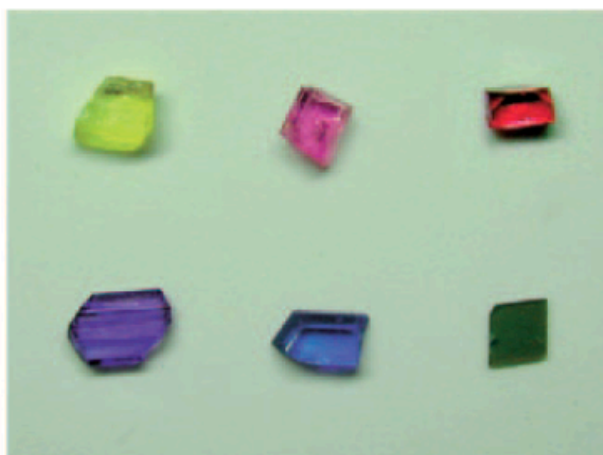
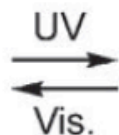
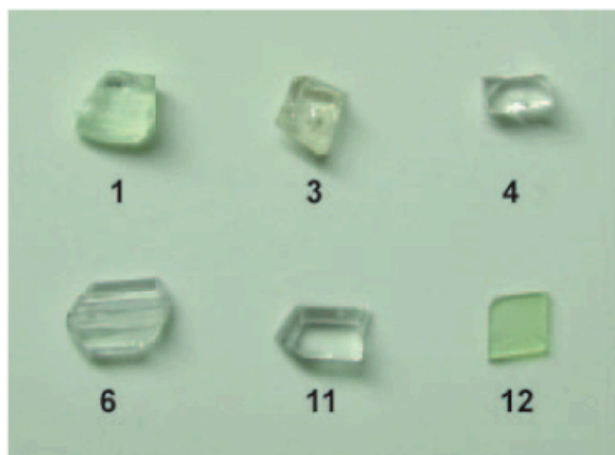
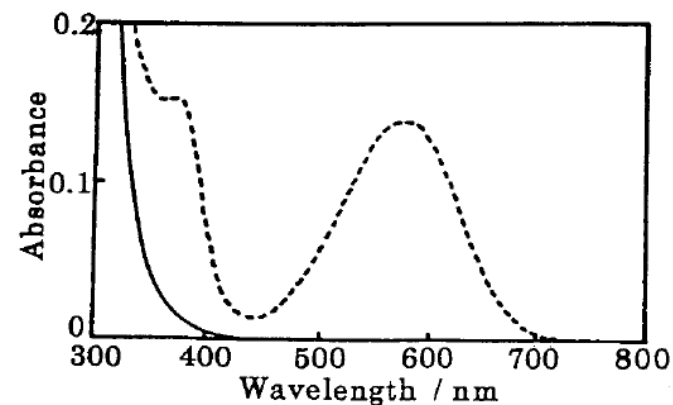
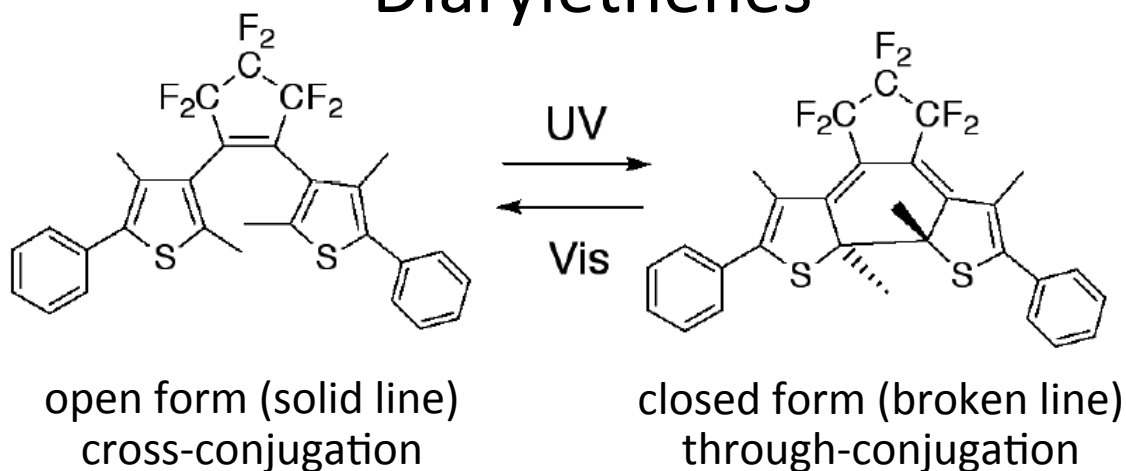


