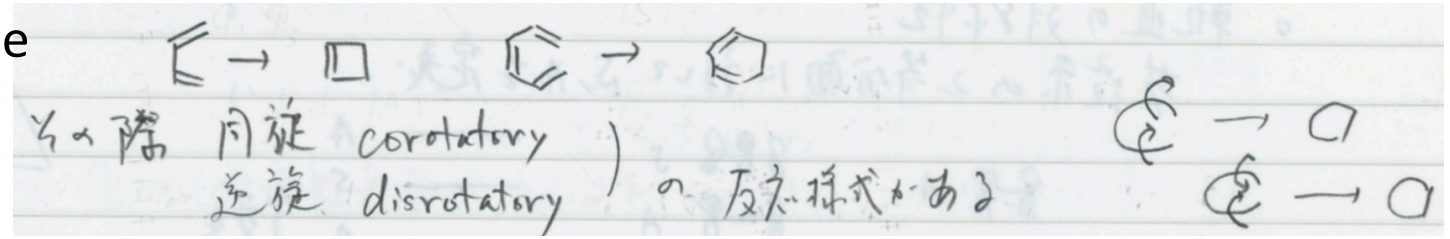
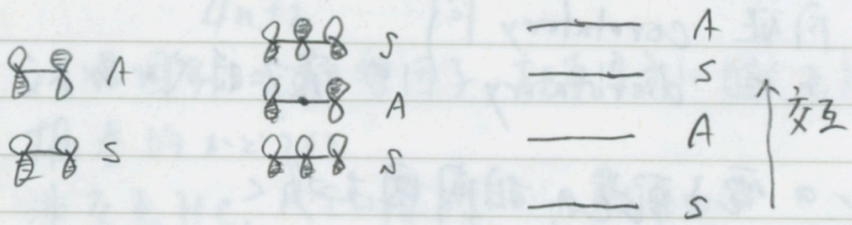
Woodward−Hoffman rule

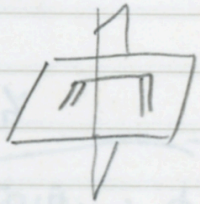
pericyclic reactions

ペリ環状反応



☞ Orbital symmetry :





Symmetry/Antisymmetry with respect to reflection.

closed-shell polyenes は 元々二重結合を結合的

(LUMO 一重 結合的)

$4n+2\ \pi$ HOMO S LUMO A

$4n\ \pi$ A S

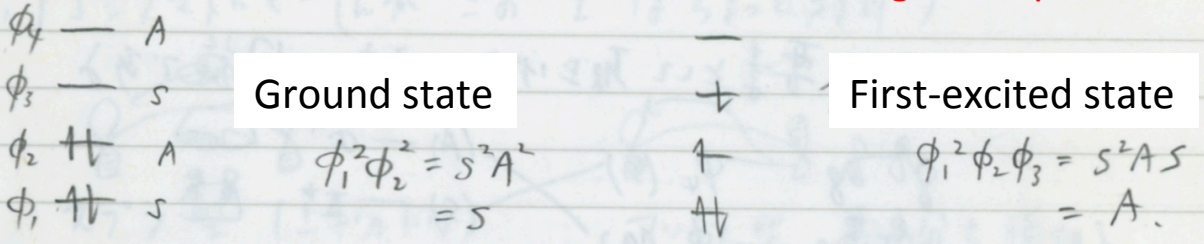
open-shell (radical) polyenes

$4n+3\ \pi$ SOMO A

$4n+1\ \pi$ S

☞ Electron-configurational symmetry :

Algebraic product of S(+1) and A(-1).



Ground state

$\phi_1^2\phi_2^2 = S^2A^2 = S$

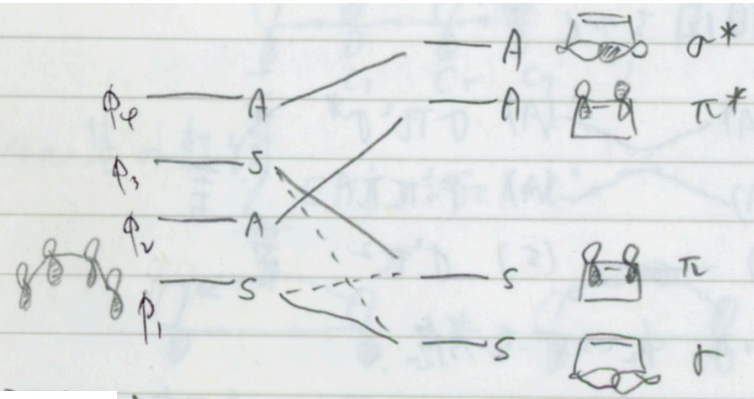
First-excited state

$\phi_1^2\phi_2\phi_3 = S^2AS = A$.

Orbital symmetry conservation law

MO's conserve the orbital symmetry with respective to the symmetry of transformation.

Ex) butadiene – cyclobutene interconversion: orbital–correlation diagram.



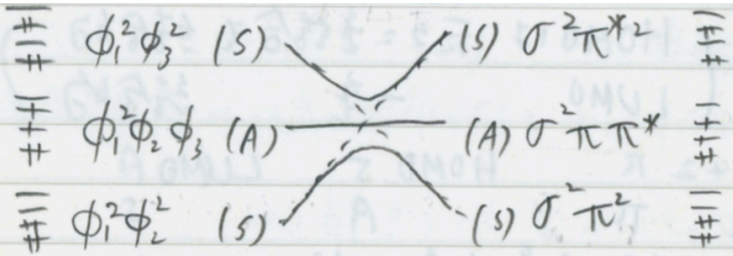
Only S – S and A – A transformations are allowed.

