

分子結晶中の反応

Chemical reactions involving solid materials

- Solid phase reactions
polypeptide synthesis
- Solvent free reactions
chemical reactions between two (or more) solids
in the absence of solvent
- ◆ **Solid-state reactions**
chemical reactions of molecules in the solid state
unimolecular or bimolecular

格子中の分子配列を利用した反応

Reactions under control of crystal lattice

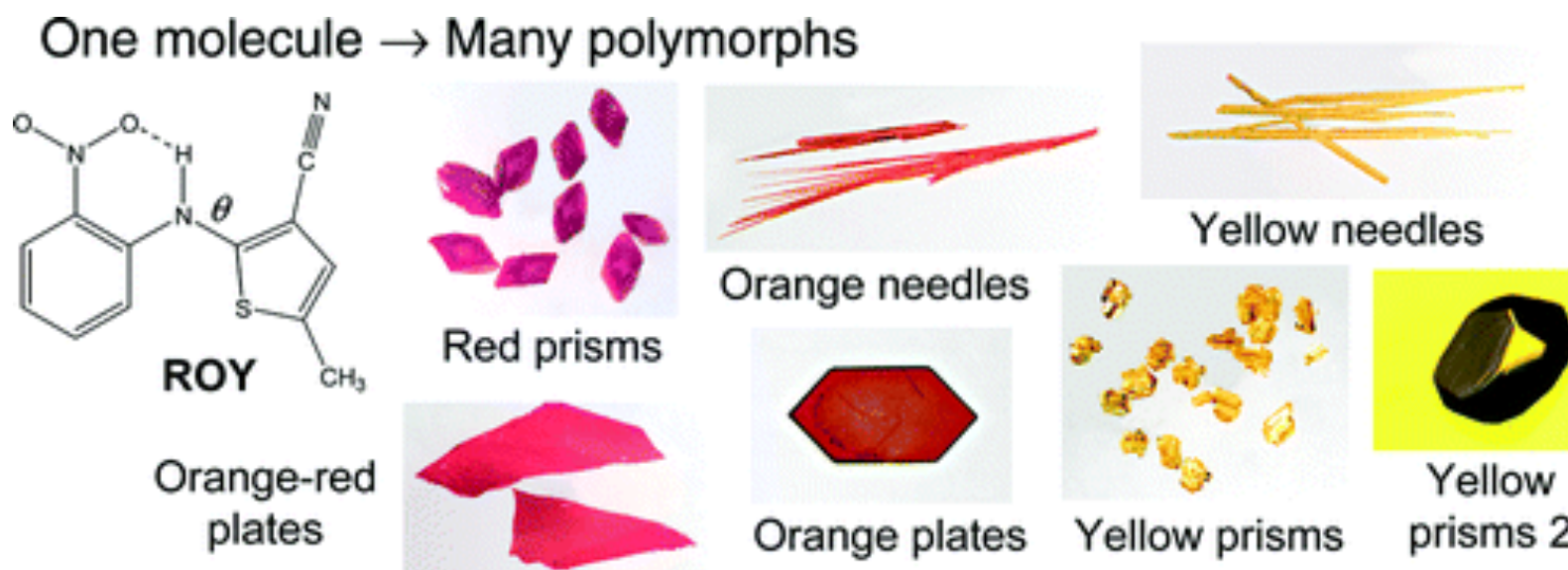
Topochemistry

G. M. J. Schmidt (1964)

- The major factor responsible for the course of the chemical reaction is the molecular packing arrangement in the crystal.
- The intrinsic reactivity of the molecule is less important than the nature of the packing.
- Topochemical principle: *reaction in the solid state occurs with a minimum of atomic or molecular movement.*

Polymorphism

- **Polymorphism** is the phenomenon where the same chemical compound exists in more than one crystal structure.



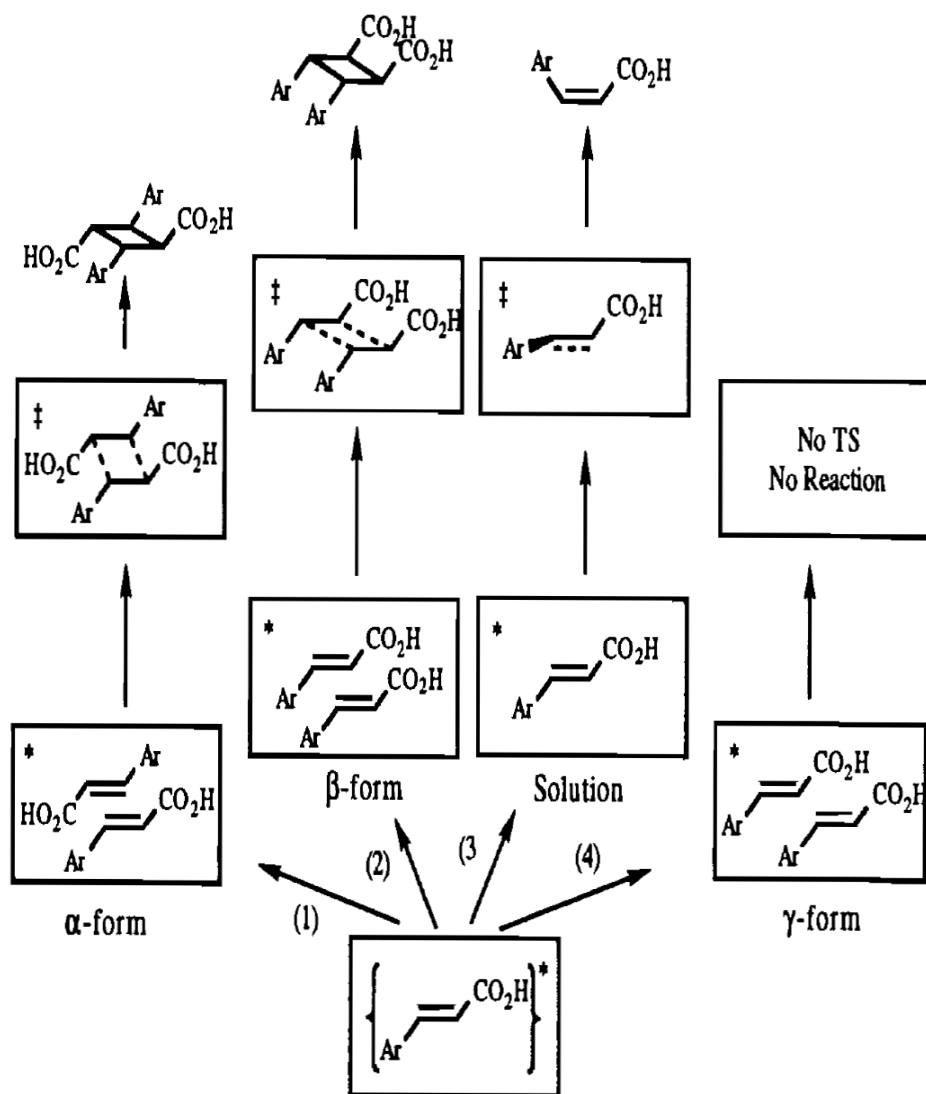
Cf. **Isomorphism** is the phenomenon where different chemical compounds show the same crystal structure.

Photochemistry of *trans*-cinnamic acids

[2 + 2] photodimerization

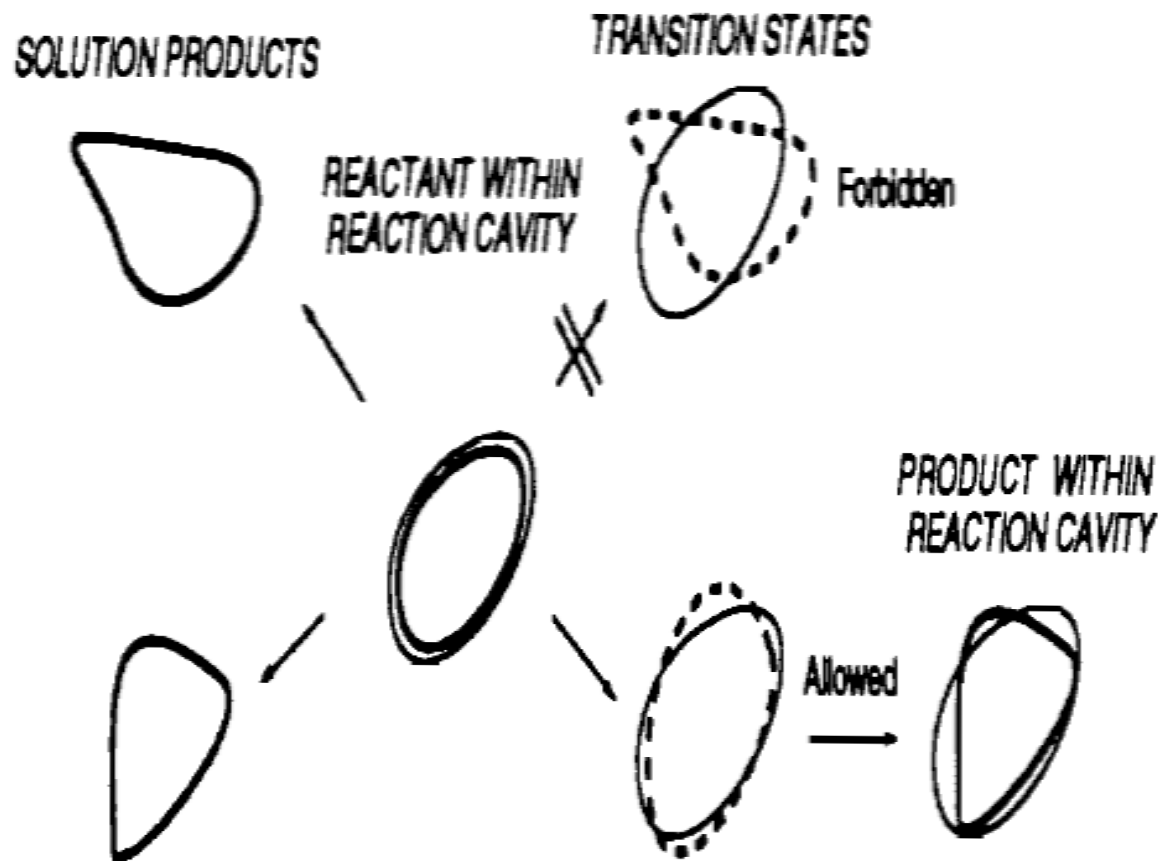
Schmidt's law

The photodimerization may occur only when the two C=C are parallel to each other and with a center-to-center distance shorter than *ca.* 4.1 Å.



Topochemical reaction: reactions that occur under the influence and control of crystalline media.