Solid state chemistry

ex.1) photochromic materials

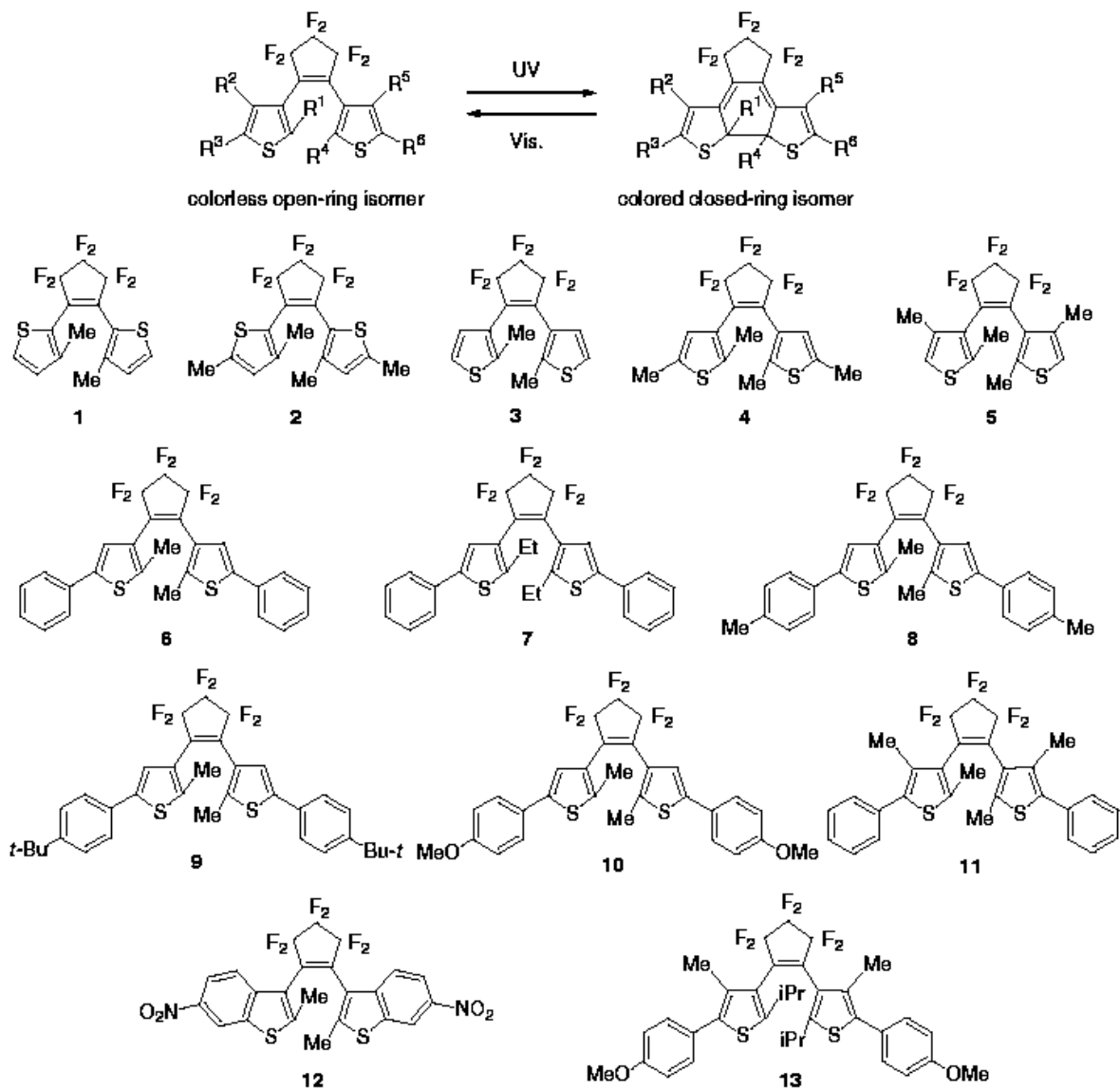
Diarylethenes



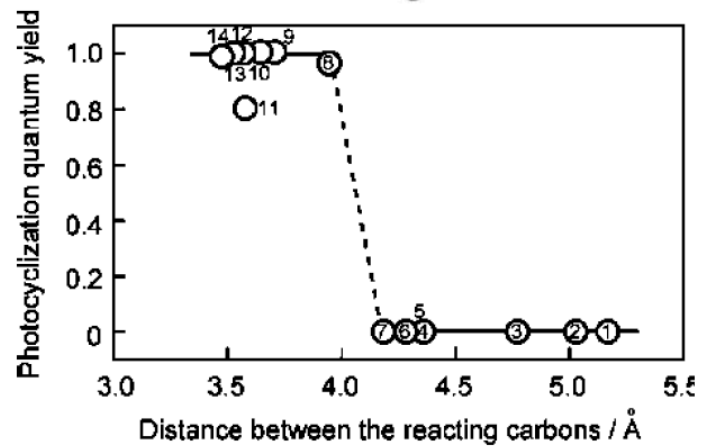
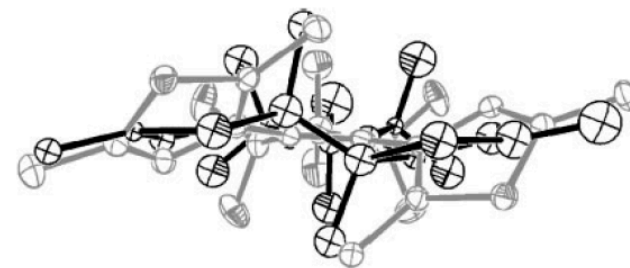
M. Irie et al.,