No-crossing law

Orbital-correlation lines must not cross each other when they have the same symmetry.

Ex) butadiene – cyclobutene interconversion: configuration–correlation diagram.

Note that reflection symmetry is applied to disrotatory reaction.



ϕ_1–σ, ϕ_2–π^*, ϕ_3–π, and ϕ_4–σ^* relations are applied.

The correlation curve implies the energy surface on the reaction coordinate.

$\phi_1^2\phi_2^2$ (S) ⟷ $\sigma^2\pi^2$ (S)

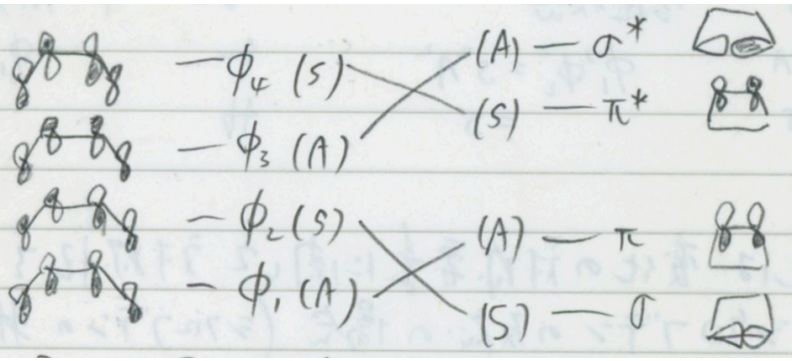
$\phi_1^2\phi_2\phi_3$ (A) ⟷ $\sigma^2\pi\pi^*$

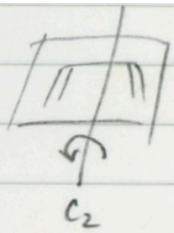
forbidden

allowed ☜ photo-conditions: disrotatory

Two-fold rotation symmetry is applied to conrotatory reaction.

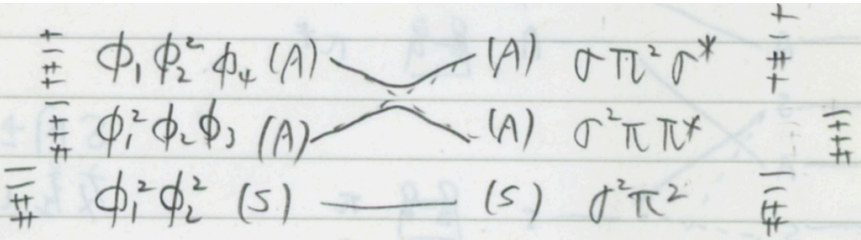
Orbital-correlation diagram:



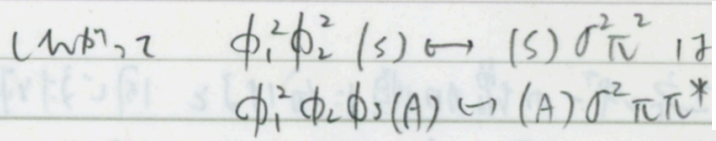


Symmetry/Antisymmetry
with respect to two-fold rotation.

Electron-configuration-correlation diagram:



ϕ_1–π, ϕ_2–σ, ϕ_3–σ^*, and ϕ_4–π^* relations are applied.



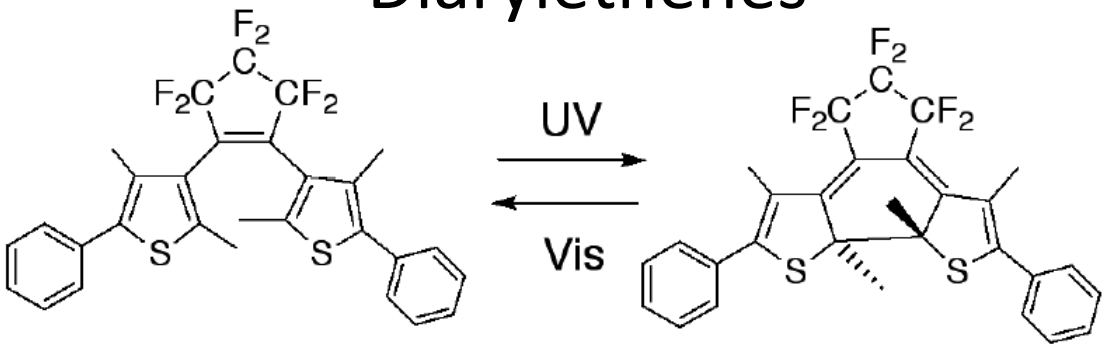
allowed ☜ thermal conditions: conrotatory
forbidden

Selectivity rule:
Newly formed double bond: symmetrical HOMO leads to disrotatory while antisymmetrical HOMO leads to conrotatory.

thermal conditions:	$4n$ 電子	conrotatory
	$4n+2$	disrotatory
photo conditions:	$4n$	disrotatory
	$4n+2$	conrotatory

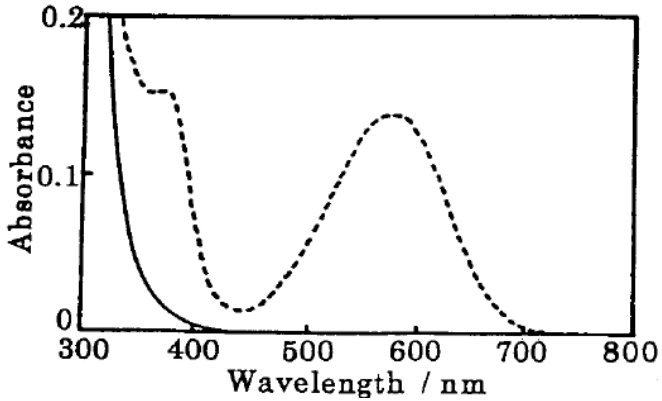
Solid sate chemistry
ex.1) photochromic materials