Reaction cavity



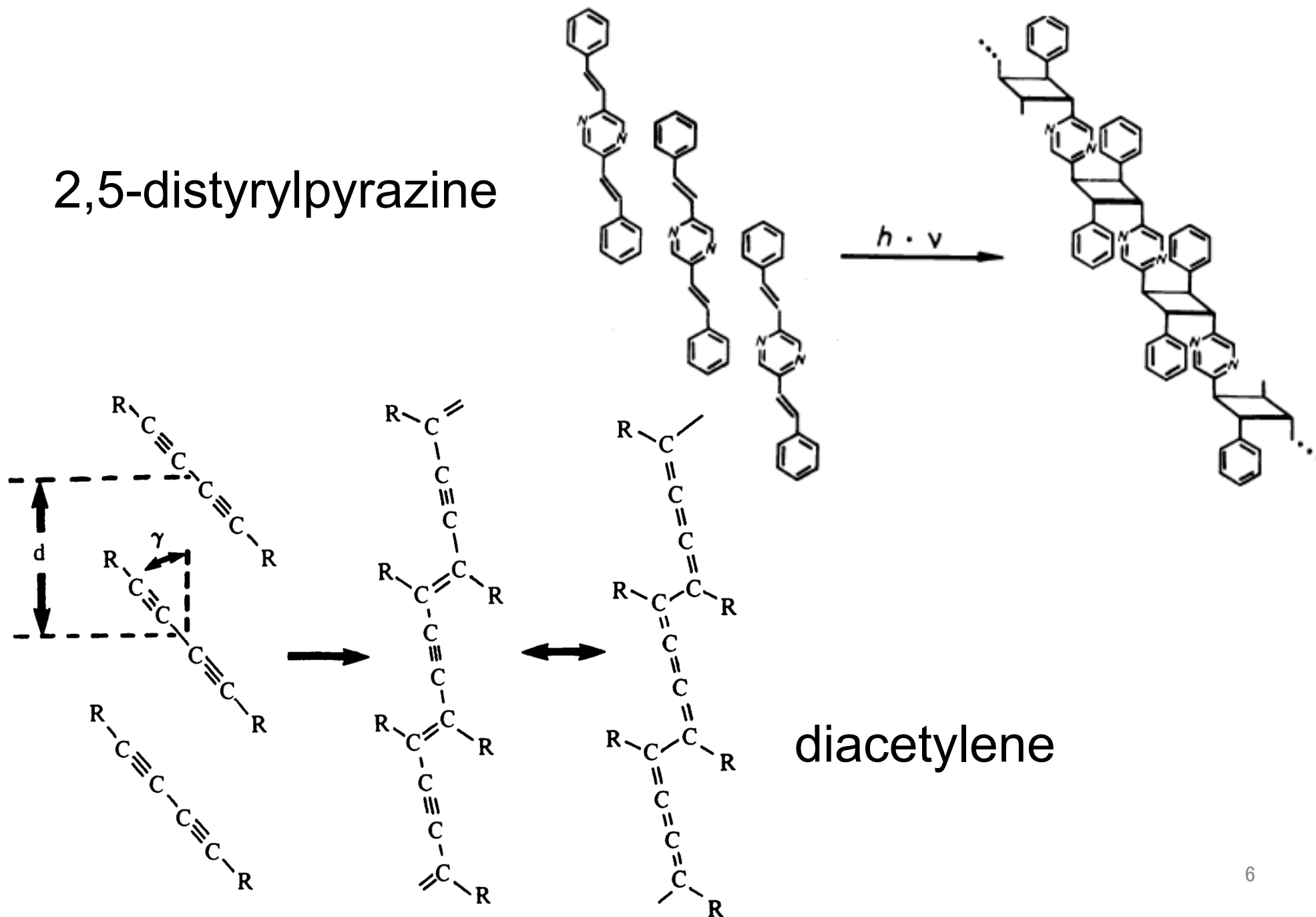
M. D. Cohen (1975)

The reaction cavity is surrounded by the contact surface of the molecules inside it with the surrounding molecules.

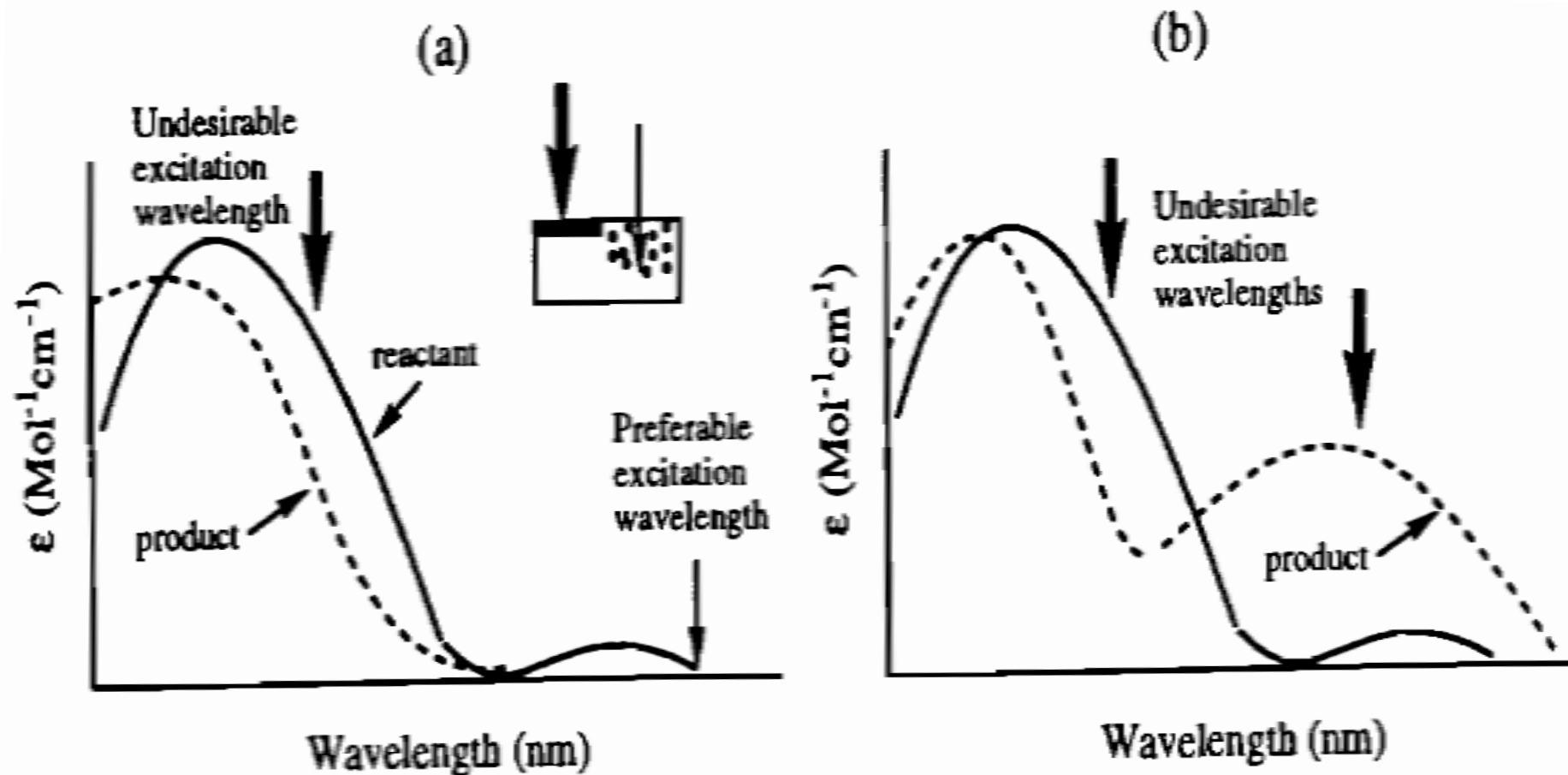
The preferred reaction will be that which proceeds with minimal distortion of the surface of the reaction cavity.

Photopolymerizations in crystals

2,5-distyrylpyrazine

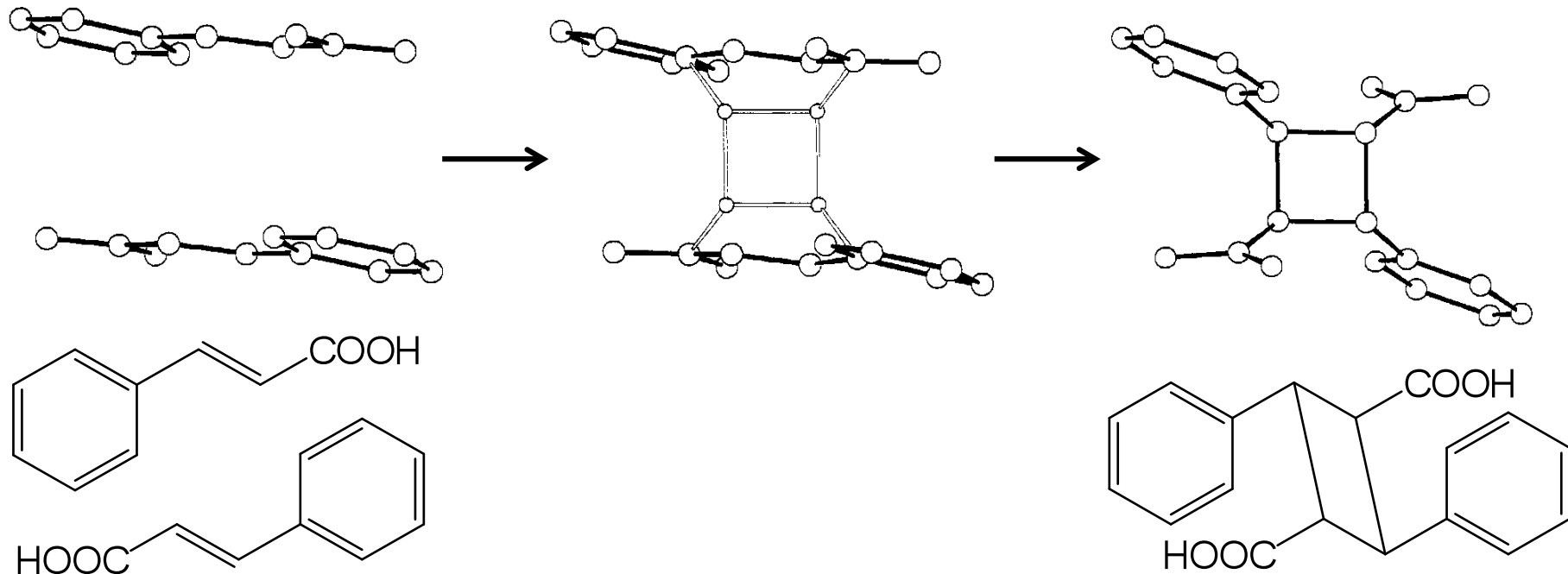


Irradiation wavelength for photoreactions



- Homogeneous distribution of product can be achieved only by irradiation with long wavelength light.