Bull. Chem. Soc. Jpn.,
2004, *77*, 195.

Solid state chemistry

ex.1) photochromic materials



Reaction – structure relation



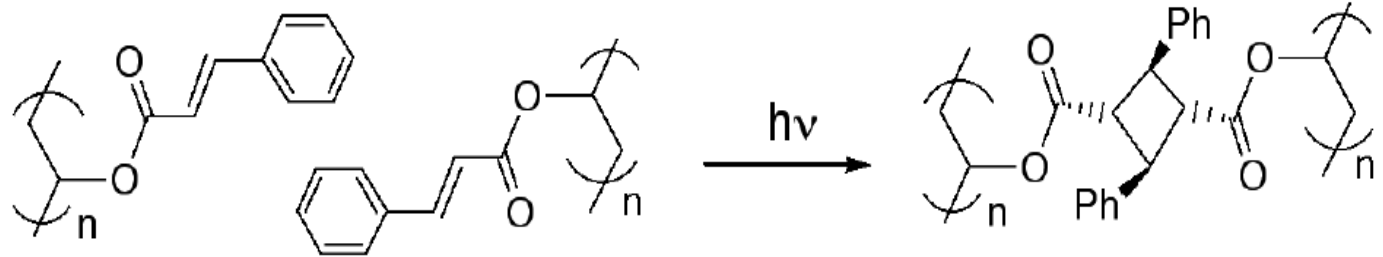
M. Irie et al.,
Bull. Chem. Soc. Jpn.,
2004, *77*, 195.