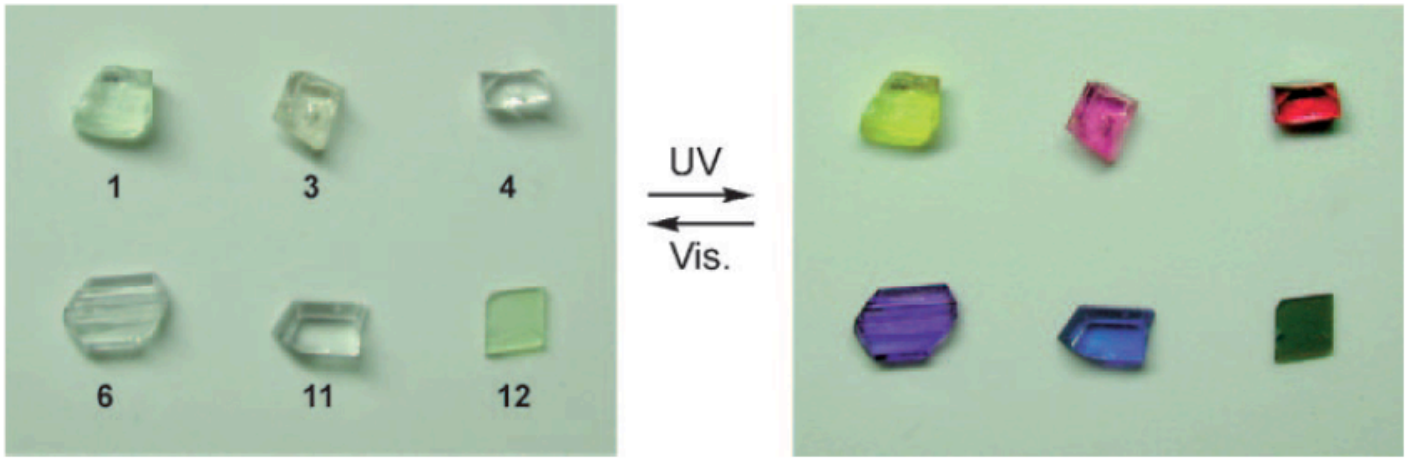
Diarylethenes



open form (solid line)
cross-conjugation

closed form (broken line)
through-conjugation

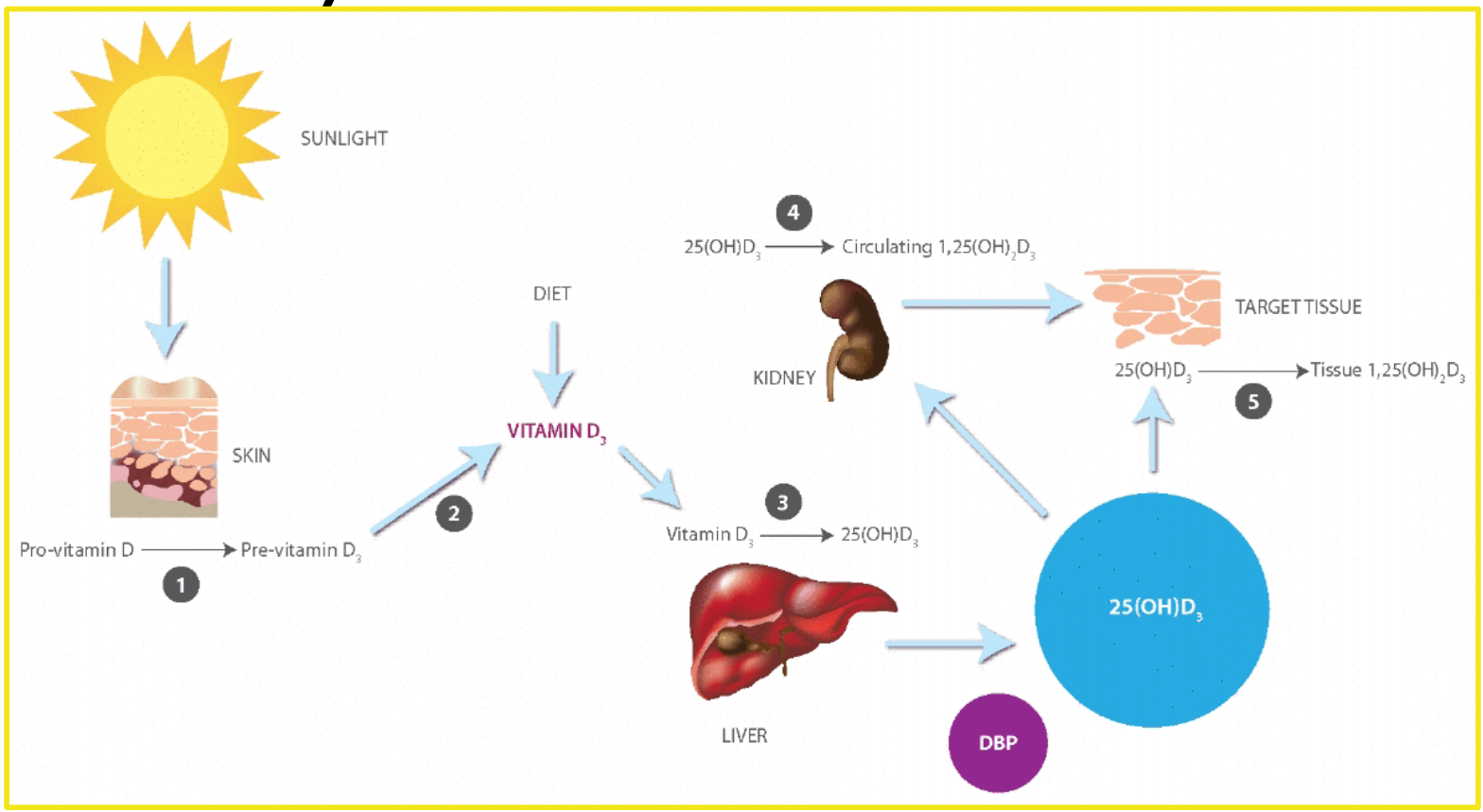


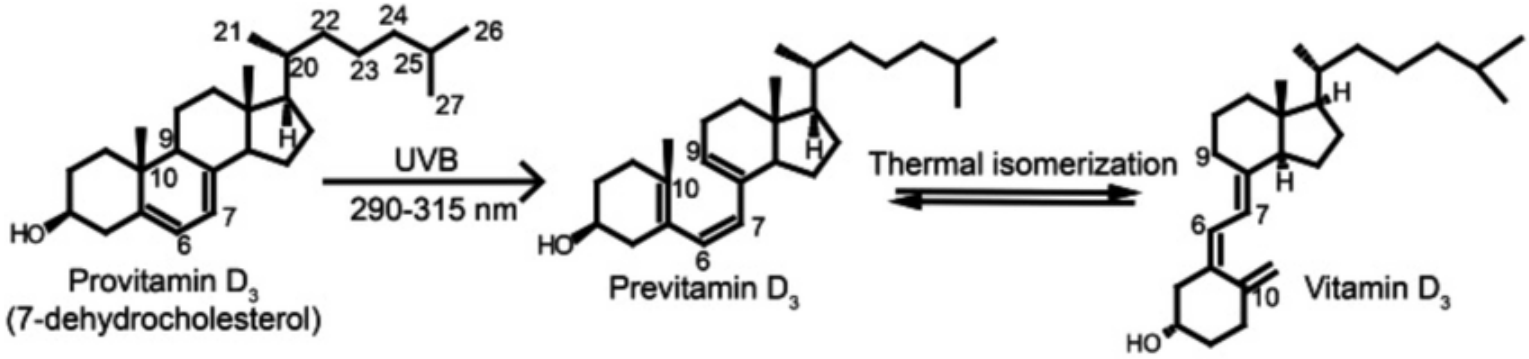


M. Irie et al.,
Bull. Chem. Soc. Jpn.,
2004, *77*, 195.

Solid sate chemistry
ex.5) vitamin D3

Vitamin-D deficiency rickets (くる病), a disorder that becomes apparent during infancy or childhood, is the result of