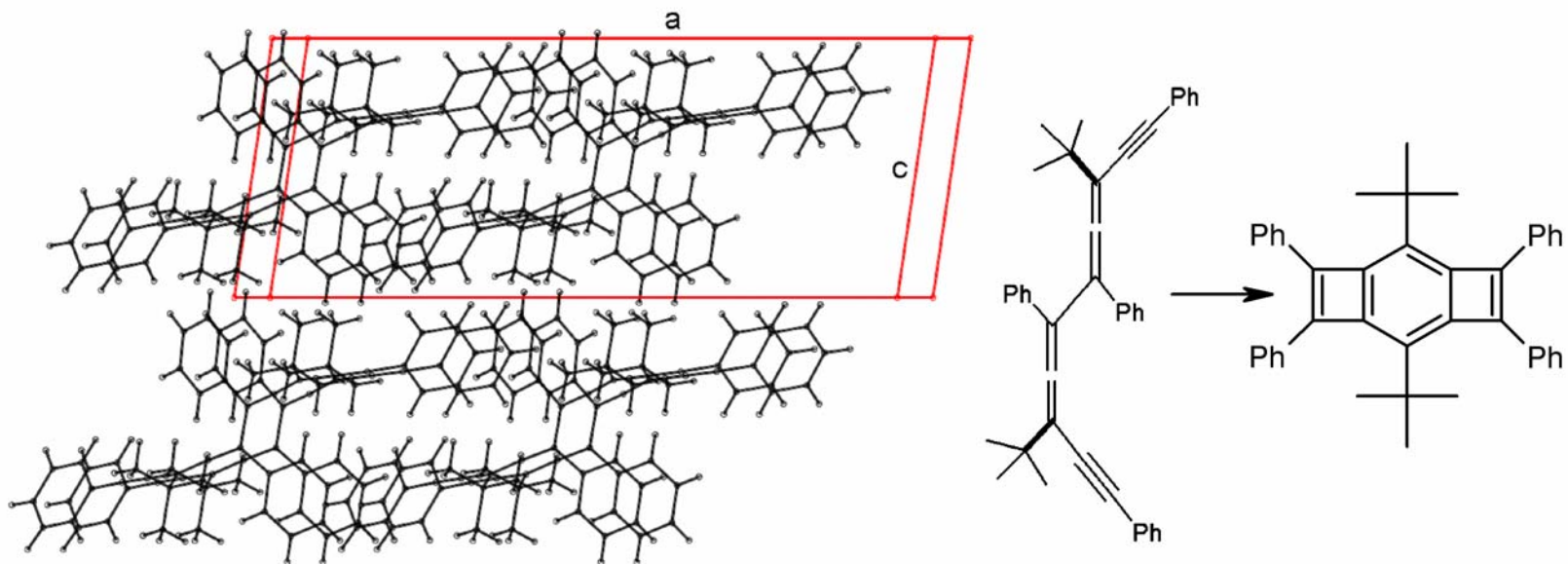
When appreciating physics: Polymer cannot migrate it must therefore not become longer but may become shorter, as is experimentally found

After 100 polymerization steps the reacting monomer has to migrate for a 9 \AA distance (different limit than with 1,3-diacetylenes)

Reactions for non-polymerizing „R“are: E/Z-isomerization, [2+2]-dimerization, or none

Beware of rare initial phase transitions before polymerization!

A highly interlocked monolayered bis-diallene



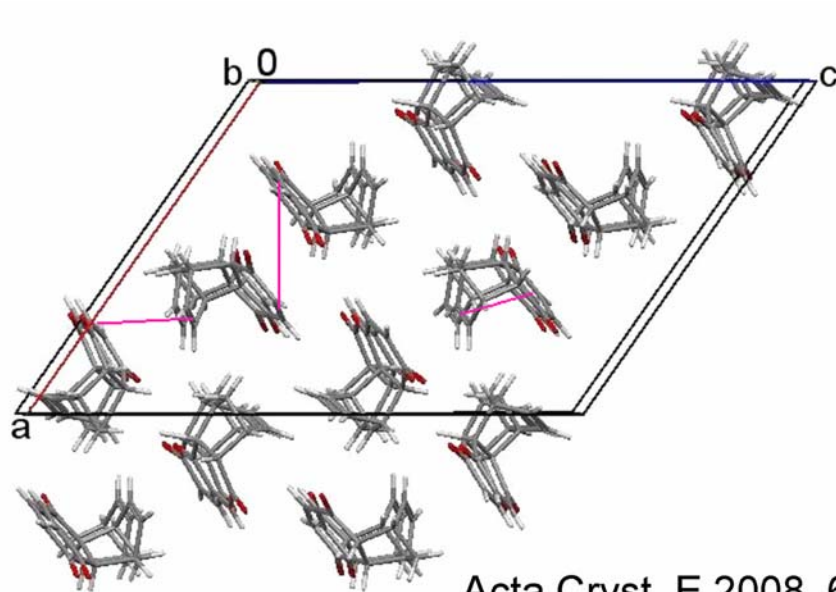
Prediction: cannot migrate in the bulk and cannot cyclize in the crystal bulk

But thermolysis at 140-150°C gives the blue-green color of the product without crystal change

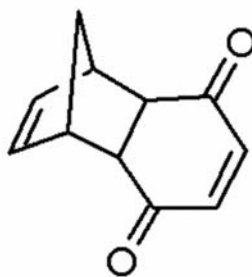
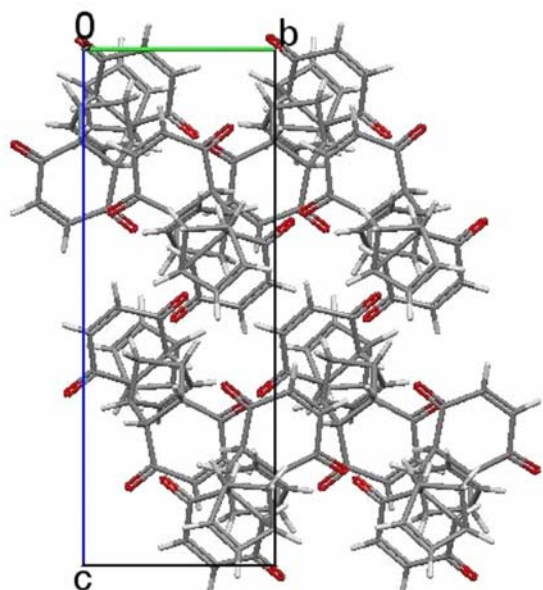
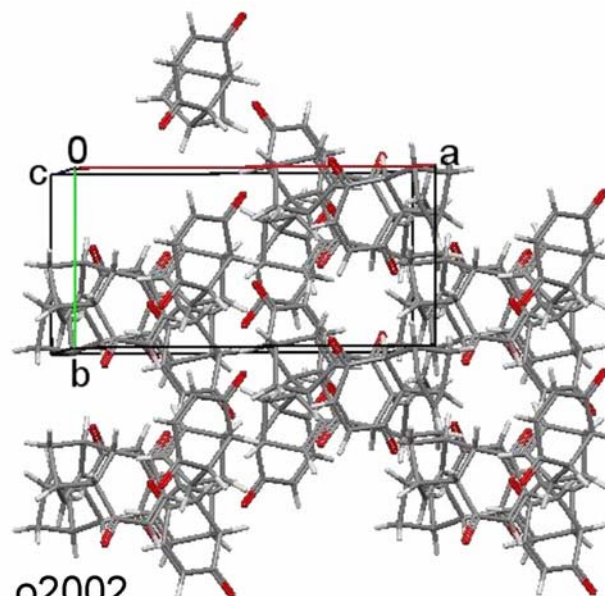
AFM analysis: There is only cyclization at the surface without disintegration

Significant conversions are obtained with milled material or in KBr pellet

How do we analyze and proceed? A challenging system



Acta Cryst. E 2008, 64, o2002

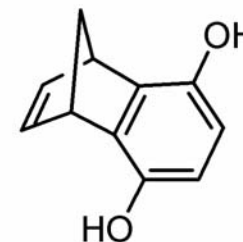


internally photocycloadds
cleavage planes under (010)
channels along [001]
channels along [100]

$P2_1/c$; $D = 1.288 \text{ g/cm}^3$; m.p. 77°C
hydroquinone-tautomer: m.p. 144°C

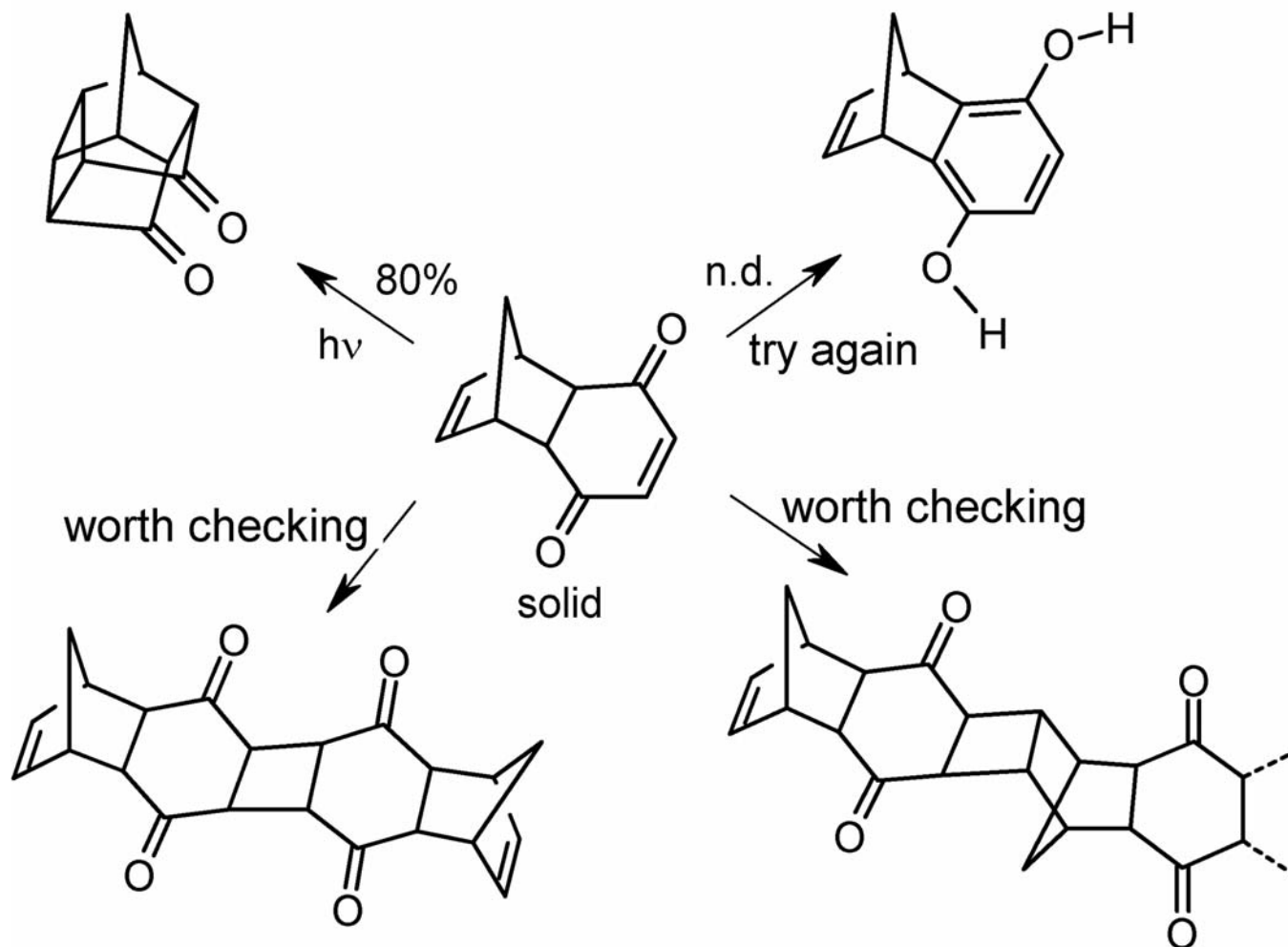
B3LYP (6-31G*): ΔE 2.8 kcal/mol

notwithstanding lattice energies



Which one of multiple reaction possibilities?