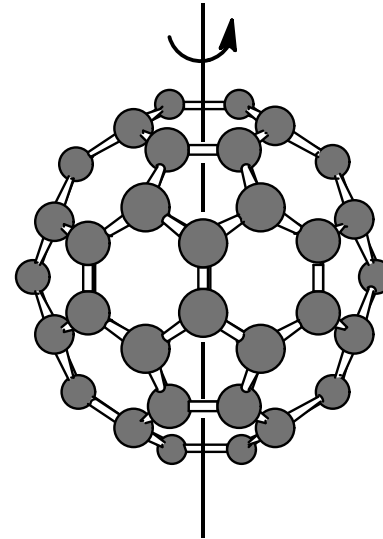
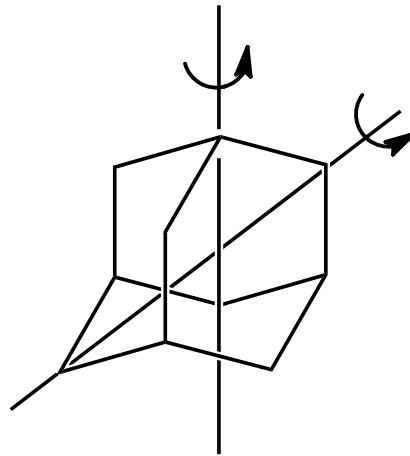
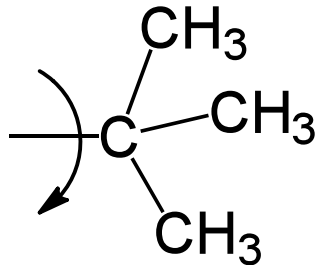
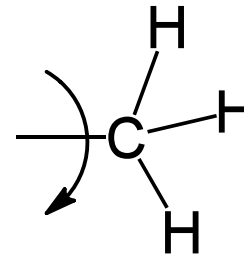
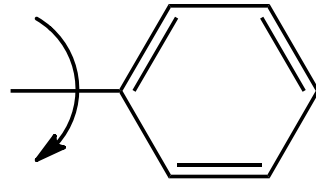
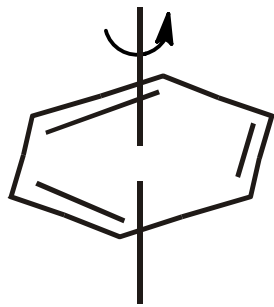
Single crystal to single crystal photodimerization of cinnamic acid



- The irradiation at absorption maximum leads to destruction of single crystals.
- Single crystal to single crystal photoreaction was achieved by irradiation at absorption tail.

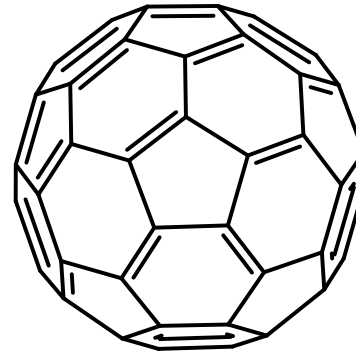
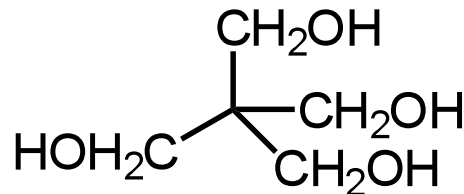
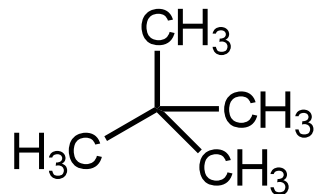
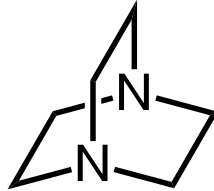
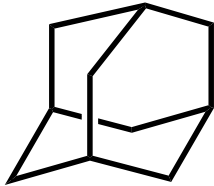
分子結晶中の分子運動

Molecular motions expected in the solid state



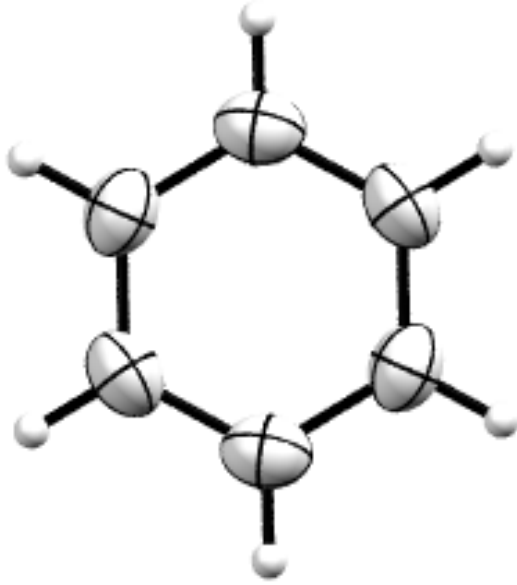
If molecular motions do not change the shapes of the molecules (volume-conserving motions), they can occur even in crystals.

Plastic crystals



- orientationally disordered
- tetrahedral or spherical molecules
- face-centered cubic
- mechanical softness
- small entropy of fusion
- an intermediate state between solid and liquid

Reorientation of planar molecules



benzene at 150 K

X-ray diffraction analysis yielded a seemingly static image of benzene with discrete atoms.

But, the molecule reorients around the 6-fold axis by “jumping” between equivalent sites.

This type of molecular motion is very difficult to detect by crystallography.

Solid-state NMR spectroscopy

^1H broad line NMR: line width, relaxation times

^{13}C CP/MAS NMR: line shape analysis, relaxation times

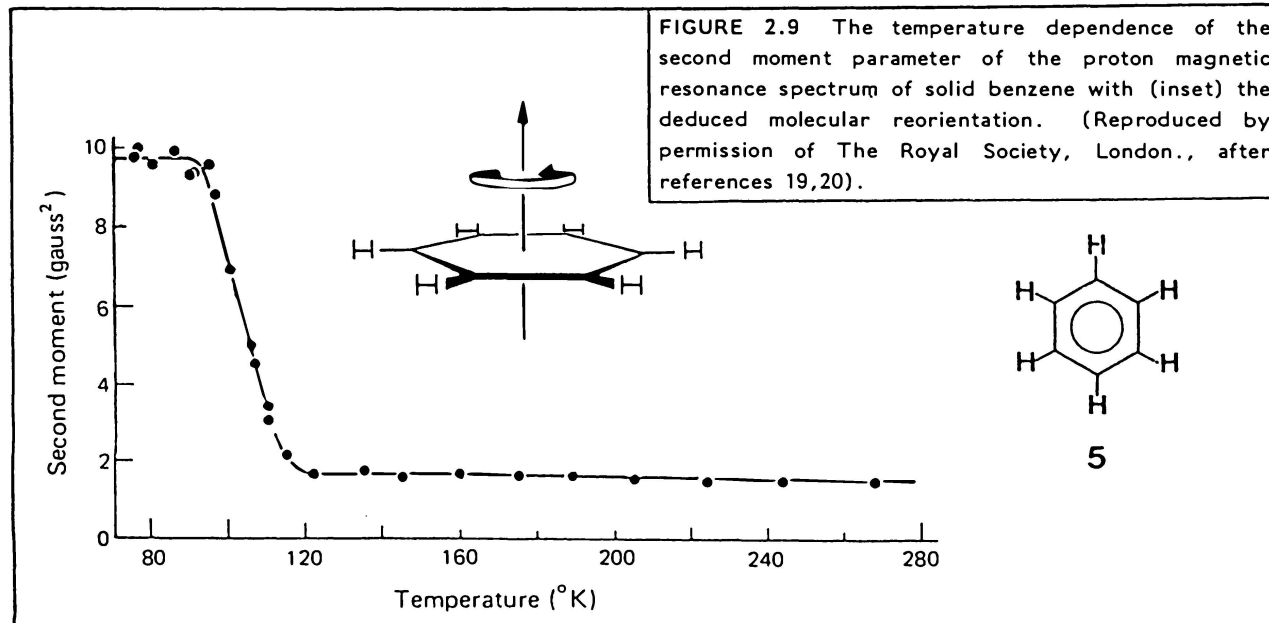
^2H quadrupolar echo NMR: line shape analysis

- Each method is sensitive to motions on a certain range of time scales.
- NMR spectroscopy allows us to obtain information on molecular motions over a wide range of time scales.
- Interpretation of the spectra usually requires the information of the crystal structures.
- X-ray and NMR are complementary techniques.

“Solid State NMR for Chemists”, C.A. Fyfe (1983).

Reorientation of benzene in crystal

Second moment analysis of benzene



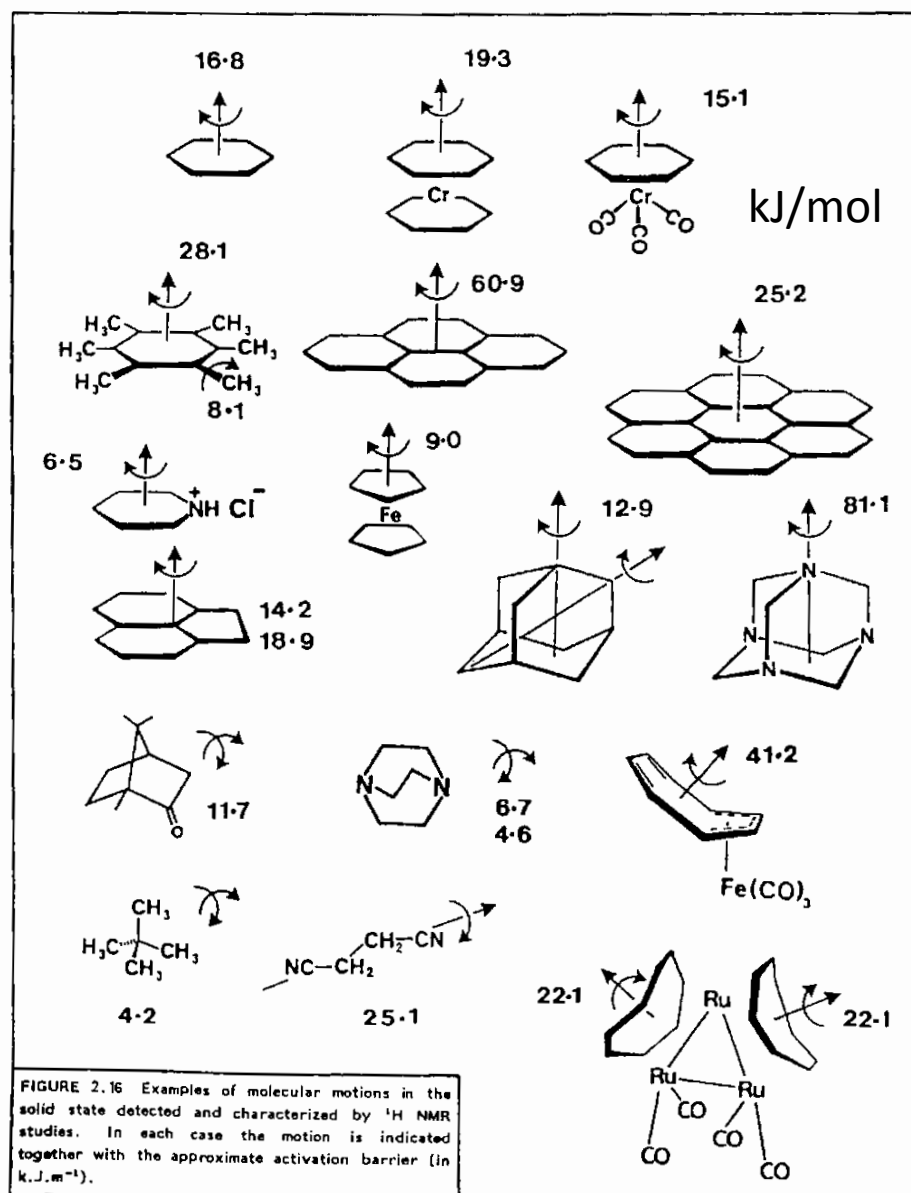
$$M_2 \propto \sum_{i,j} \left(\frac{3\cos^2\theta_{ij} - 1}{r_{ij}^3} \right)^2$$

Molecular motion reduces the average dipolar interaction and causes a narrowing of the spectrum.