insufficient amounts of vitamin D in the body. The deficiency of vitamin D may be caused by poor nutrition, a lack of exposure to the sun, or ….





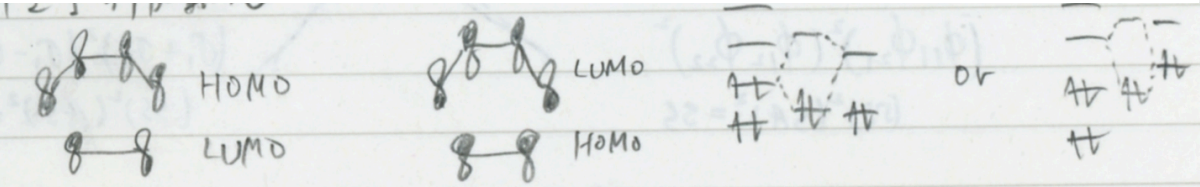
Woodward−Hoffman rule

cycloaddition reactions
協奏的環化

supra: on one side of the plane
antara: across the plane

[4+2]cycloaddition

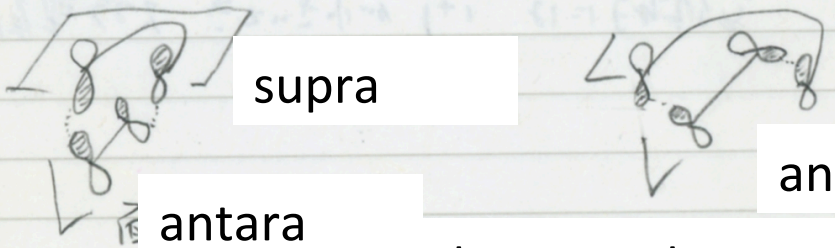
Ex) Diels-Alder reaction



thermal conditions: supra–supra (or antara-antara)