J.C.S. 1964, 3062



These were a few examples of intramolecular and dimerization reactions. I could of course tell a lot more systems, but there are further important advances

Intermediate summary (much more than money saving)

All failures and „unexpected“ results of topochemistry are artificial: **everything is expected** from molecular migrations within crystals .

Use easy **convincing arguments** at the molecular level, on undebatable physical basis, strictly with crystal packing.

Avoid extremely **complicated hypotheses** and simulations and waste of time (\$).

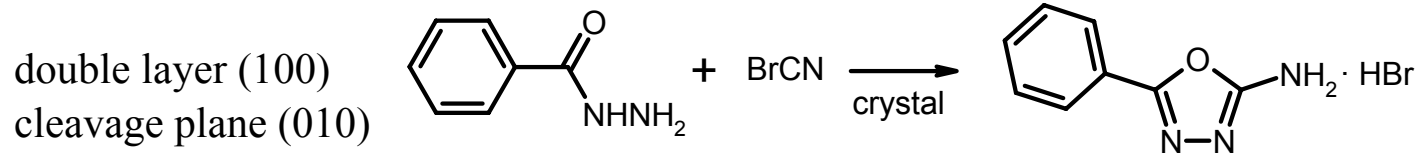
Available crystal packing allows valid **predictions** including unique cases.

I apply this now for **gas-solid and solid-solid reactions** that ensue, but are **only thinkable on the basis of anisotropic molecular migrations**.

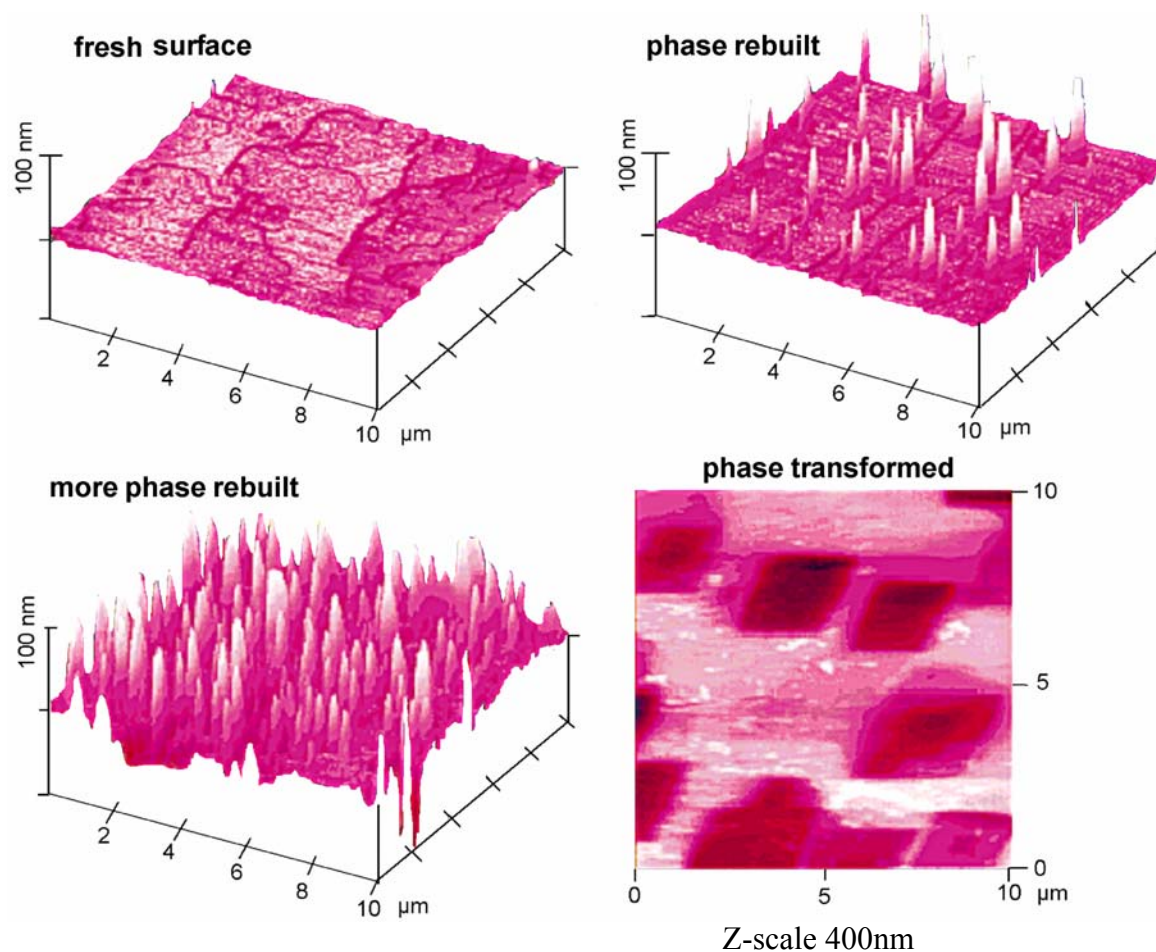
These profit also from self assembled crystal packing allowing to perform them at mostly 100°C lower reaction temperature than corresponding liquid phase reactions

Gas-solid reactions: a phase-rebuilding mechanism example

Channels or cleavage planes are required for the molecular migrations!

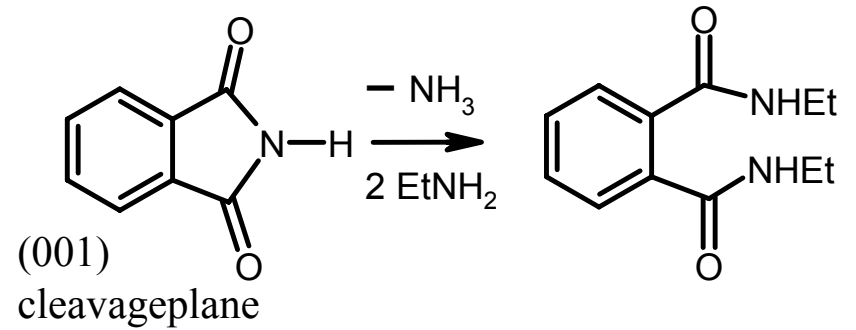
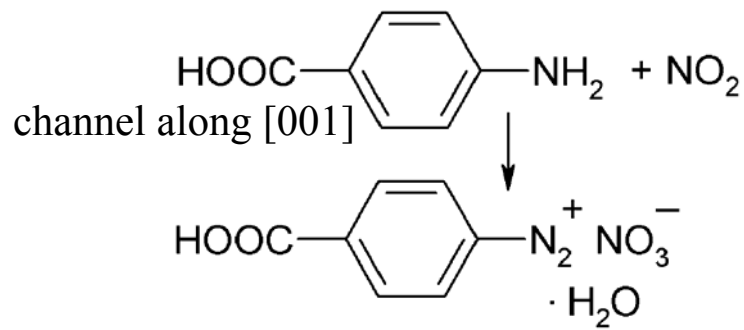


AFM

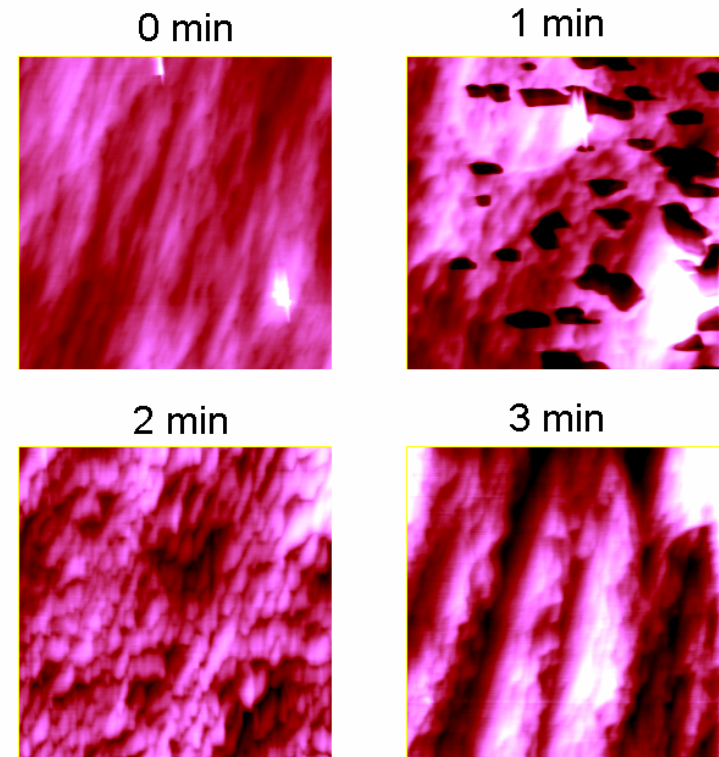
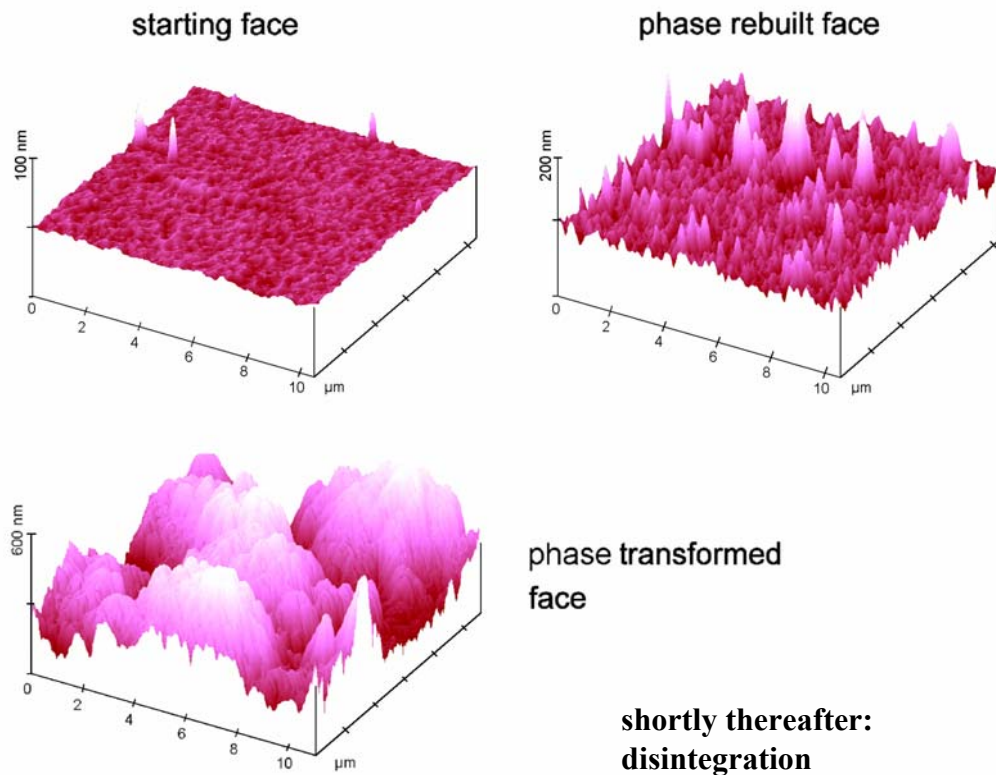


shortly thereafter
disintegration
follows as the
third step with
formation of
fresh surface