Line narrowing was observed above 90 K and interpreted in terms of fast reorientation around the 6-fold axis.

Reorientation of molecules in crystals

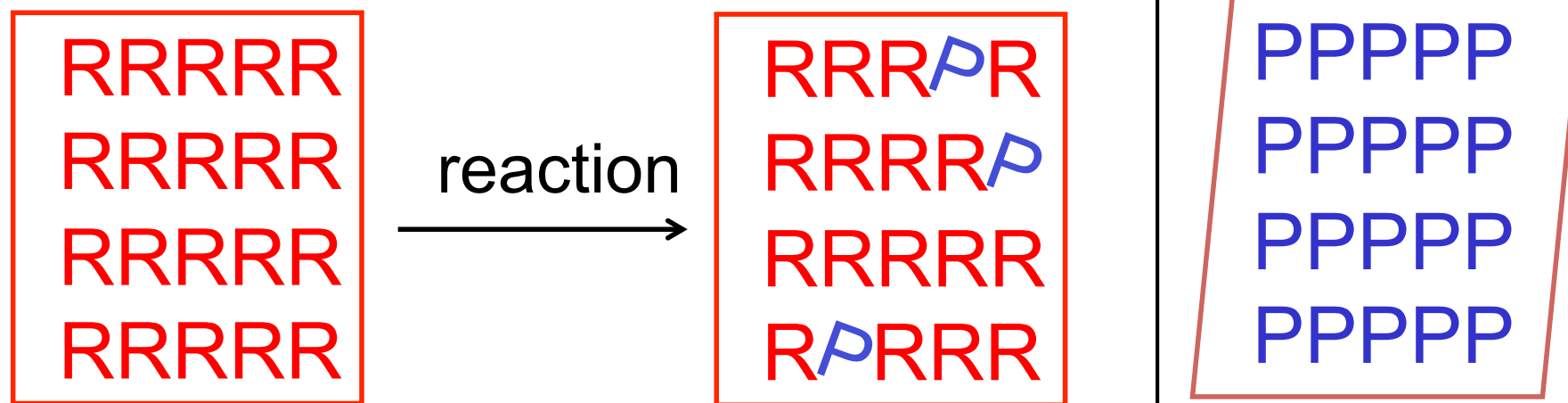
A variety of molecules undergo reorientations even in crystals.



X-ray diffraction studies on molecular motions

- ADP(atomic displacement parameter) analysis
 - Force constants and potential barriers can be estimated in favorable cases.
- Disorder analysis
 - Molecular motions can be recognized from the presence of two (or more) orientations (conformations) of molecules.
 - Motions on any time scales can be detected.