[i + j]cycloaddition

supra–supra or antara–antara
supra–antara or antara–supra



supra

antara–antara

antara

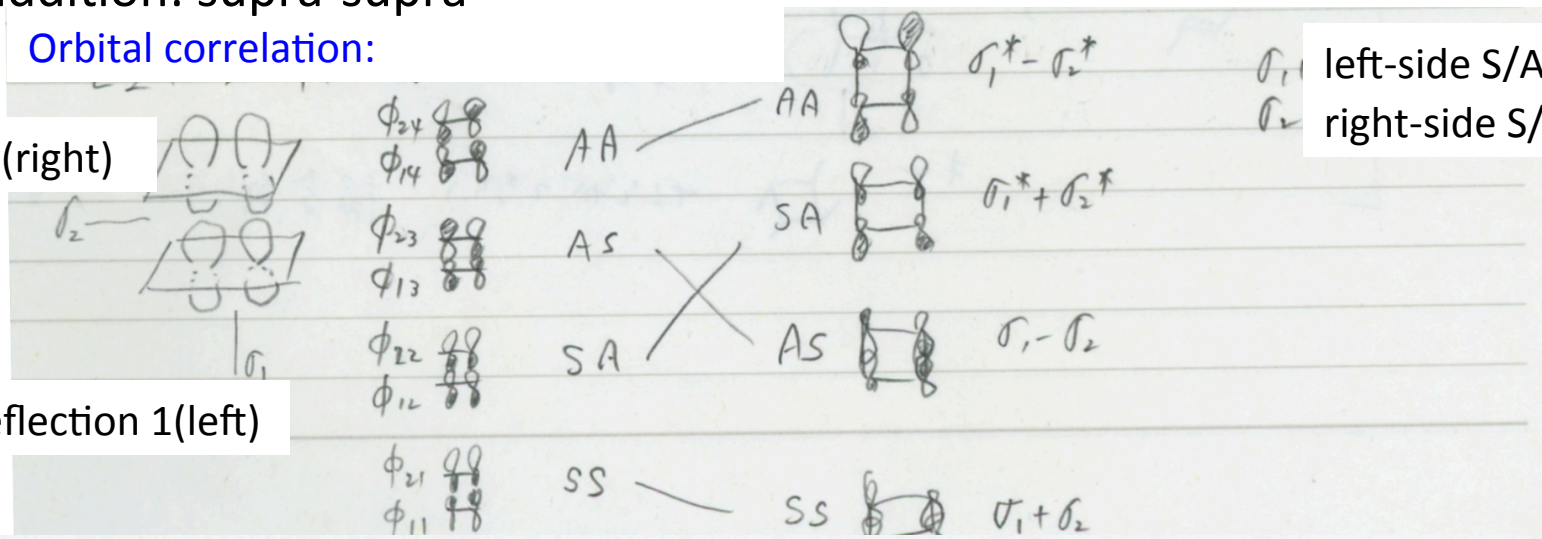
when i+j is large.

If i + j is small, only supra is sterically possible.

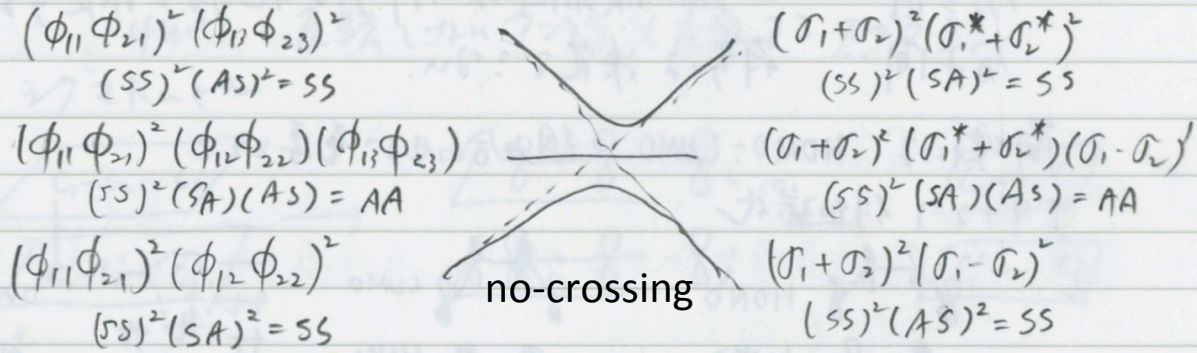
thermally allowed. (photo. forbidden)
photochemically allowed. (them. fobiden)

[2+2]cycloaddition: supra-supra

Orbital correlation:



Electron-configuration correlation:



Therefore, thermally forbidden and photochemically allowed.

[i + j]cycloaddition : photo.

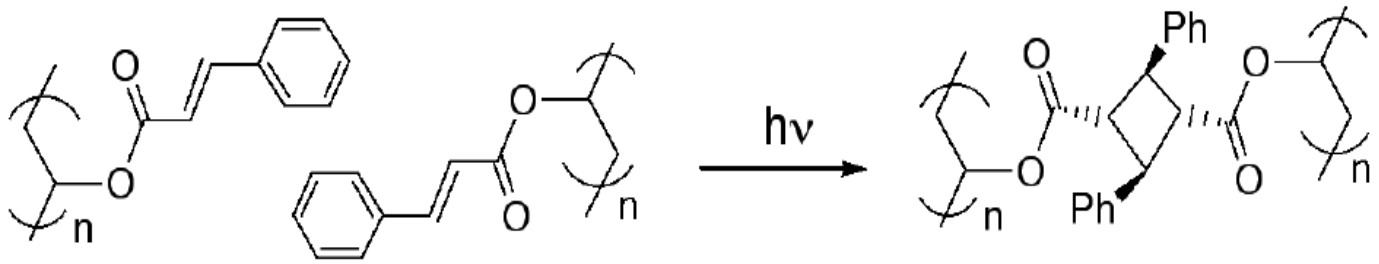
$i+j = 4n+2$ supra–antara or antara–supra

$i+j = 4n$ supra–supra or antara–antara

If i + j is small, only supra is sterically possible.