Gas-solid reactions: phase-rebuilding mechanism II



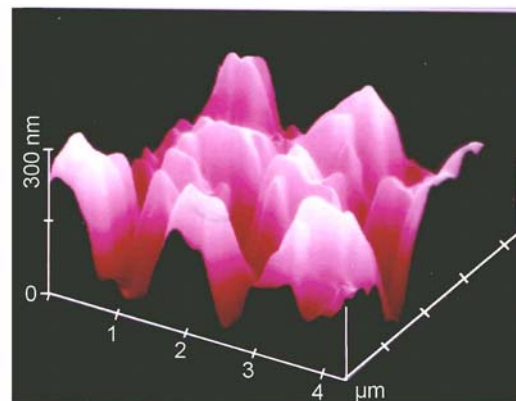
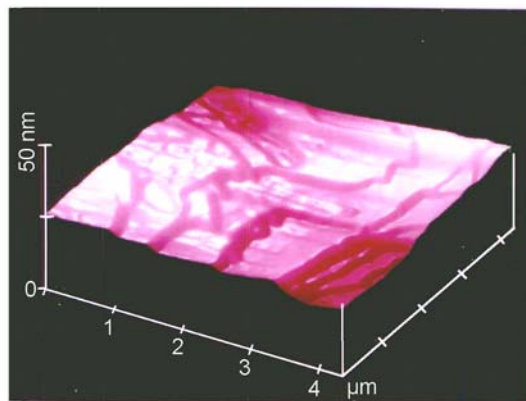
(syringe directly at the AFM stage)



27
interaction time with 3 ml gas; Z-scale 50 nm

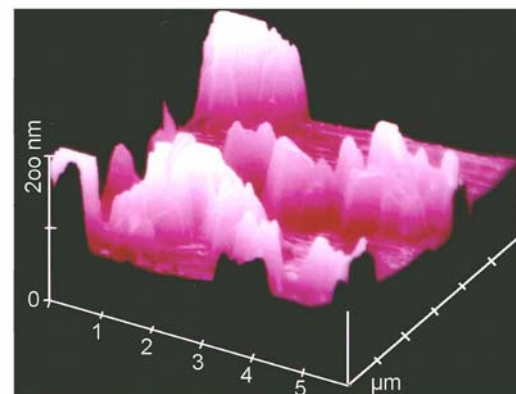
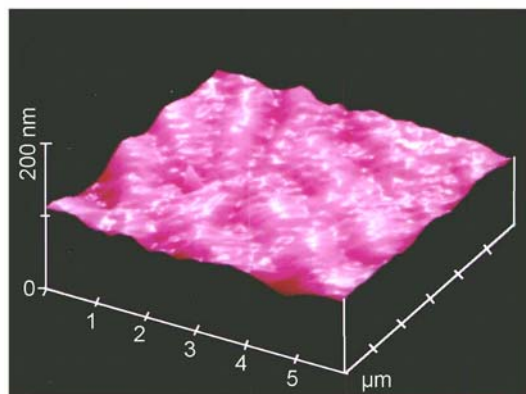
Face selectivity with cinnamic acids' Br₂-addition

α -cinn. t=0
(010)



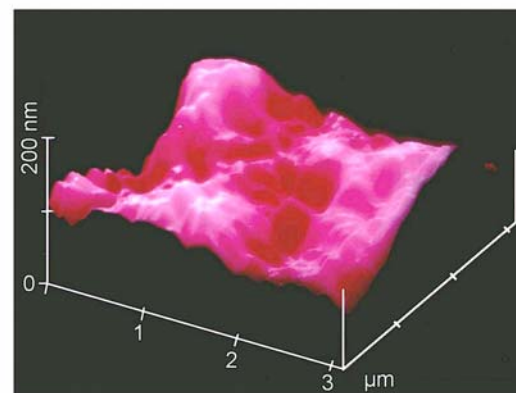
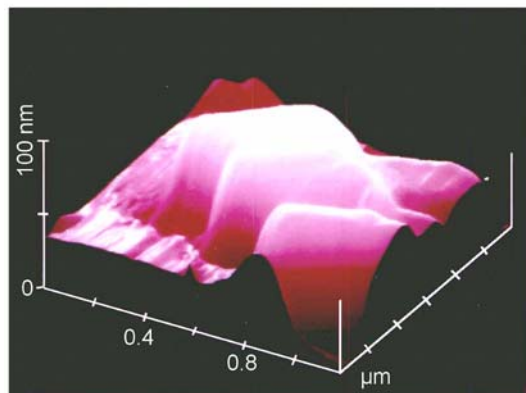
α -cinn. (010)
+ Br₂ gas

β -cinn. t=0
(100)



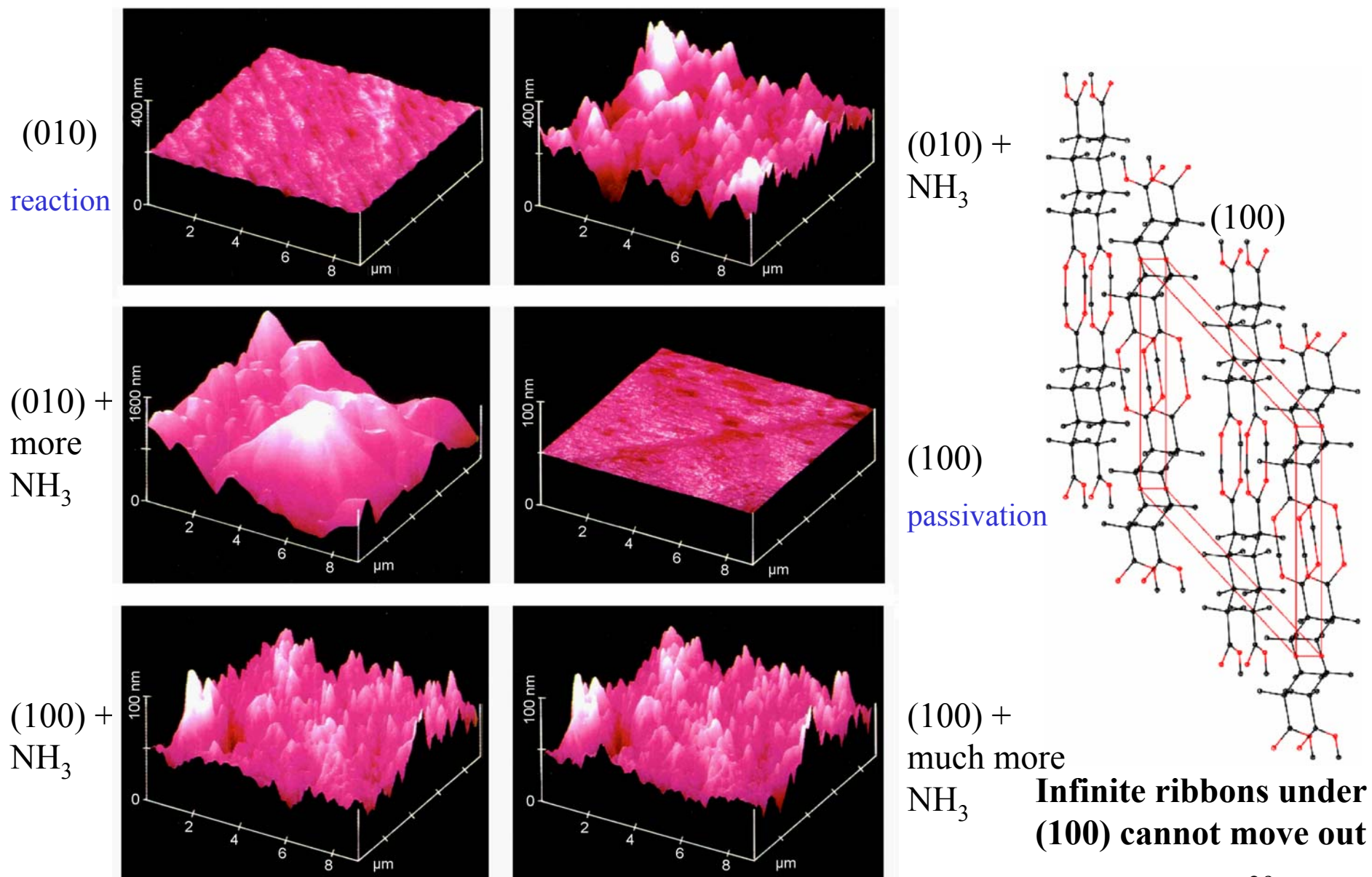
β -cinn. (100)
+ Br₂ gas

β -cinn. (100)
+ more Br₂ gas



β -cinn. (010)
+ Br₂ gas

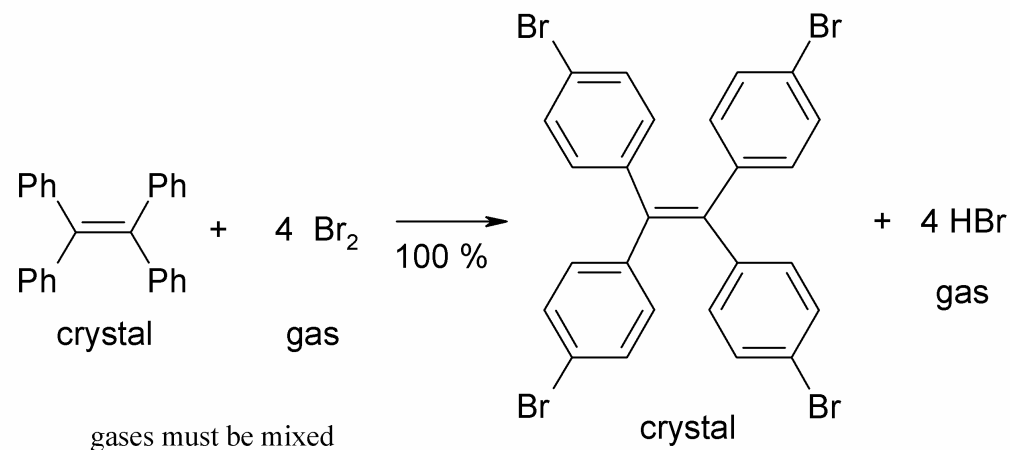
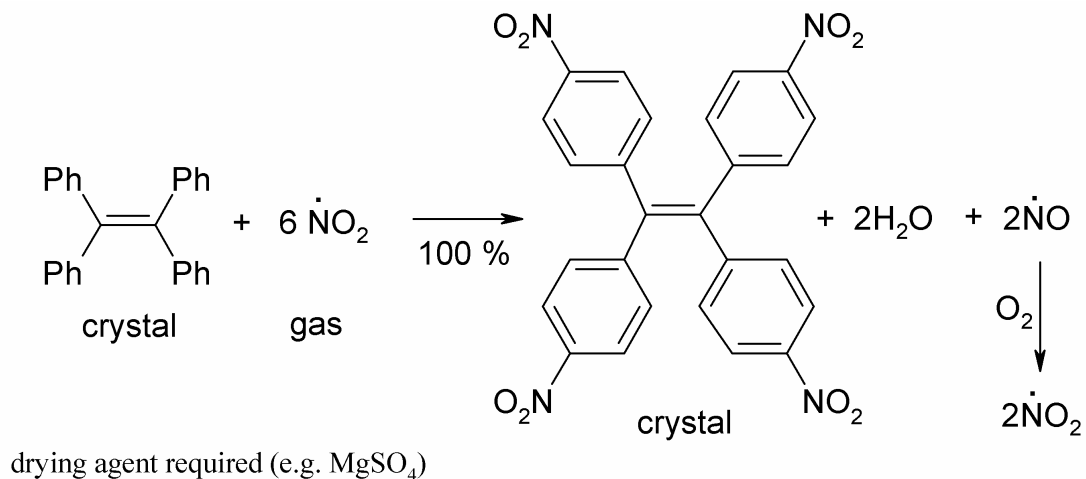
Face selectivity and surface passivation; adipic acid