Observation of solid-state reactions by X-ray diffraction analysis



reactant

after reaction

product

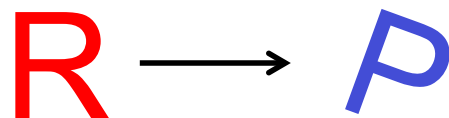
observed structure

R

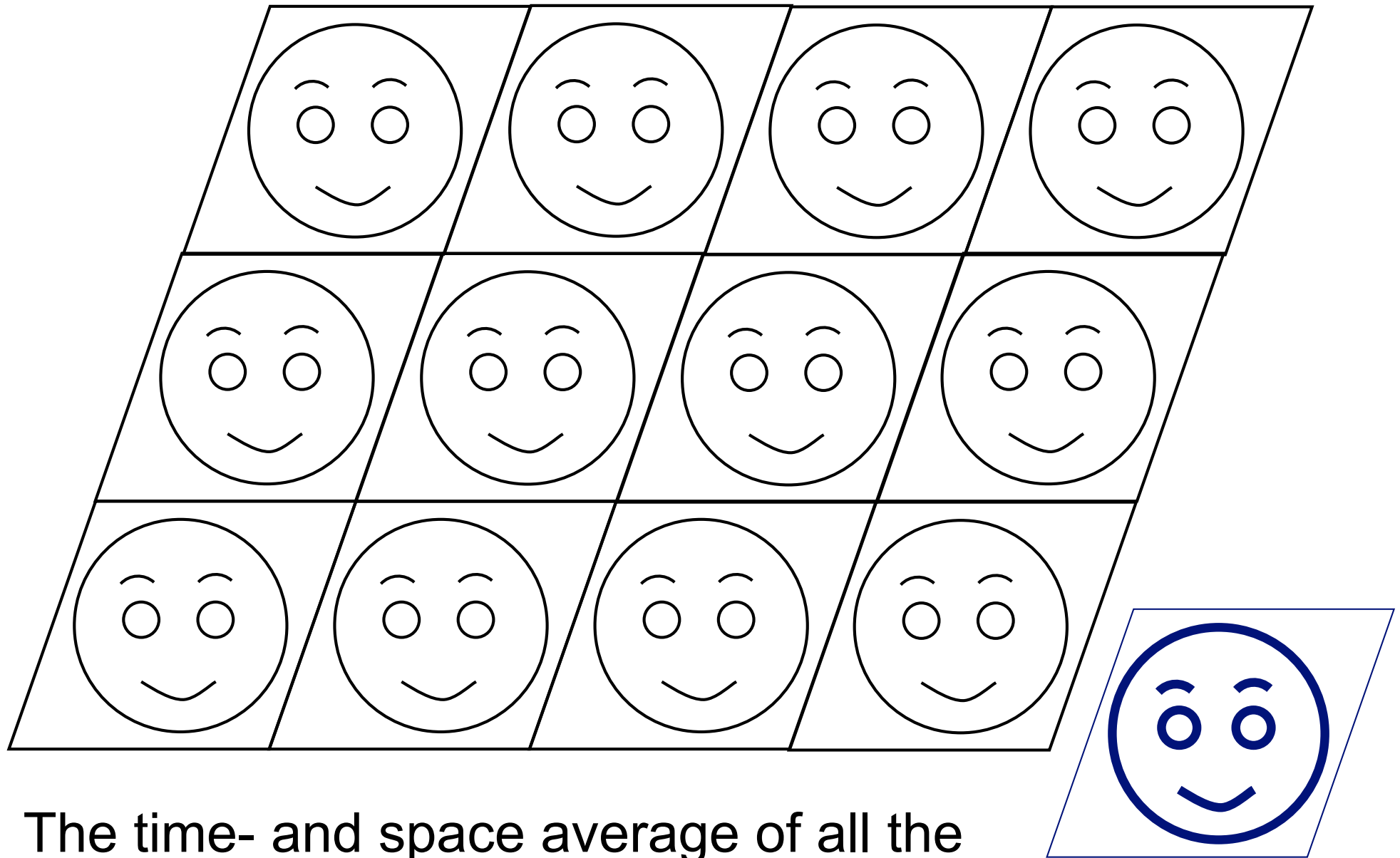
R

P

structural changes in the reaction

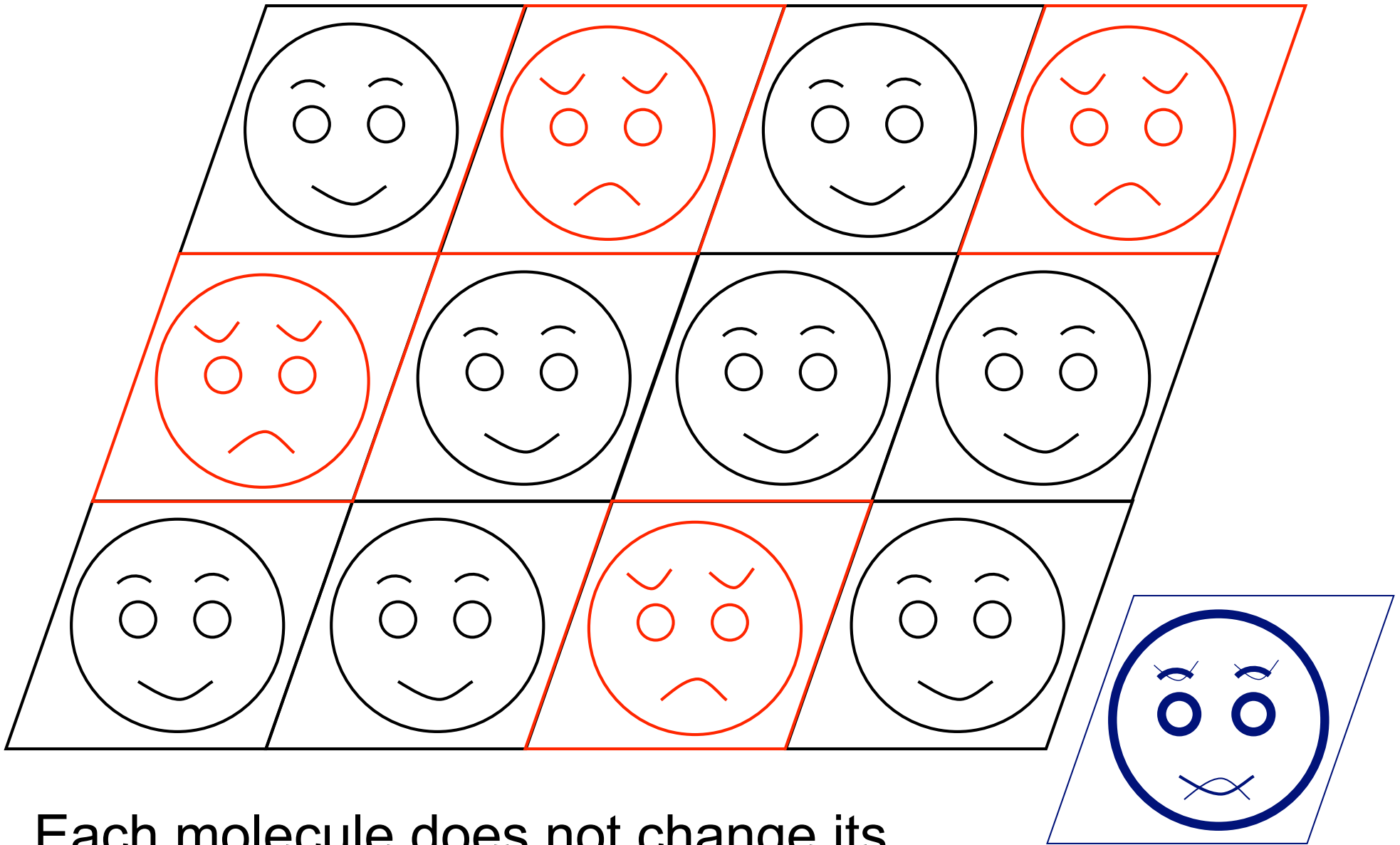


Molecular structure obtained by diffraction



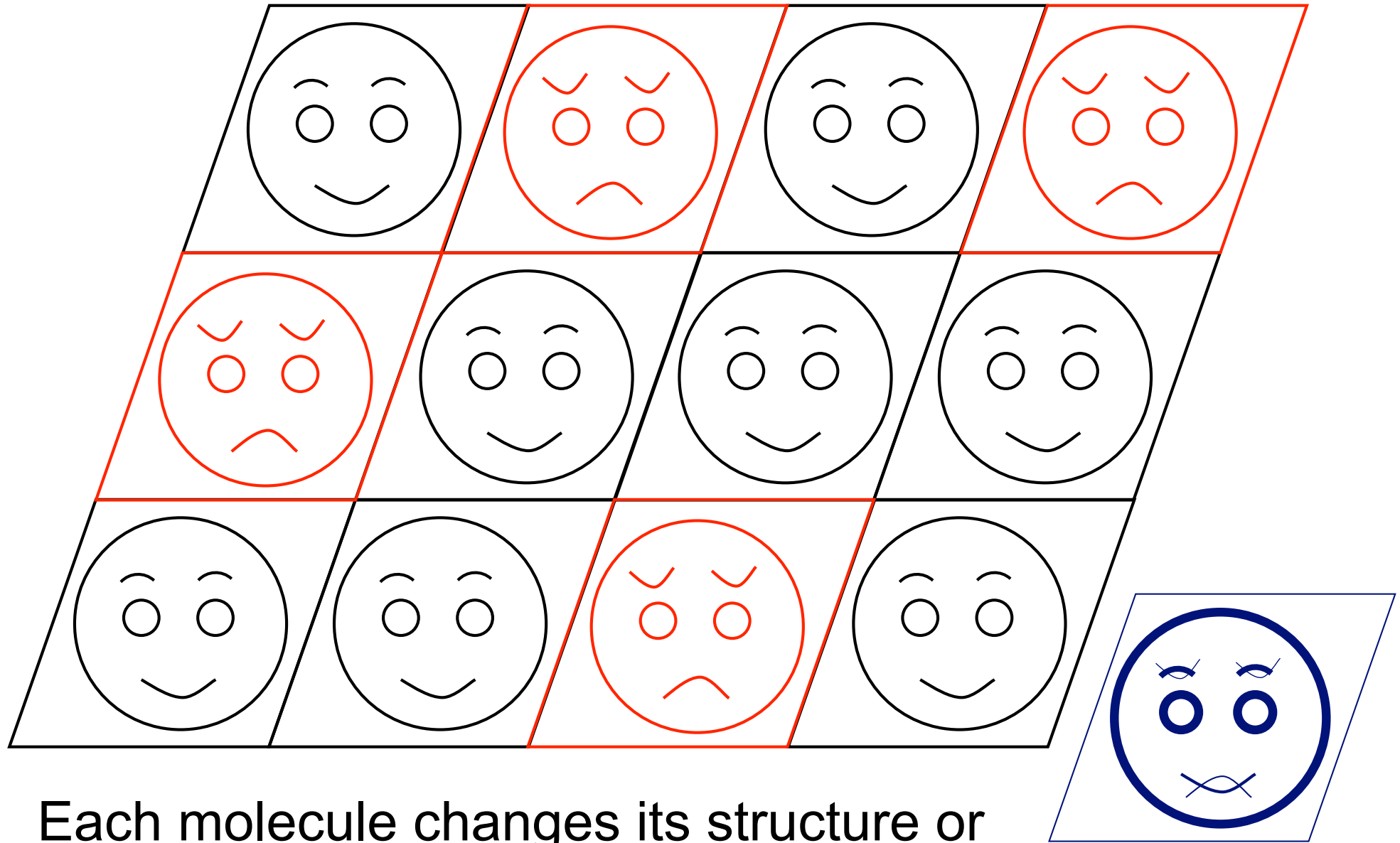
The time- and space average of all the molecules in the crystal.

Disordered crystal (static disorder)



Each molecule does not change its structure or orientation.

Disordered crystal (dynamic disorder)



Each molecule changes its structure or orientation.

Disorders frequently observed in crystal structures

- CH_3 , CF_3 , ^tBu groups attached to an aromatic ring
- long alkyl chains
- non-planar rings
- planar aromatic rings
- small solvent molecules
- ions (BF_4^- , ClO_4^- , PF_6^-)

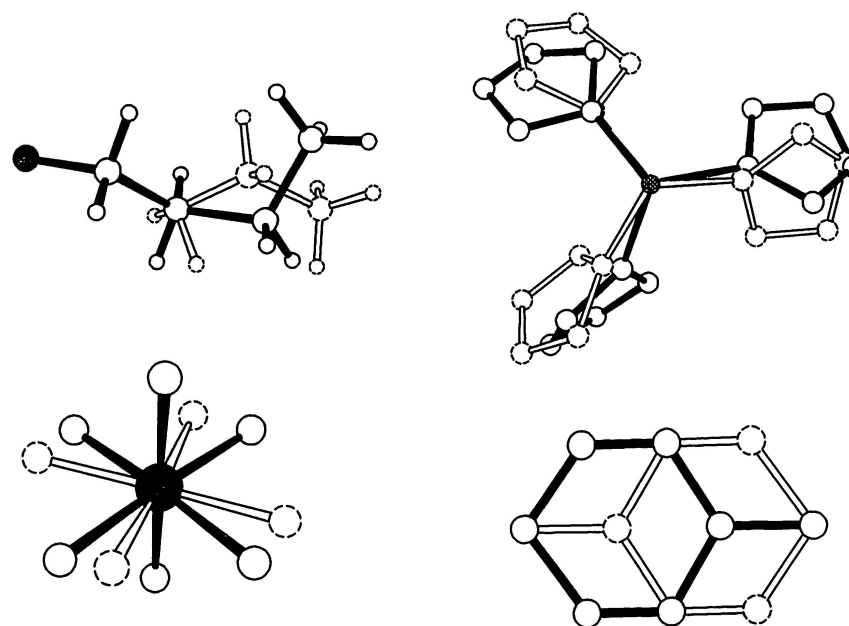
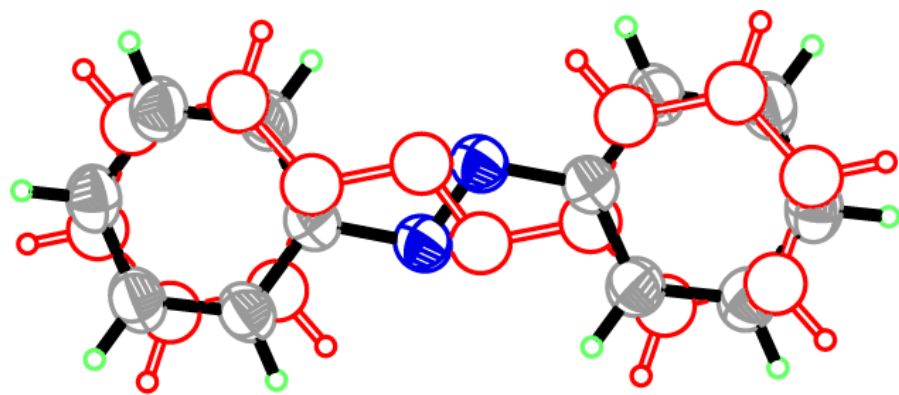
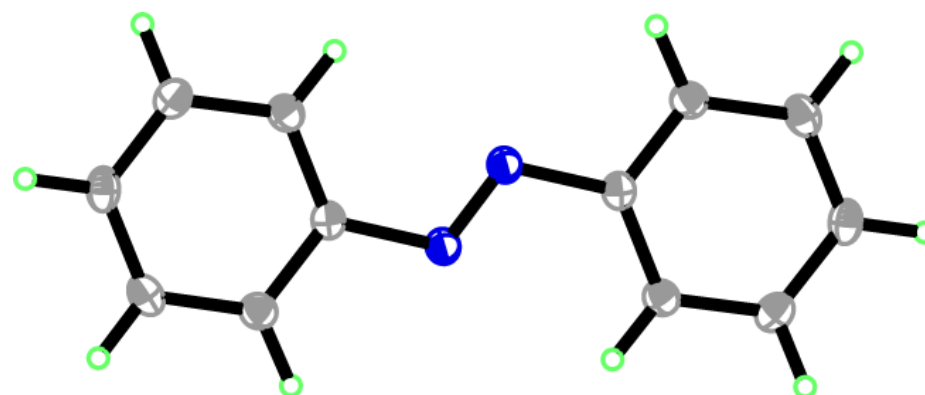


Fig. 4.2 Some examples of disorder: top left, an *n*-butyl chain in which the last two carbon atoms (with their hydrogen atoms) adopt two alternative positions; top right, three disordered the ligands coordinated to a metal atom; bottom left, an AsF_6^- anion with two orientations related by rotation about one of the linear FAsF units; bottom right, a toluene solvent molecule disordered over an inversion centre (hydrogen atoms not located!).