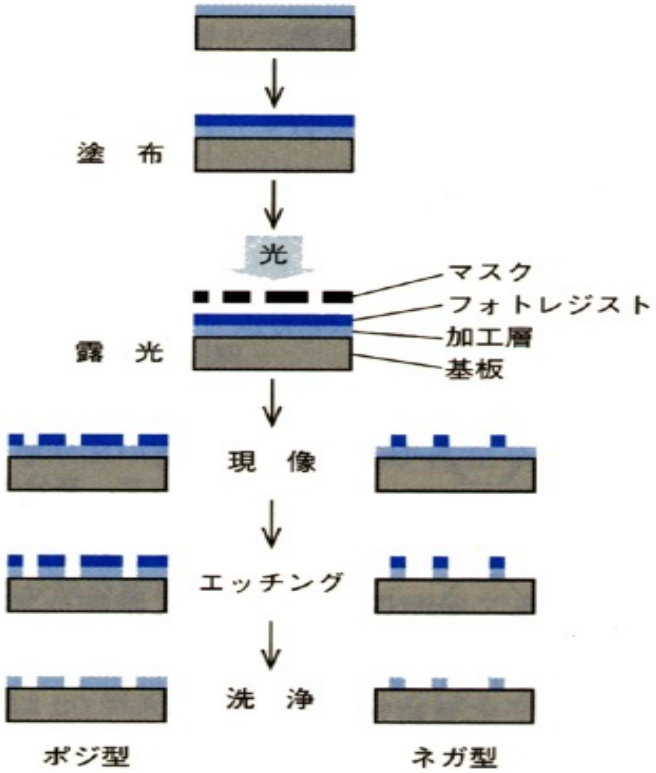
Solid sate chemistry
ex.2) photoresist

KPR (Kodak Co. Ltd.)



cross-linked polymers

lithography:



substrate

paint for masking

exposure

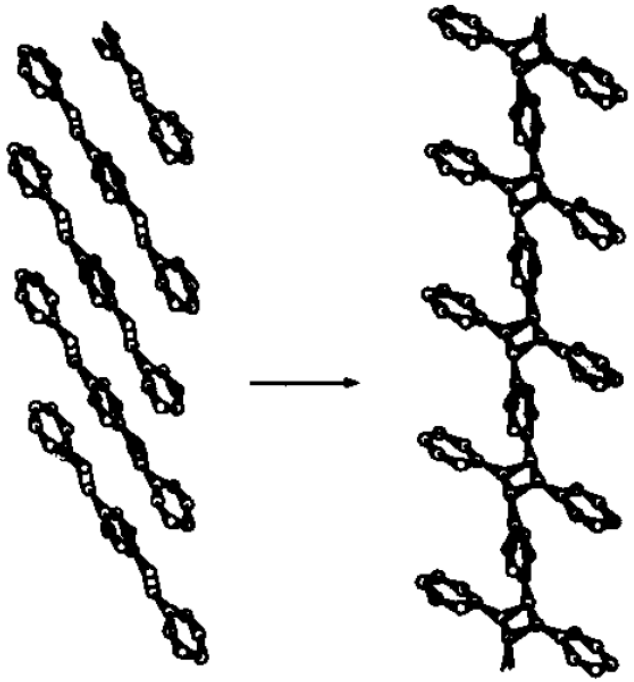
developing a photo

etching (positive/negative types)

wash

Solid sate chemistry

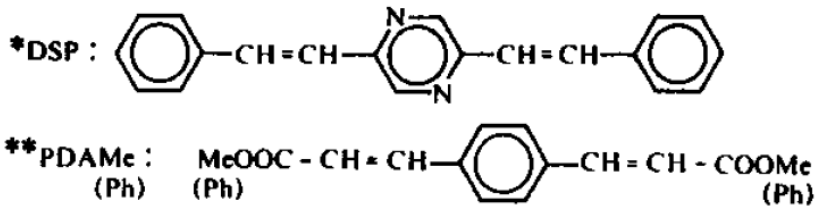
ex.4) photo-polymerization



α-phase distylylpyrazine (DSP)