Curtin and Paul remained puzzled in JACS (3) and Science (1)

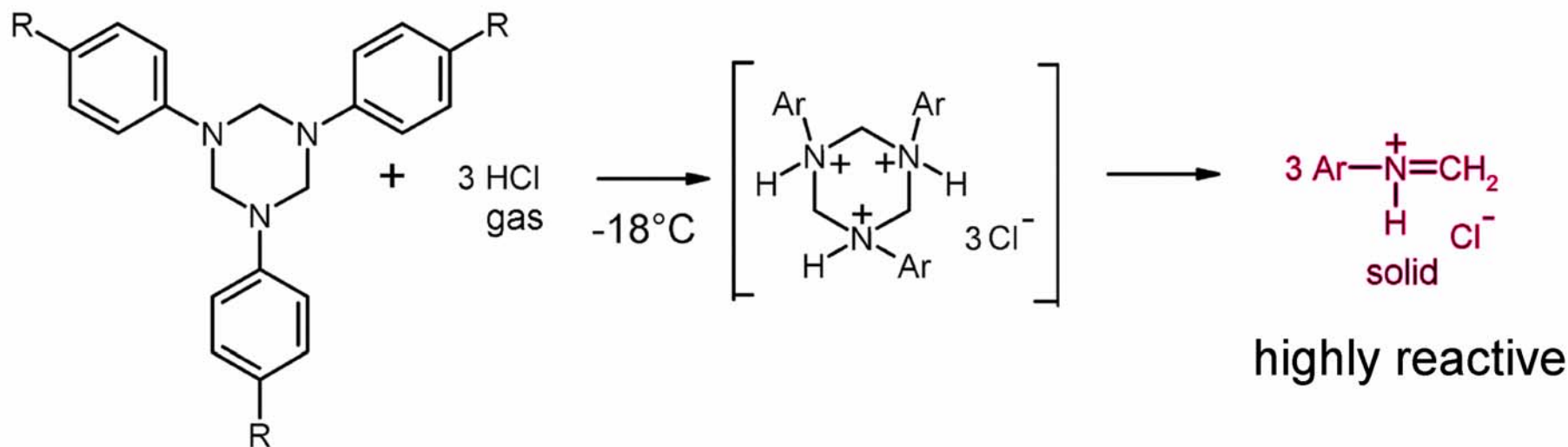
Quantitative specific gas-solid tetrasubstitutions

layered with channels

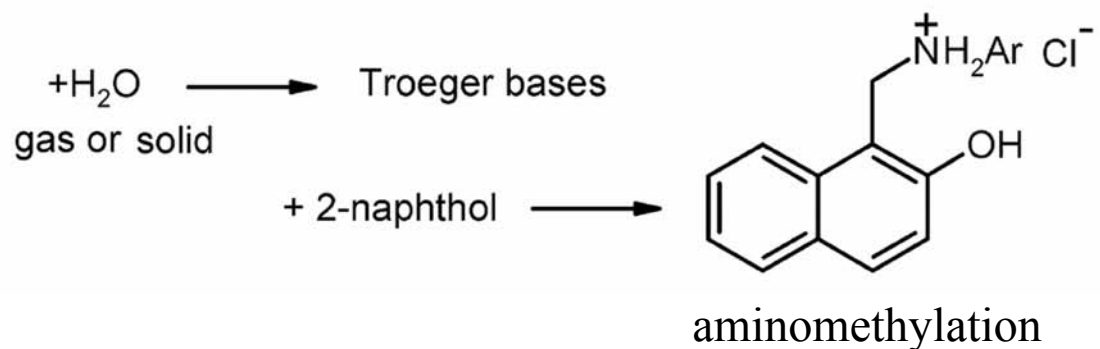


Clearly, the higher level of sustainability

Unprecedented aminomethylene hydrochlorides

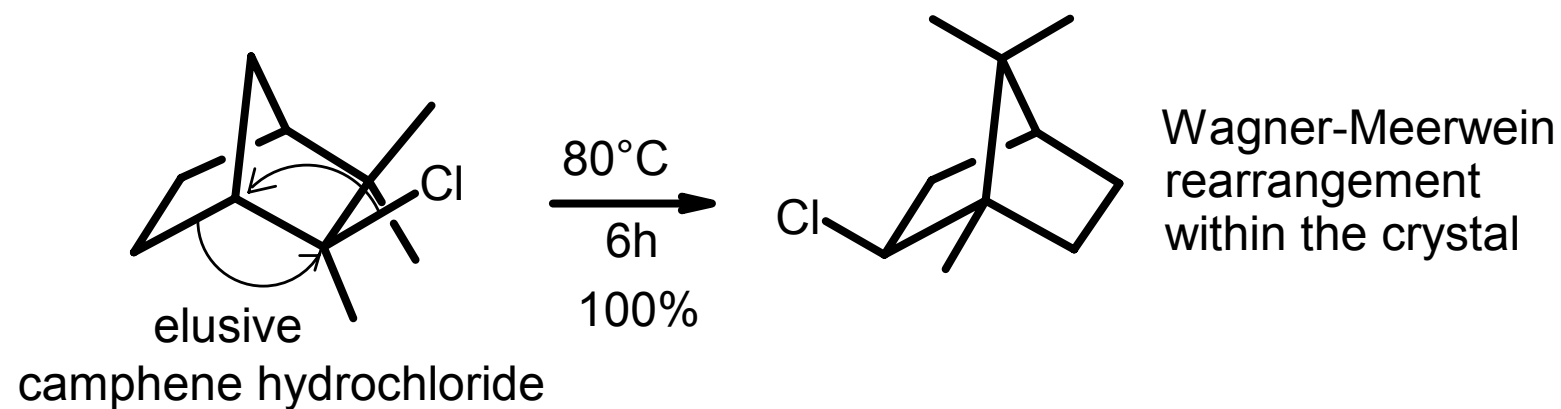
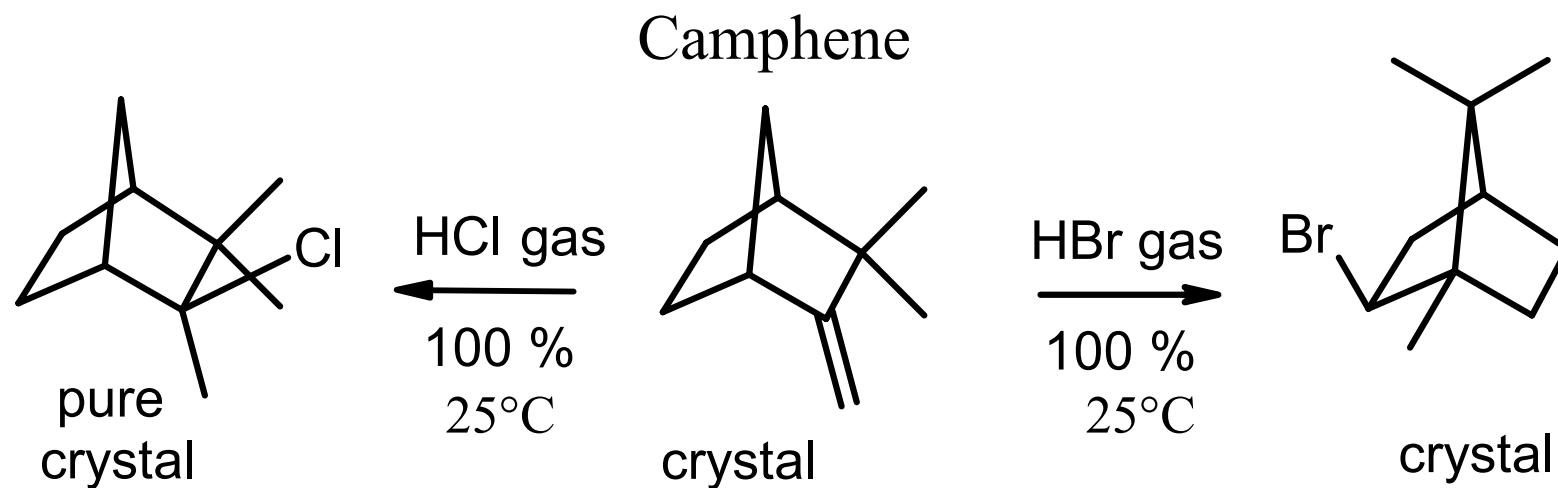


(R=H; Me; OMe)
 All have multiple channels at least in 3 directions and two also cleavage planes



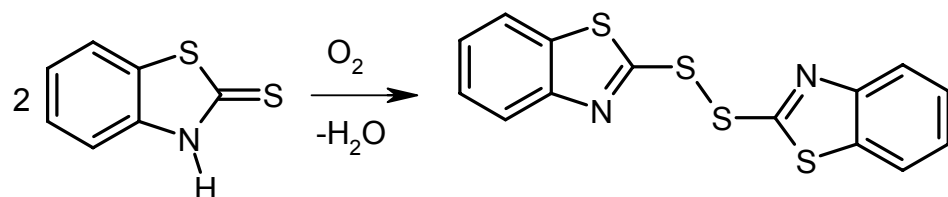
These reagents are only stable in the solid state (IR: 1733 and 1714 cm⁻¹) and must be reacted in the solid state