Temperature dependence of the disorder of azobenzene



at 300 K



at 90 K

Populations of the two conformers

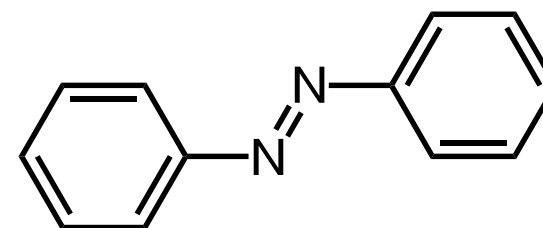
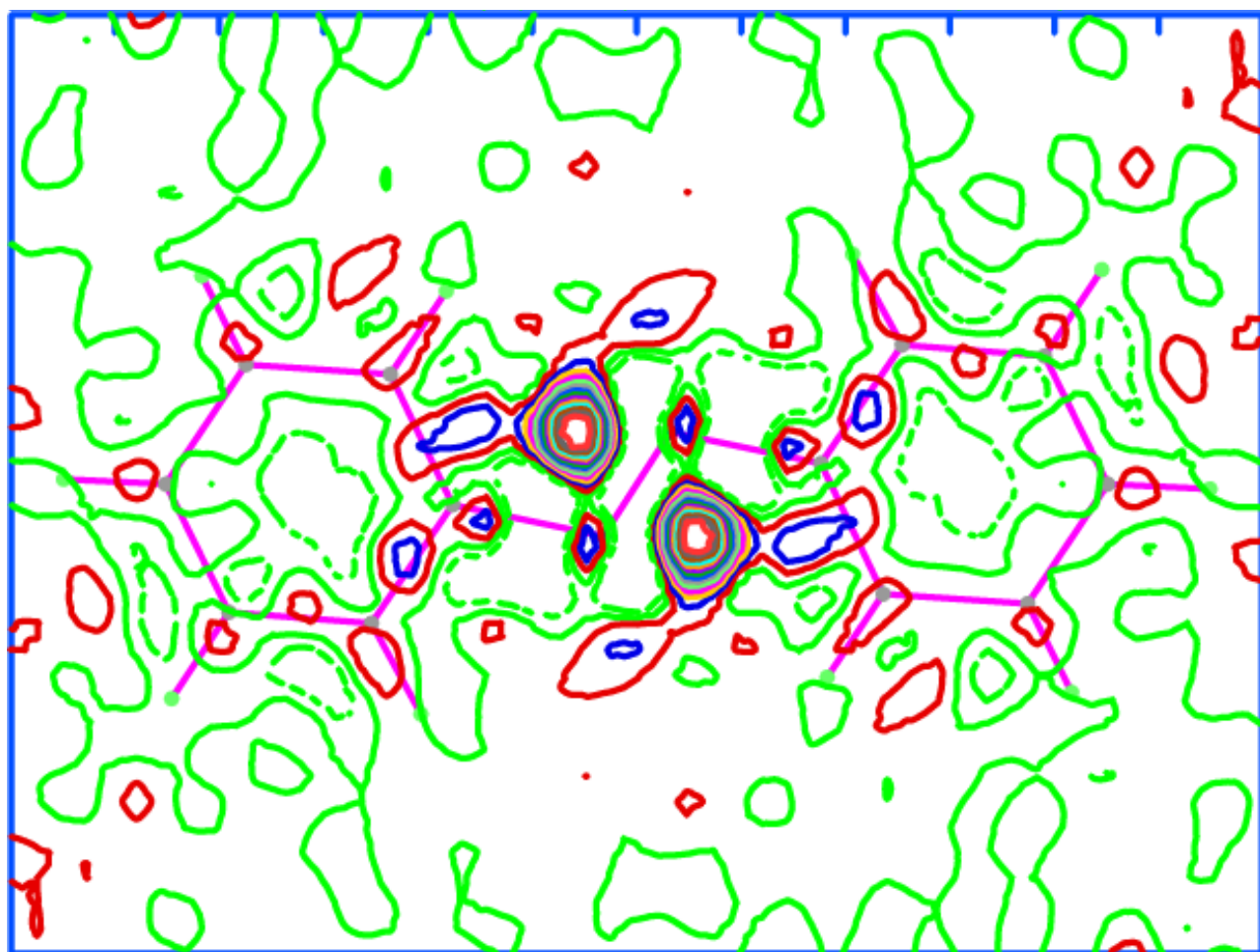
300 K	82.2(3) : 17.8(3)
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90 K	1 : 0
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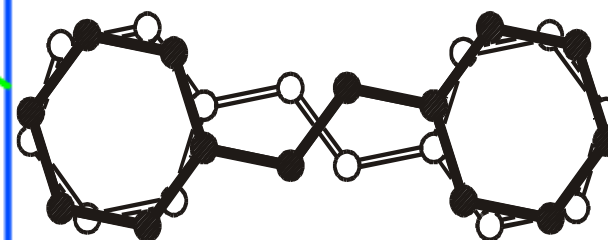
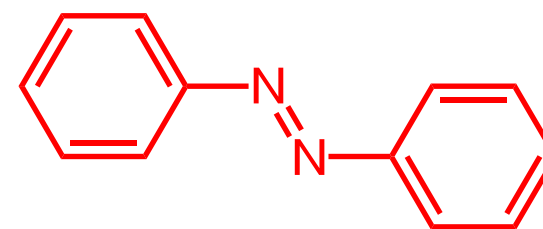
The disorder disappeared at low temperature.

→ Dynamic disorder

Electron density map of azobenzene at 300 K



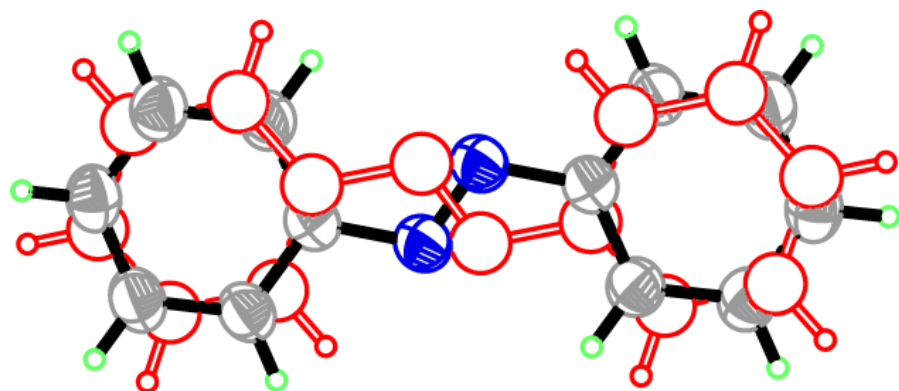
Azobenzene



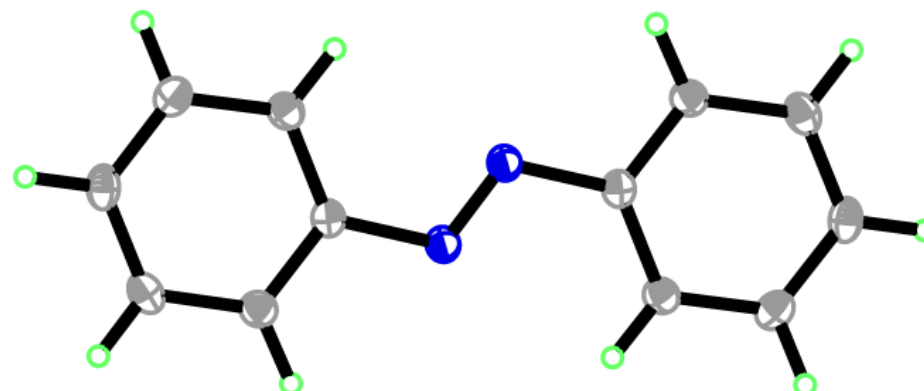
difference electron density map ($0.05 \text{ e}\text{\AA}^{-3}$ interval)

Difference electron density map reveals a minor orientation at 300 K.

Temperature dependence of the disorder of azobenzene



at 300 K



at 90 K

Populations of the two conformers

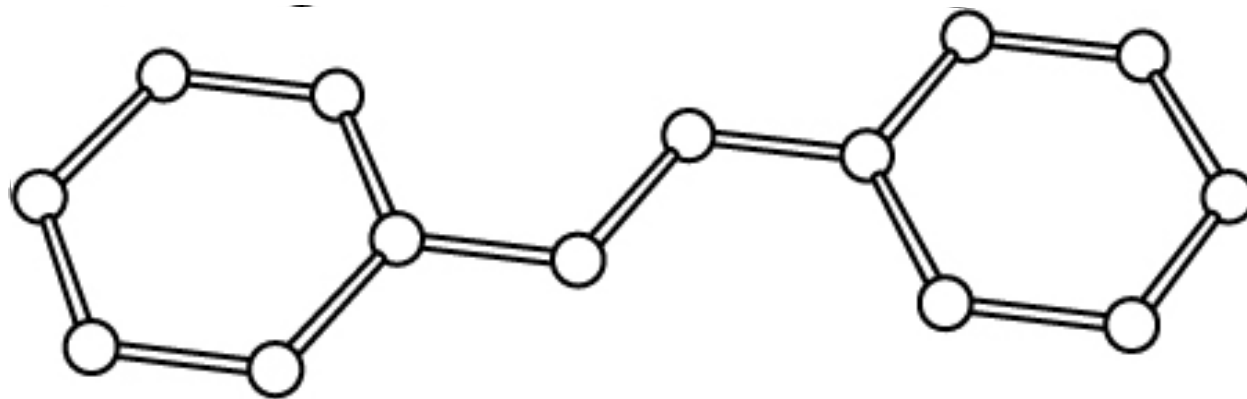
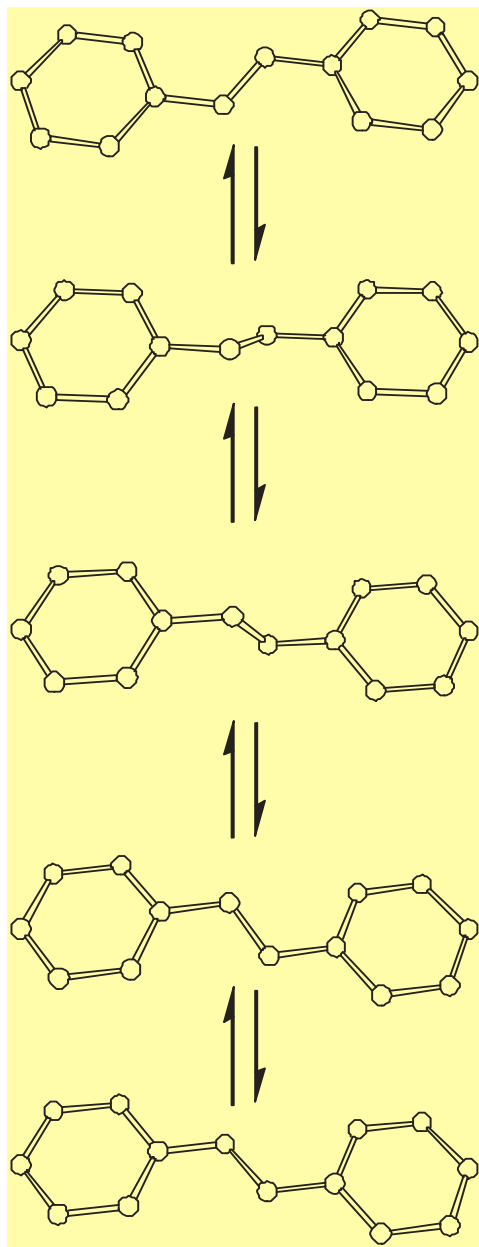
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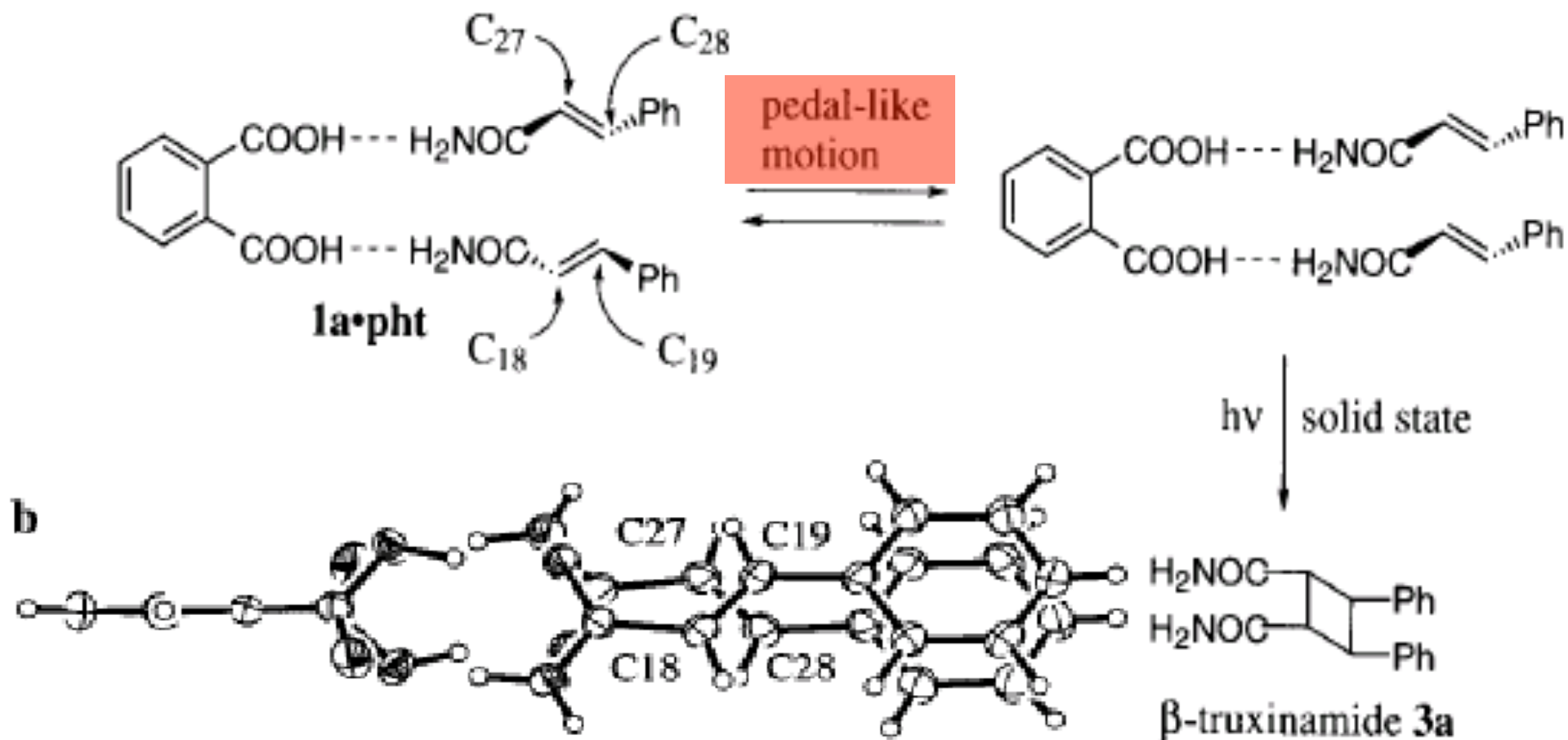
→ Dynamic disorder