Table. The cell parameters of reactive DSPs

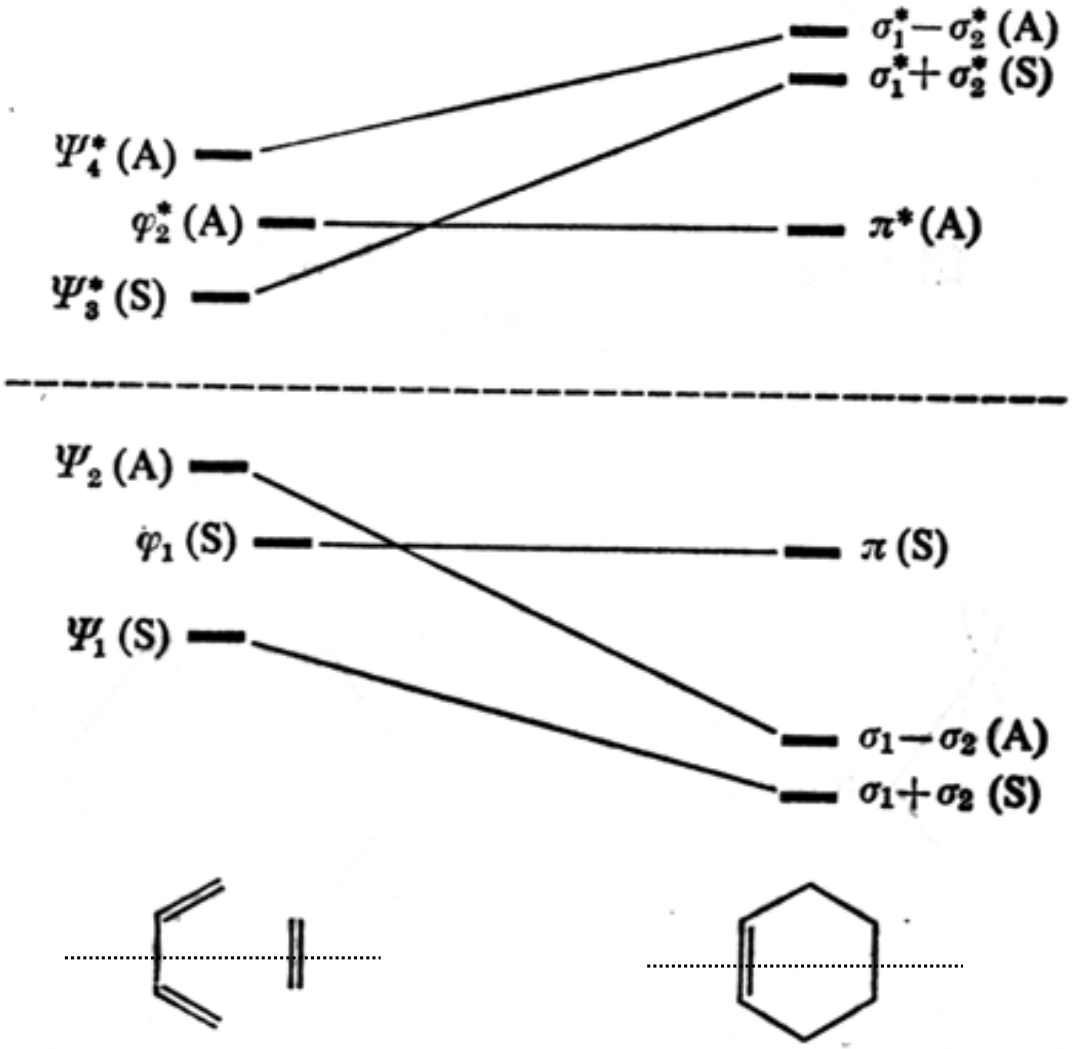
化合物	空間群	*a* (*α*)	*b* (*β*)	*c* (/nm) (*γ*) (/°)	二重結合間距離/nm
2,5-ジスチリルピラジン(DSP)* (*α* 相)					
monomer	*Pbca*	2.0638	0.9599	0.7655	0.3939
polymer		1.836	1.088	0.752	
1,4-フェニレンジアクリル酸ジメチルエステル(PDAMe)**					
monomer	$P\bar{1}$	0.7148 (98.97)	0.8382 (116.85)	0.5844 (78.06)	0.3957
polymer	$P\bar{1}$	0.782 (107.8)	0.742 (106.0)	0.604 (78.8)	
1,4-フェニレンジアクリル酸ジフェニルエステル(PDAPh)**					
monomer	$P2_1/c$	0.6917	1.8584 (101.87)	0.7557	0.3917
polymer	$P2_1/c$	0.750	1.73 (102.0)	0.750	

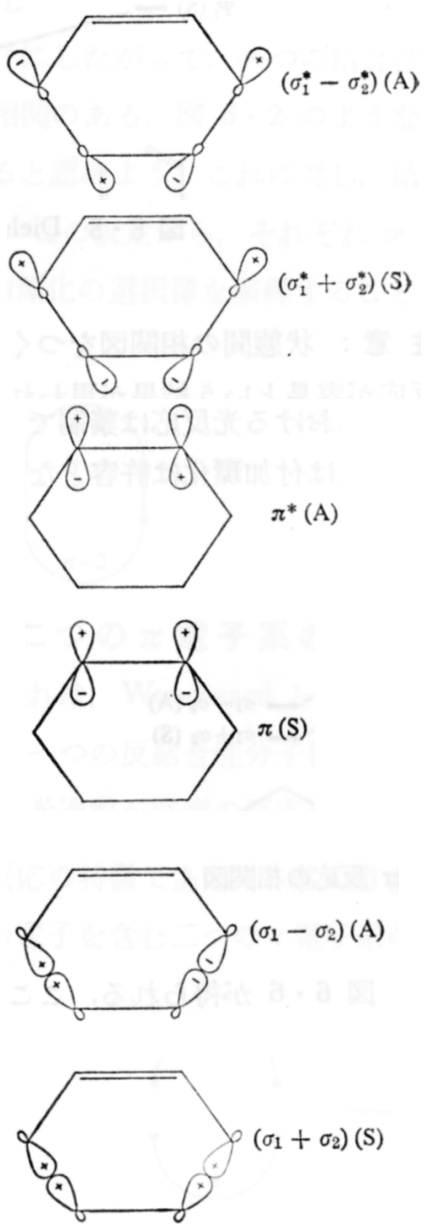


Explain why 2π + 2π cycloaddition reactions are allowed in photo-process and forbidden in thermal-process.