Gas-solid synthesis of elusive and rearranged products



Single double-layer's impeding gives island formation

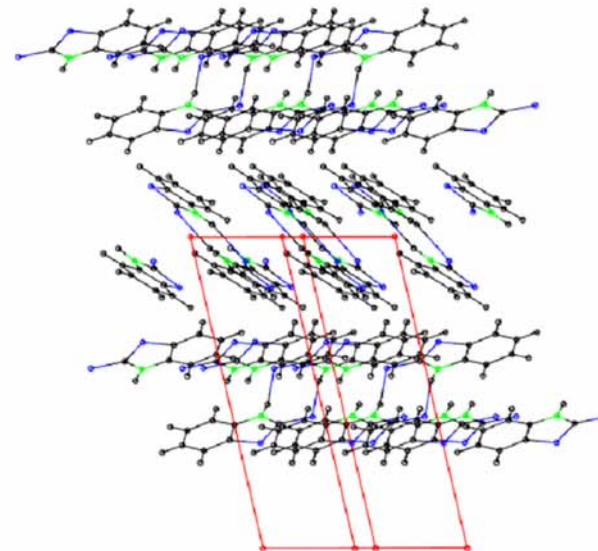
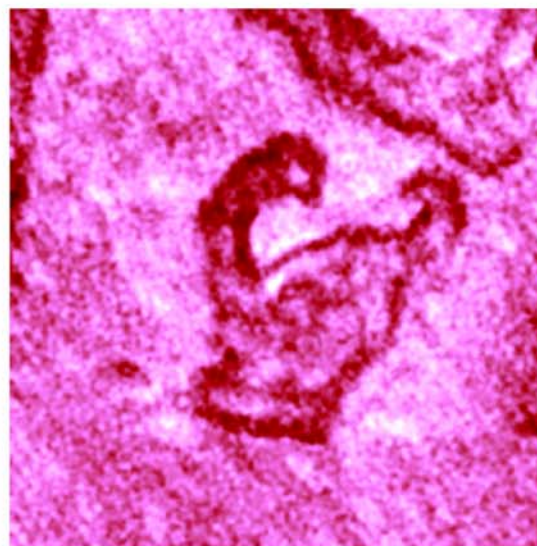
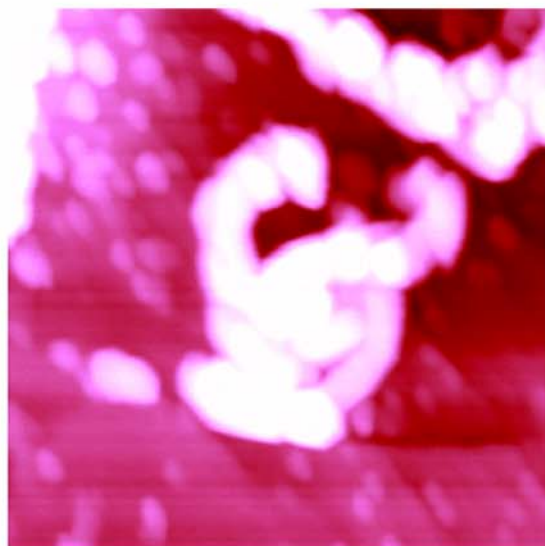
protected autoxidization of thin 2-mercaptobenzothiazole scales on (001)



AFM

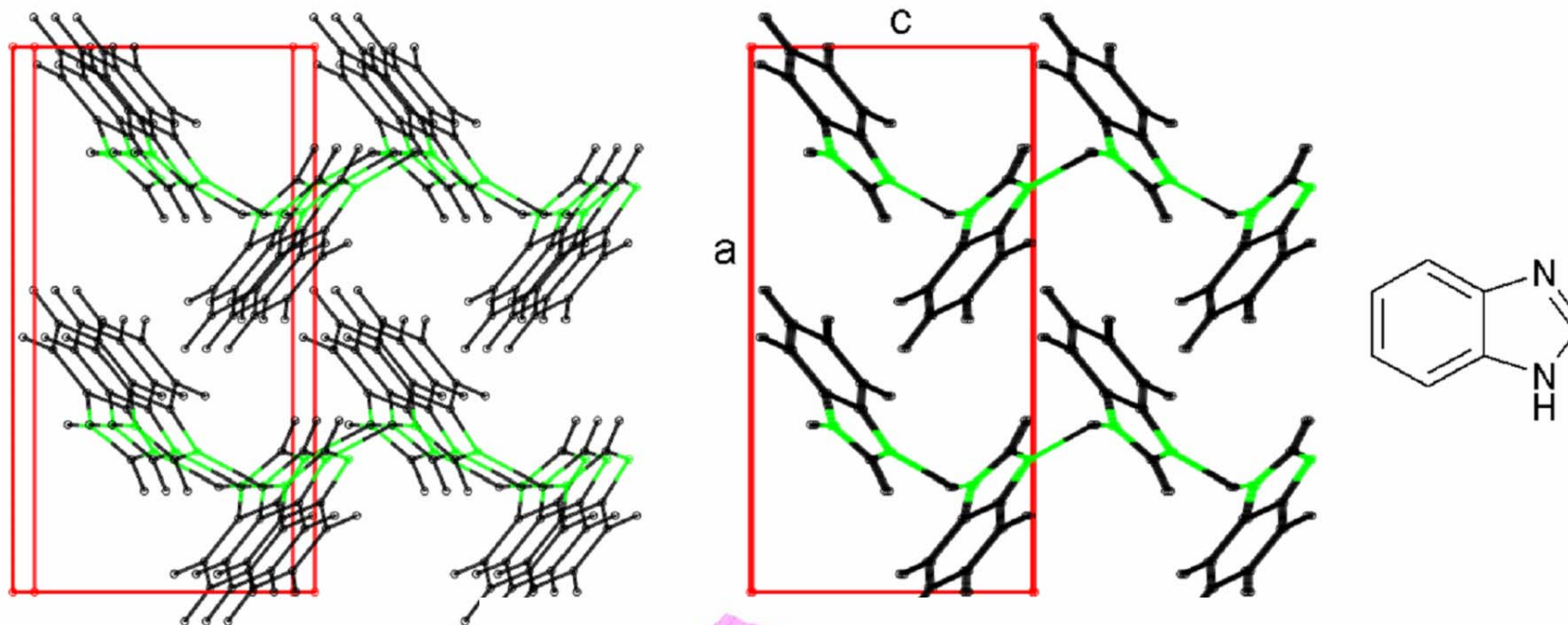
SNOM

(001) on top



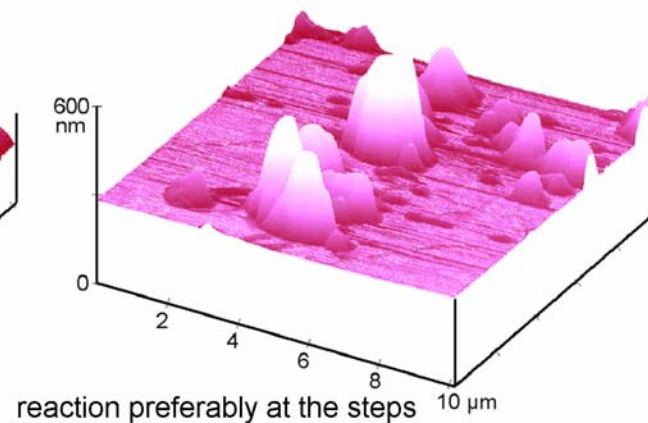
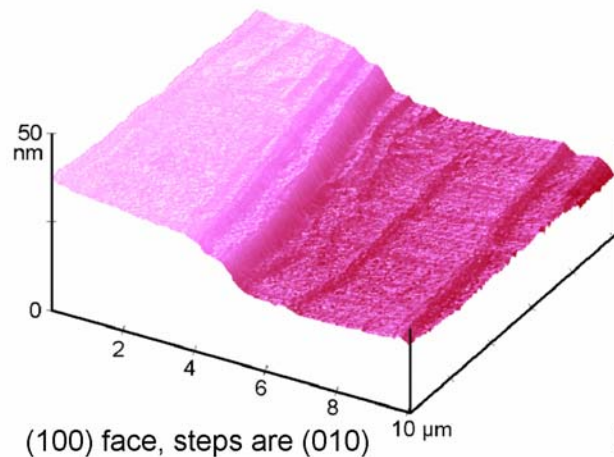
The chemical contrast in the SNOM is precisely at the sites of the islands that have grown on the flat unattacked surface: chemical reaction only around initiating sites: single double-layer protects

Beautiful channels along [010] of benzimidazole



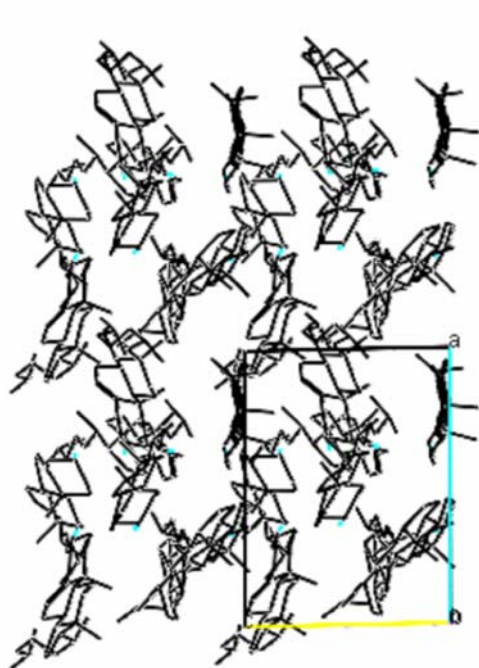
Gas-solid reaction with
ClCN on the AFM,
similarly with HCl

Solid-solid reaction with
 Ph_3CCl and $(\text{HCHO})_n$

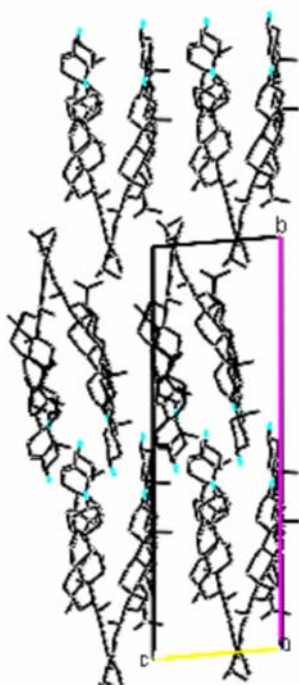


Preparative: complete; further applications are clearly predicted

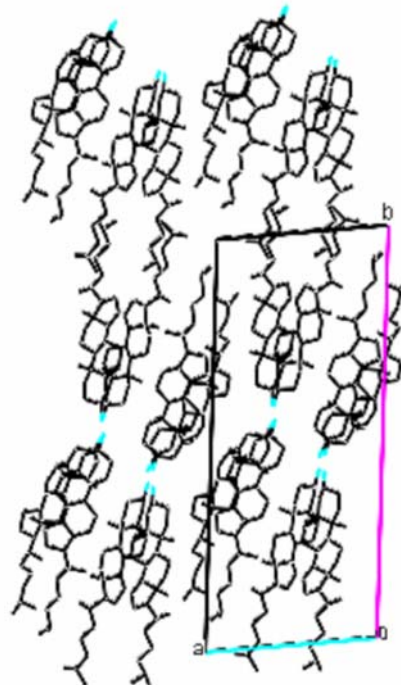
Multiple irregular channels of cholesterol for solid-state reactivity



[010]

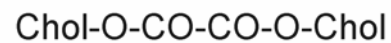
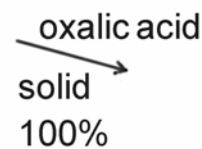
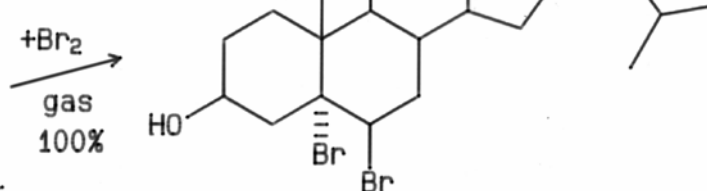
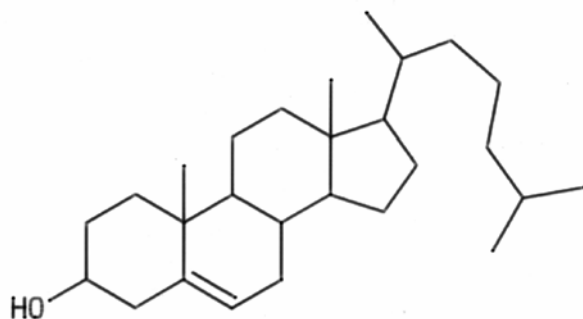


[100]



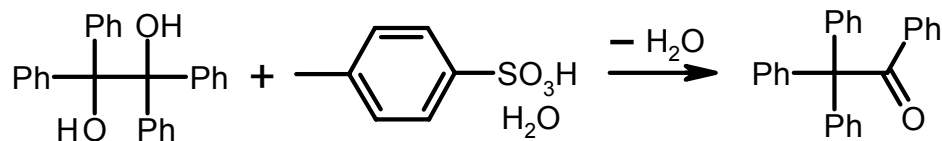
[001]

industrial applications:



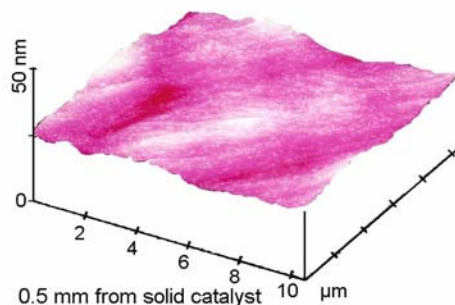
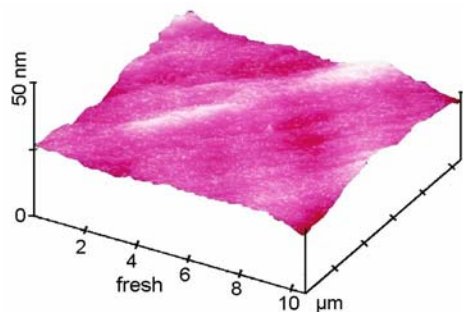
numerous further steroid syntheses

Remarkable face-selectivity, solid-solid pinacol rearrangement

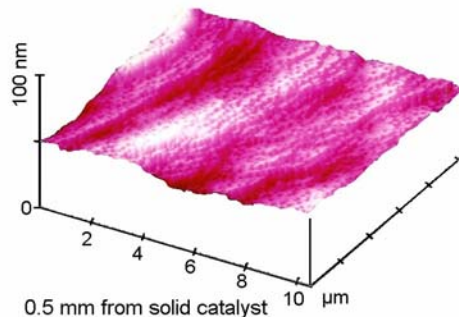
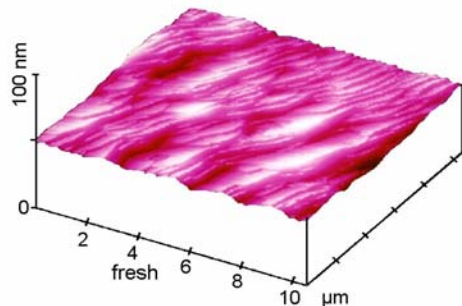


apolar channels along [010];
infinite OH...O ribbons exit
availably on (010)

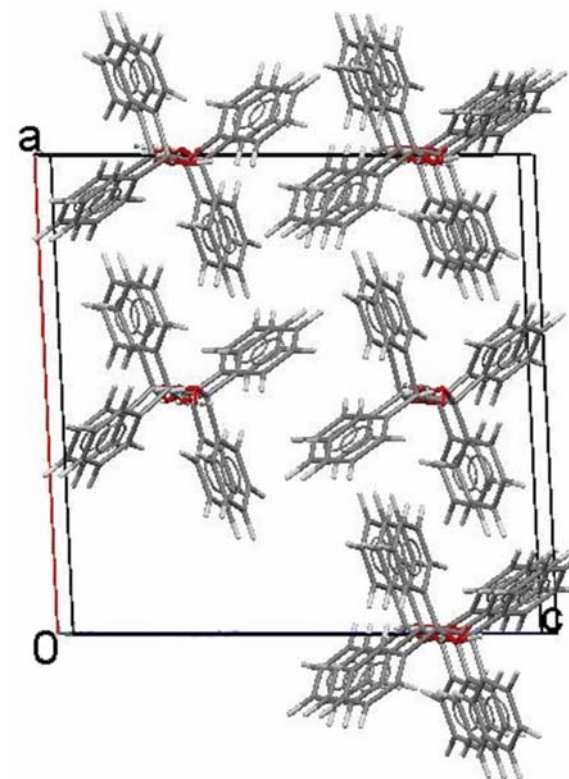
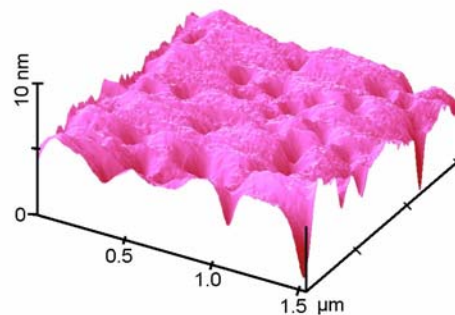
(001)
unreactive



(010)
reactive

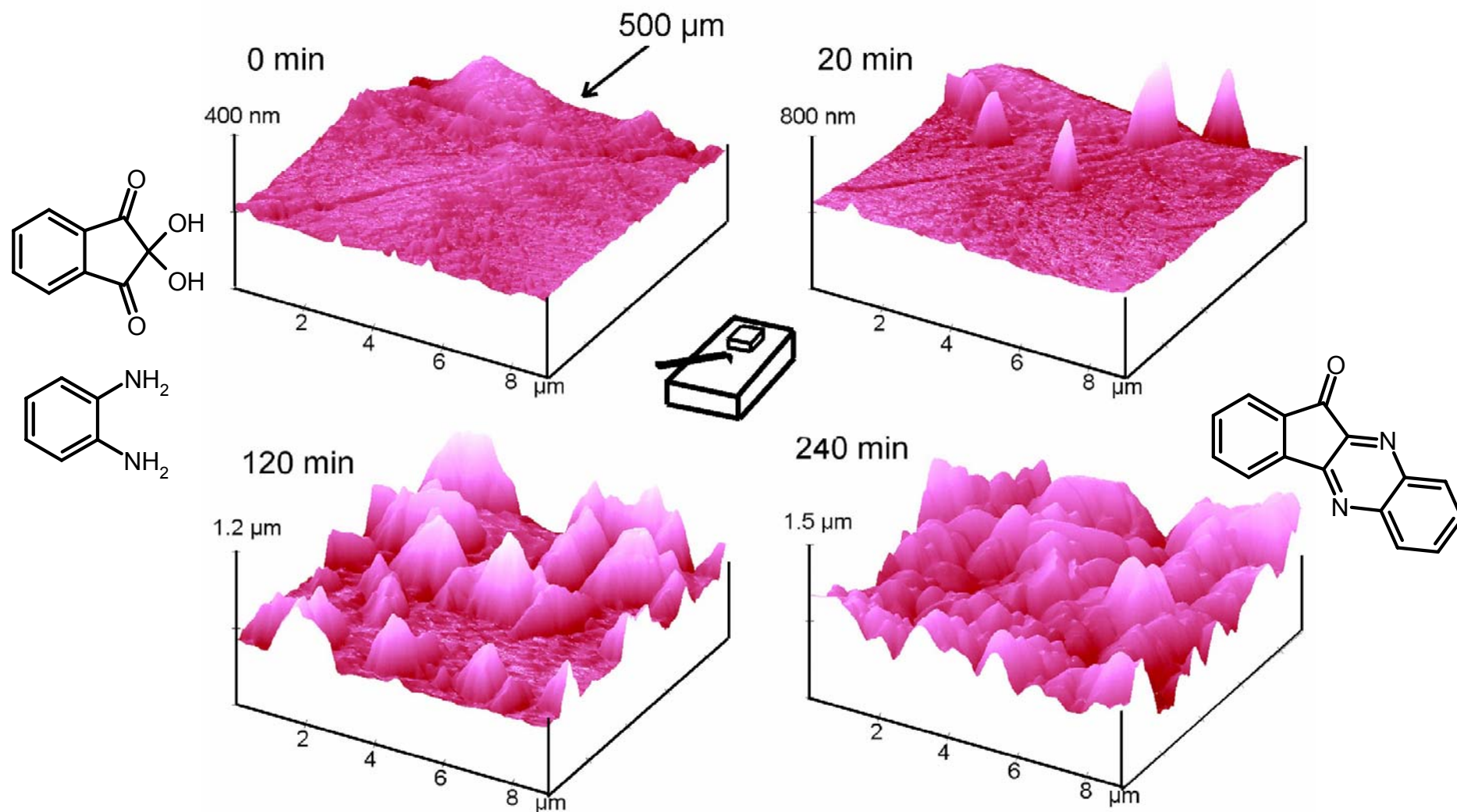


12 h, 50°C



access from top (100) or
side (001) is hindered by
the phenyls

Same mechanism with solid-solid reactions (cf gas-solid and intracrystalline)

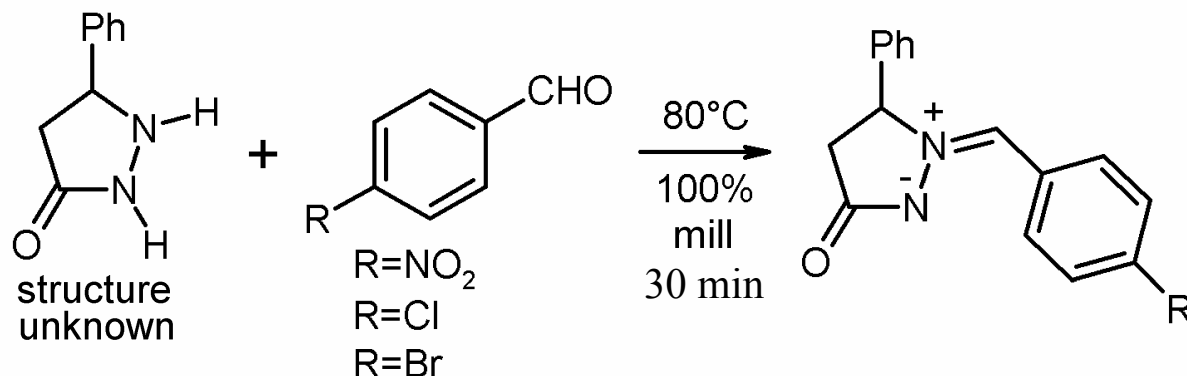


not mechanochemistry

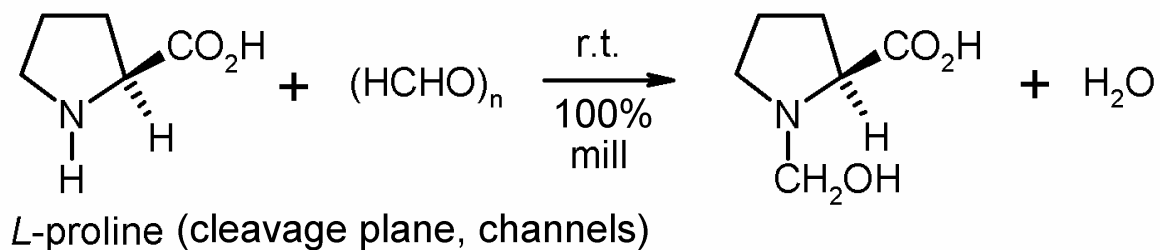
Chemically driven; everything works without mechanical interaction