Pedal motion in crystals



Azobenzenes undergo conformational interconversions through a pedal motion in crystals.

[2+2] Photodimerization of a cinnamide



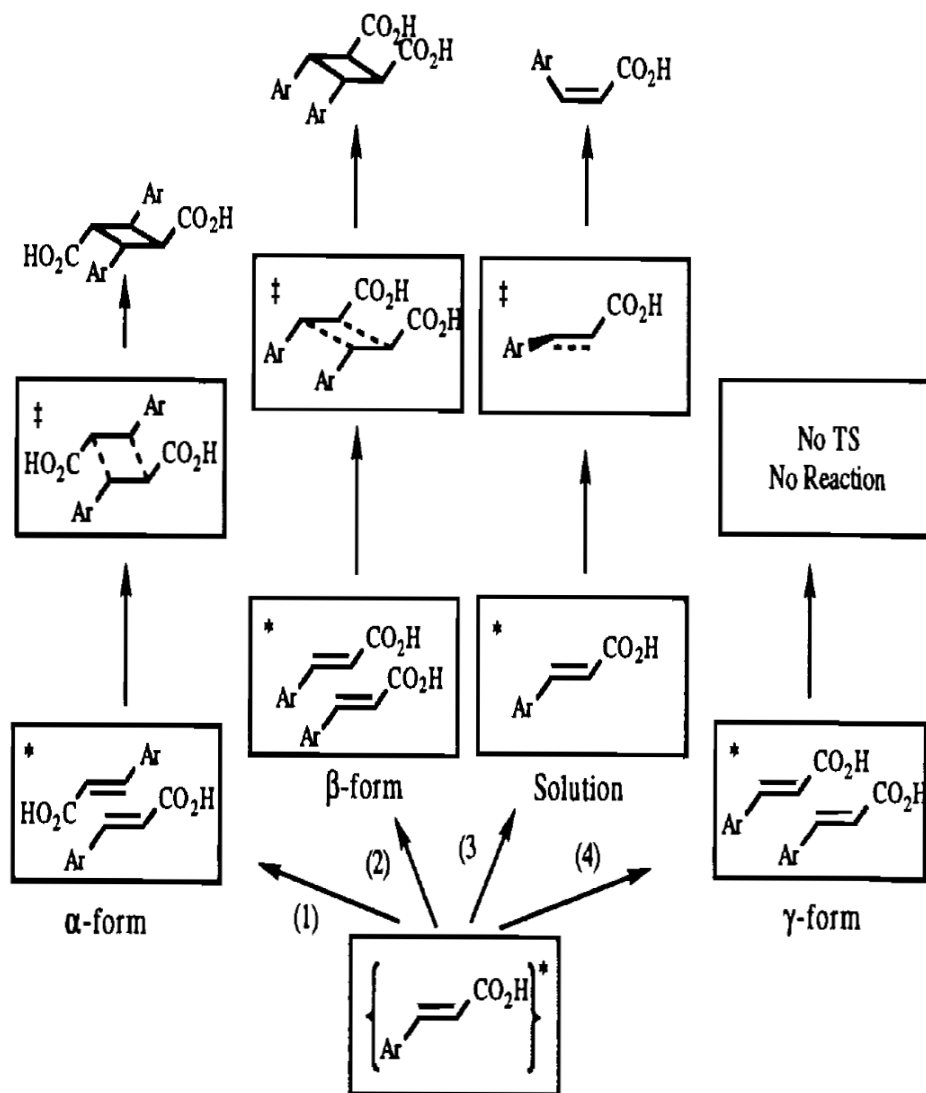
Conformational change through pedal motion takes place prior to the photoreaction.

Photochemistry of *trans*-cinnamic acids

[2 + 2] photodimerization

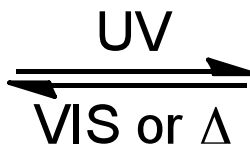
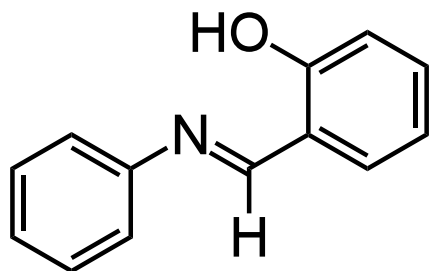
Schmidt's law

The photodimerization may occur only when the two C=C are parallel to each other and with a center-to-center distance shorter than *ca.* 4.1 Å.



Topochemical reaction: reactions that occur under the influence and control of crystalline media.

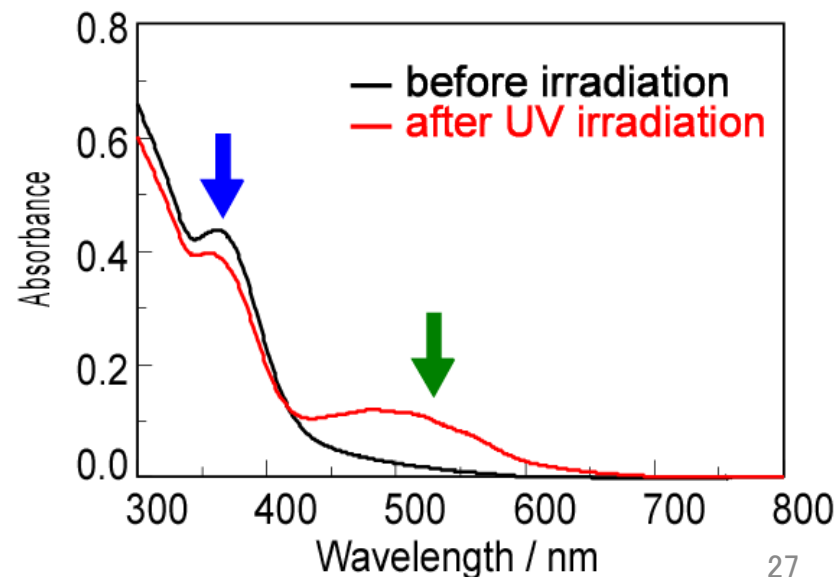
Photochromism of salicylideneanilines in crystals



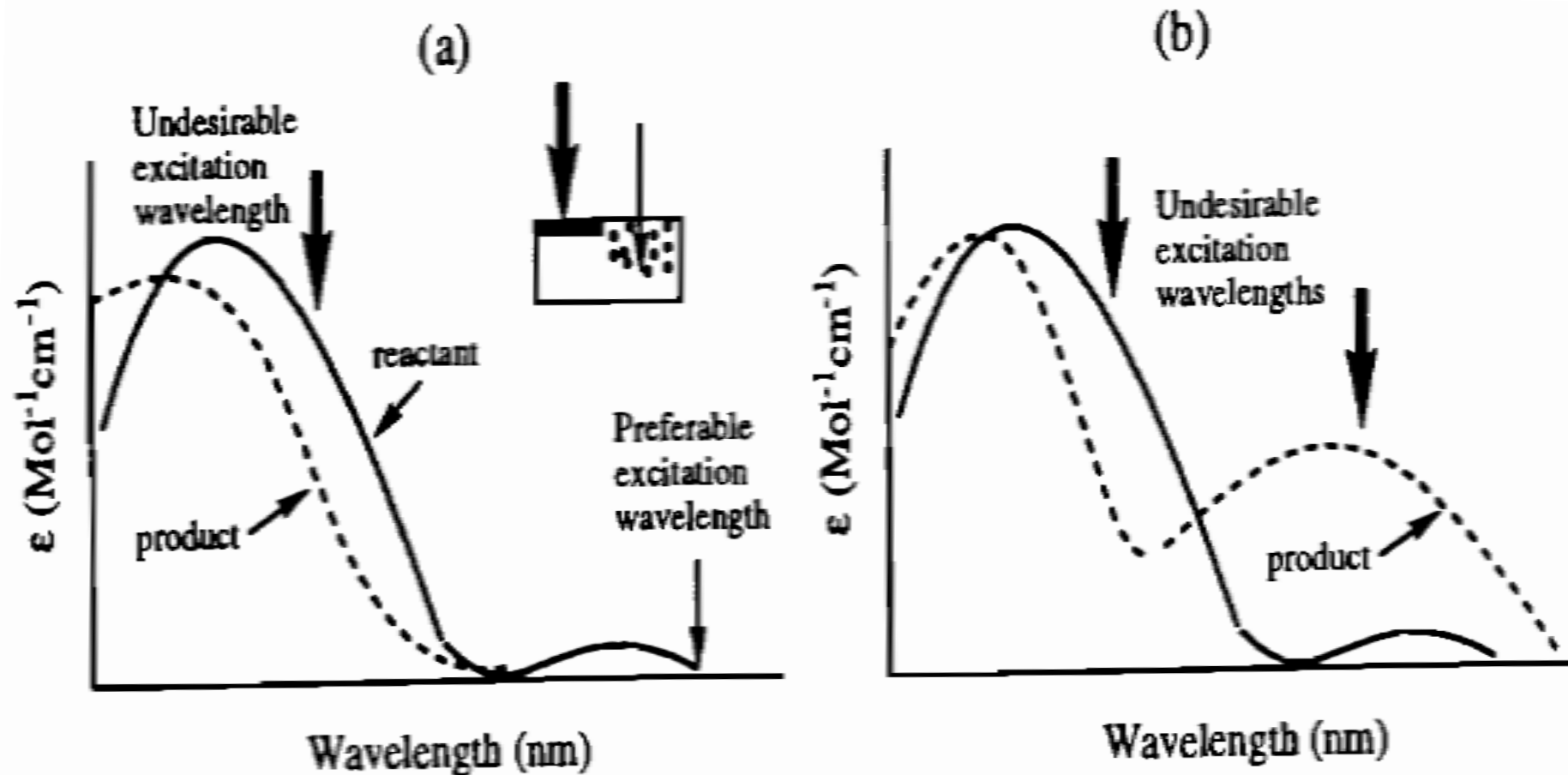
?