[4+2]cycloaddition reactions

Orbital-correlation diagram:

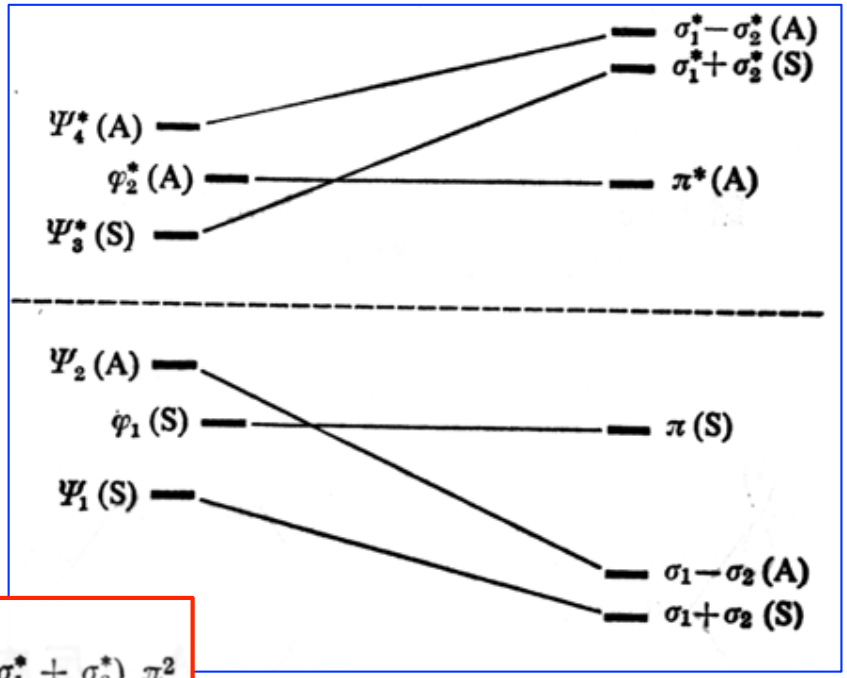


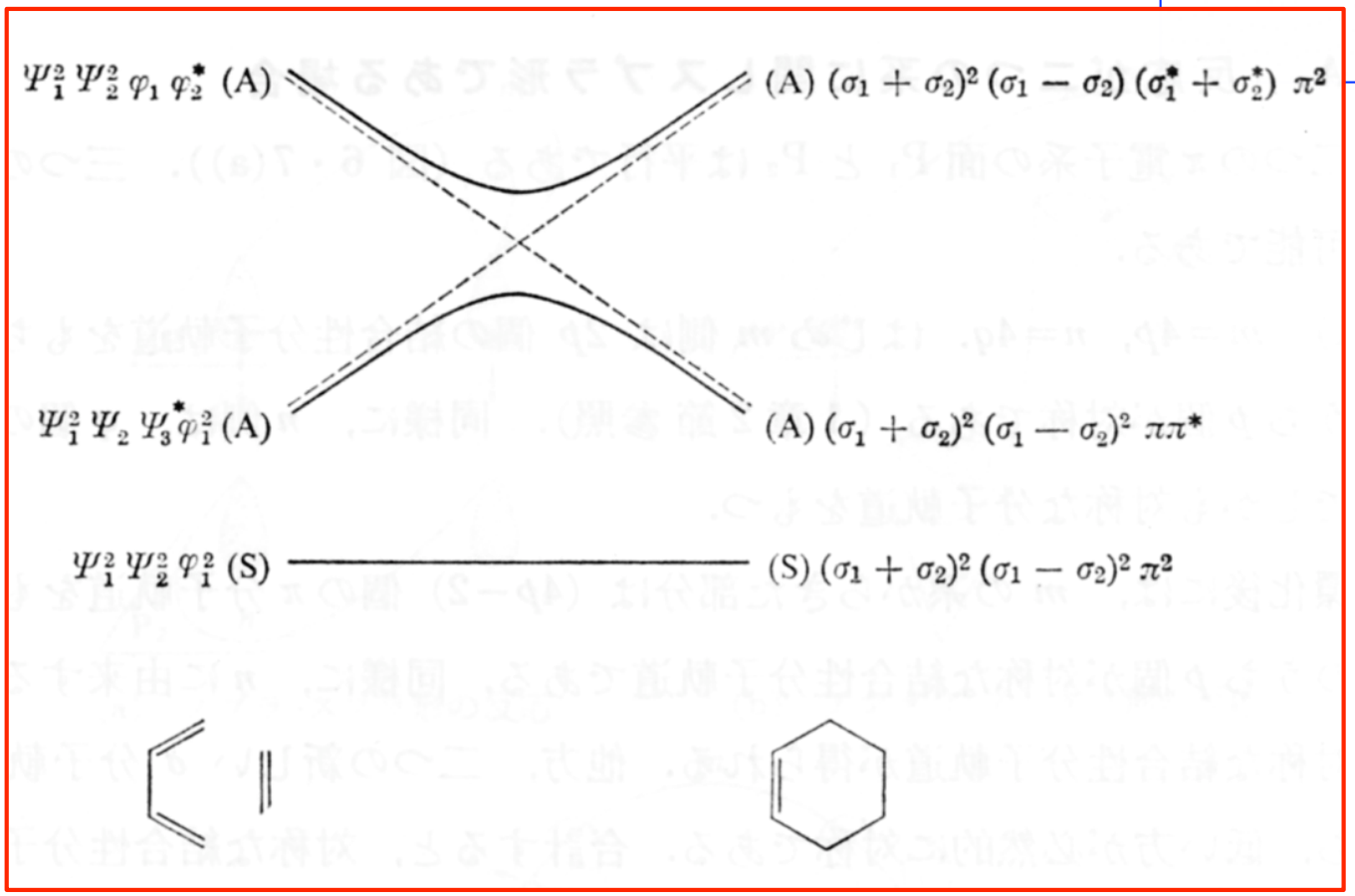


Nguyen Trong Anh著「ウッドワード-ホフマン則」（東京化学同人）

[4+2]cycloaddition reactions

Electron-configuration-correlation diagram:





Explain:

In [4+2] supra-supra, thermally allowed, and photo forbidden.

(Antara-antara and supra-supra have symmetrically the same meaning.
Supra-antara and antara-supra have the same meaning.)