Some exciting solid-solid syntheses

Azomethinimines



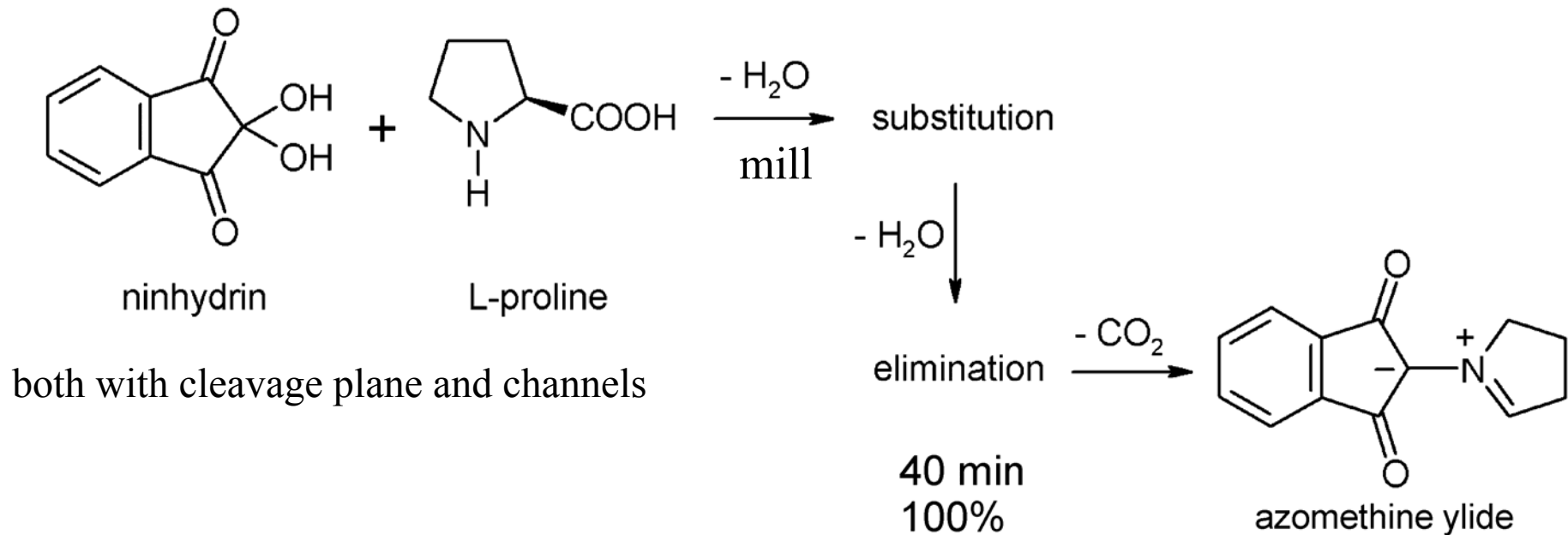
Semi-N/O-acetal (200g batches)



similarly imidazole at 0°C
similarly benzimidazole at room temperature

The higher level of sustainability

Stoichiometric solid-state cascade reaction with quantitative 200 g batches by reactive milling

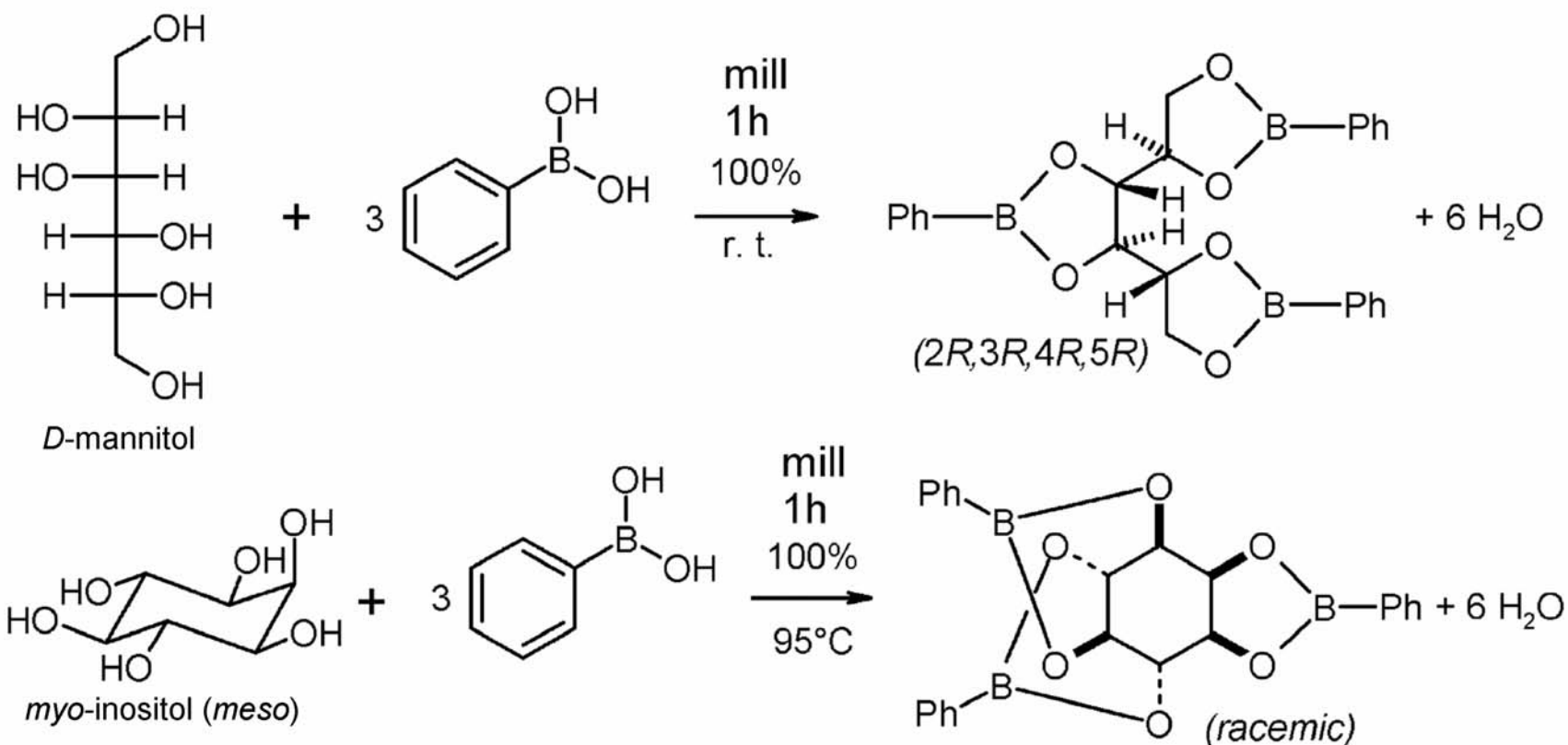


not mechanochemistry but molecular solid-state reactions

the mill comminutes and creates contacts (physics, not chemistry)

The higher level of sustainability

Protection of natural polyols



These are quantitative stoichiometric stereospecific reactions at 6 centers

D-Mannitol(β -polymorph) channels along *b* with alcoholic H-bridges; *myo*-inositol various channels in 4 directions with somewhat interlocked (001) layers, all with alcoholic H-bridges; phenylboronic acid with channel

not mechanochemistry but molecular solid-state reactions

Molecular and salt solid-solid reactions supported by milling:
comminution and contact formation (physical processes)

that is totally different from

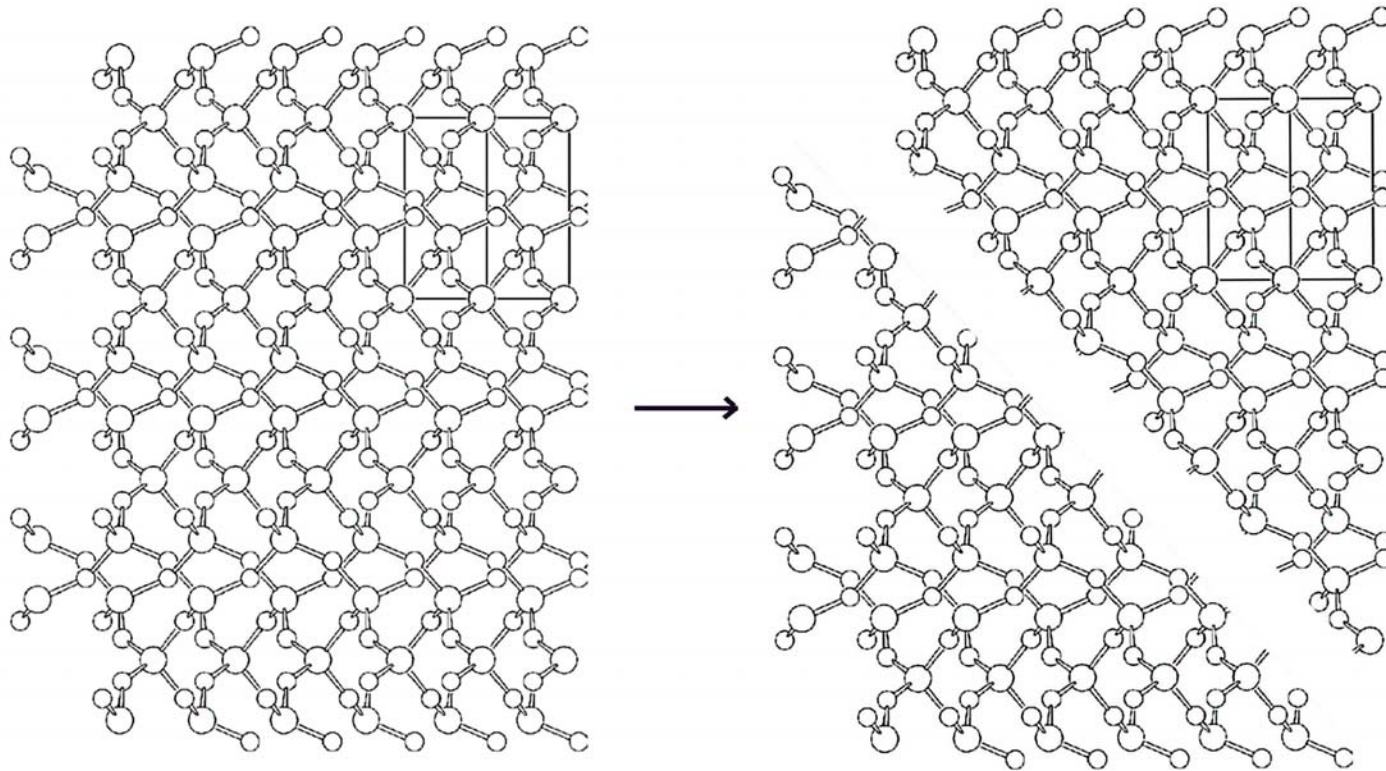
Mechanochemistry: mechanical bond-breaking by milling:
mechanical energy is used to cleave molecular bonds (chemistry)

Please distinguish „mechanical“ from „mechanochemical“ also verbatim

Topics of mechanochemical bond-breaking are with
explosives (peroxides, disulfides, diazonium salts, nitrites, etc),
infinite covalent networks (oxides, carbides, nitrides, borides,
some elements, etc), **polymers**, sheared **molecules under**
Bridgman's anvil