- Reversible color changes of crystals.
- The structure of the colored species had not been determined.

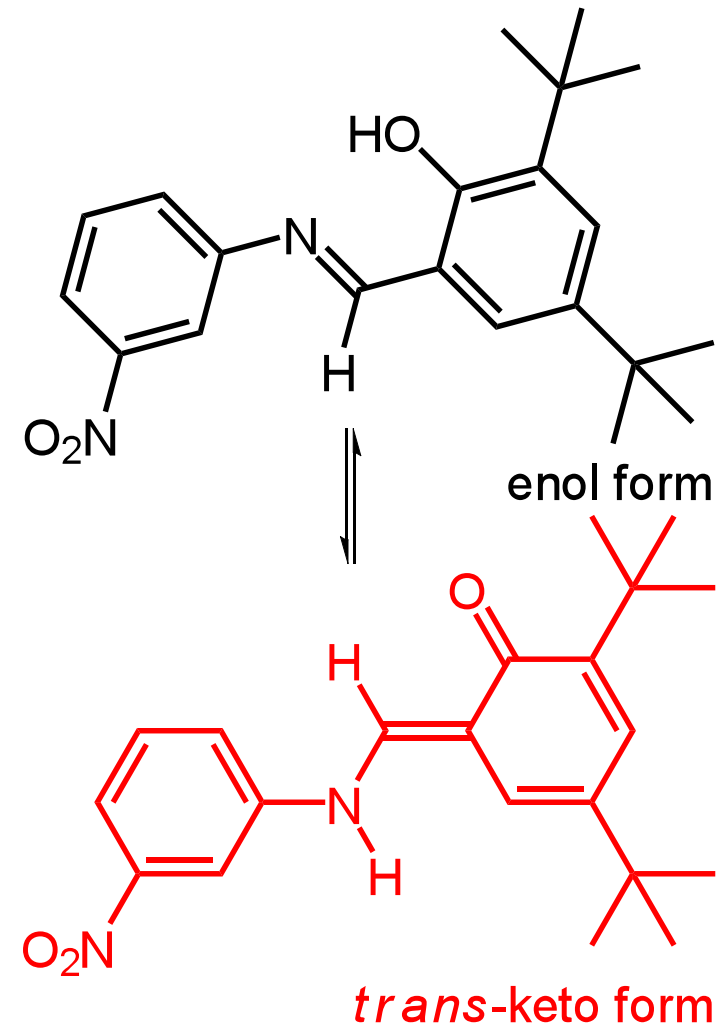
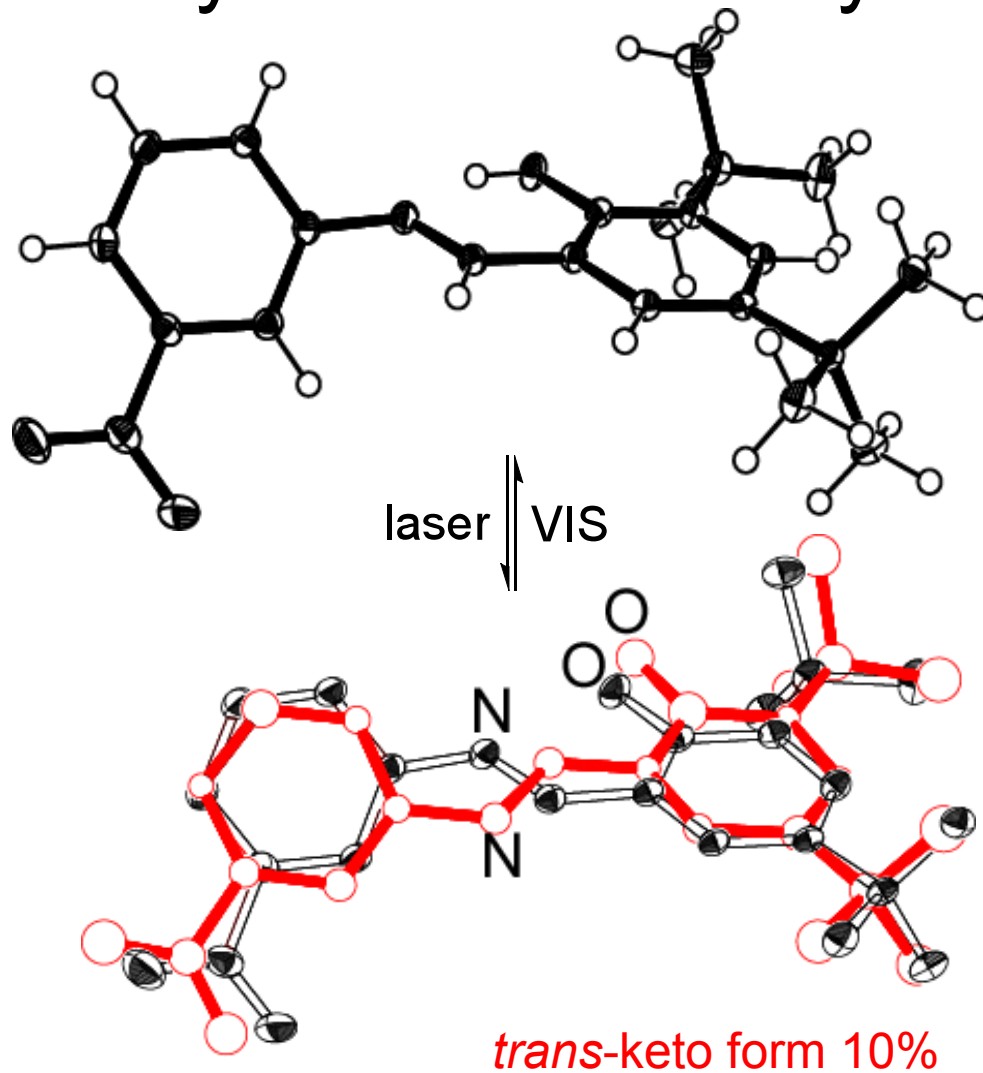


Irradiation wavelength for photoreactions



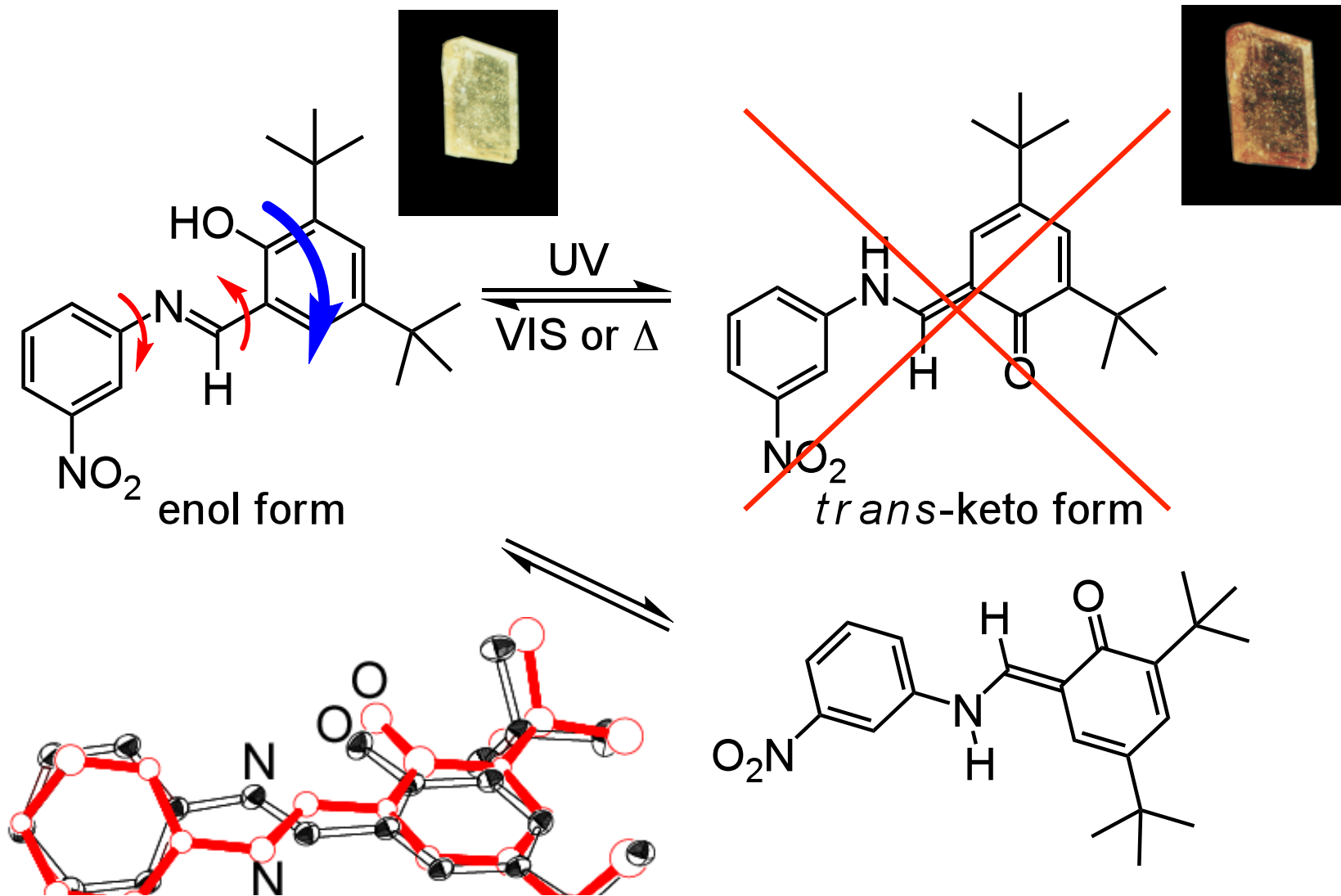
- Homogeneous distribution of product can be achieved only by irradiation with long wavelength light.

X-ray diffraction analysis of the photochromism



The colored species is the *trans*-keto form.

Mechanism of the photochromism



- (The photo-transformation proceeds through pedal motion instead of the aryl group rotation.