Countless technical applications of genuine mechanochemistry! ⁴¹

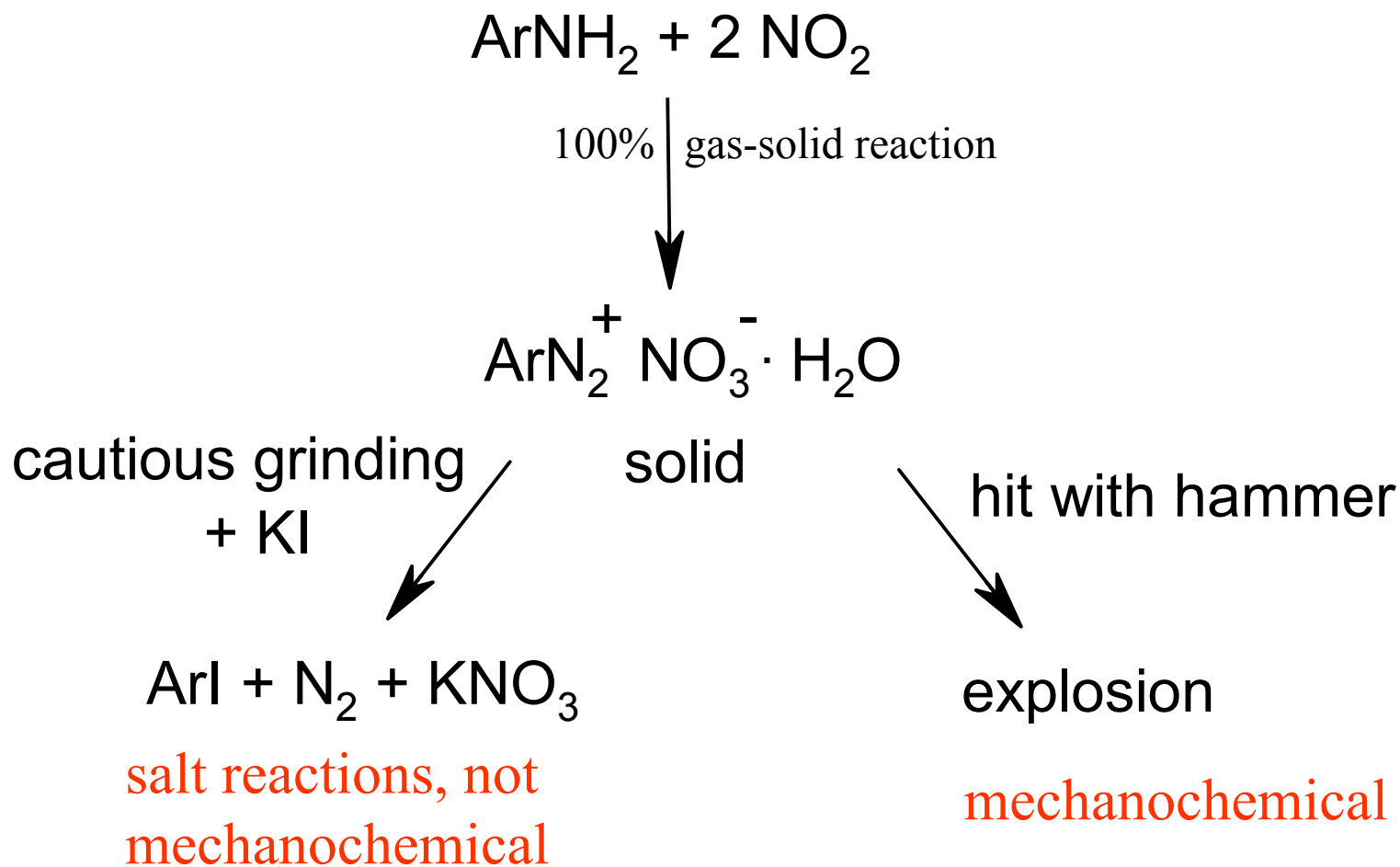
Sparkling hitting or milling of flint



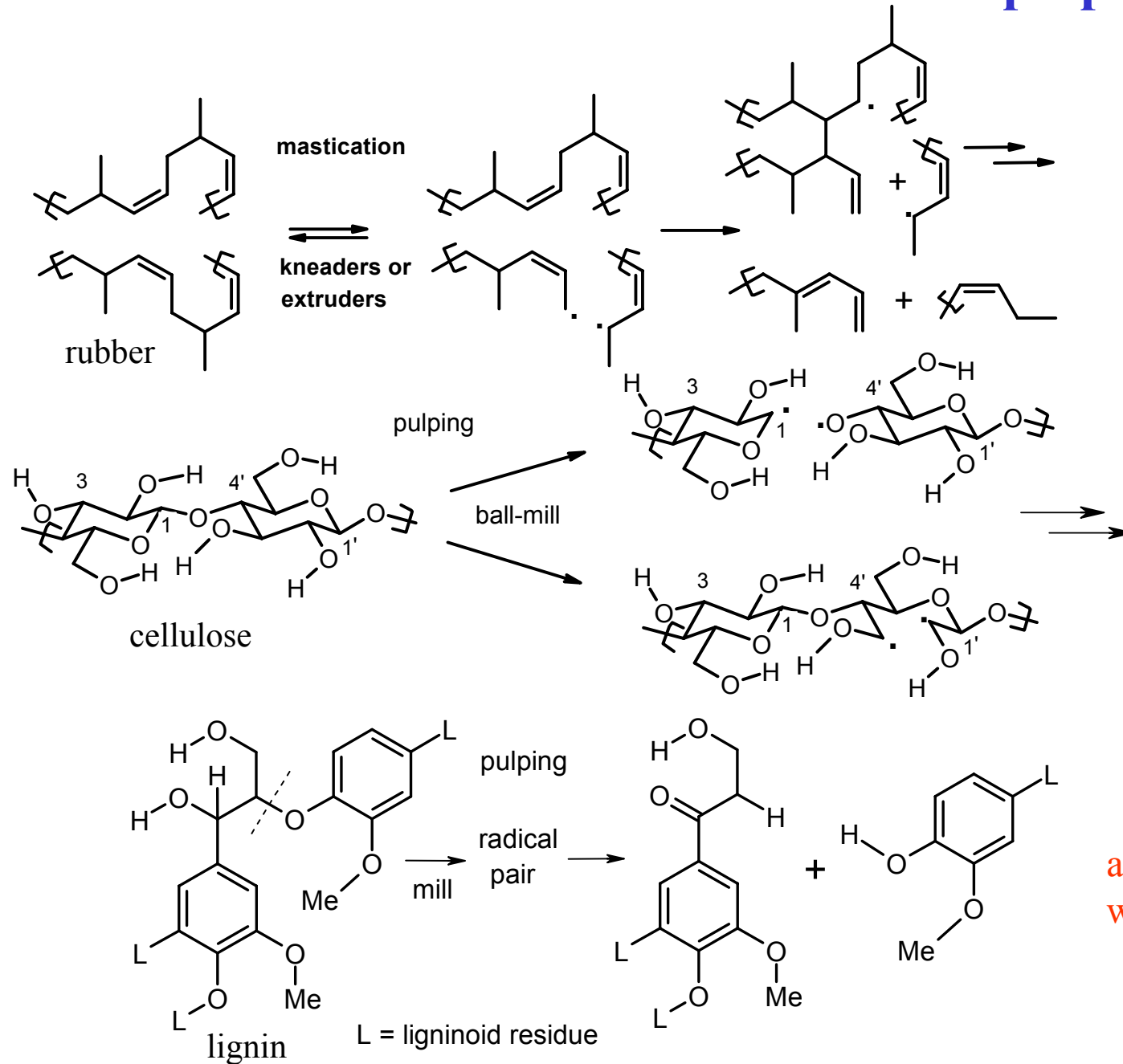
Crystal packing of α -quartz projected on (1-100) before and after cracking along the diagonal plane, indicating the radical centers on O and Si on both fracture-surfaces (Si: larger circles, O: smaller circles)

Applications of the dense surface radicals for lighters, producing silicates, initiators of radical chains, remedy of any of the (most) ⁴² poisonous organic environmental threats by complete mineralization

Distinction of molecular or salt's solid-state reactions from mechanochemical reactions

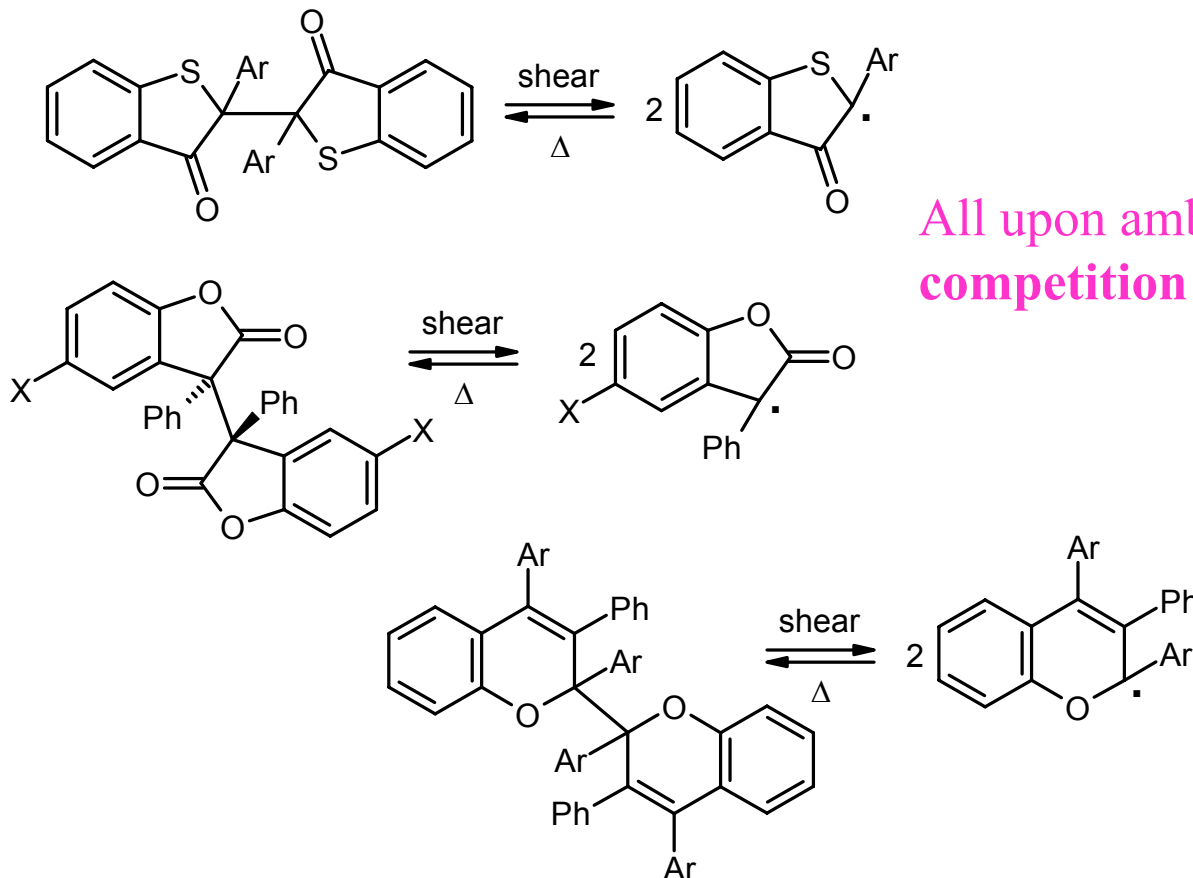


Mechanochemical mastication of rubber and pulping of wood



Mechanochemical C-C bond breaking

Weak bond molecules



All upon ambient grinding (1 bar):
competition with comminution

Strong bond molecules (such as benzene, pyridine and derivatives, phenanthrene, terphenyls, etc at -70 to -20°C) cannot escape the **shearing** under 10^5 bar (10 GPa under Bridgman's anvil): then their rings break mechanochemically

Major advancement from new mechanistic paradigm

GAS / SOLID AND SOLID / SOLID REACTIONS

the sustainable result of nanoscale mechanistic investigations

Advantages: no solvent, no liquid (decreases energy of activation)
 rapid and quantitative, usually avoiding catalysts
 new selectivities, new products
 no workup
 no wastes

**more than 1000 100% yield reactions
in 25 reaction types,
several on the kg scale**

modern techniques :

AFM (atomic force microscopy)

SNOM (scanning near – field optical microscopy)

<http://kaupp.chemie.uni-oldenburg.de>



Thank you for stepping up with science in a bright future