Fig. 4. Diarylethene derivatives showing single-crystalline photochromism.

Solid state chemistry

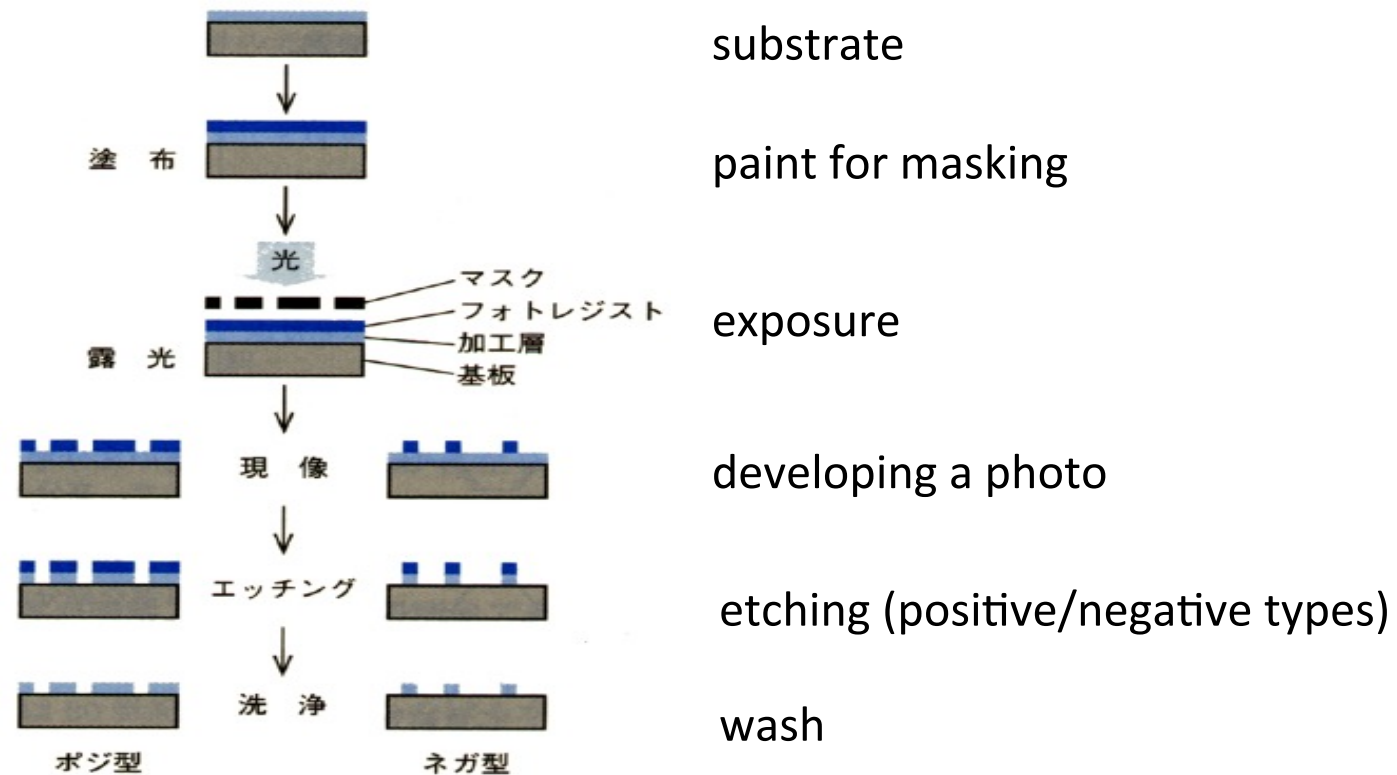
ex.2) photoresist

KPR (Kodak Co. Ltd.)



cross-linked polymers

lithography:

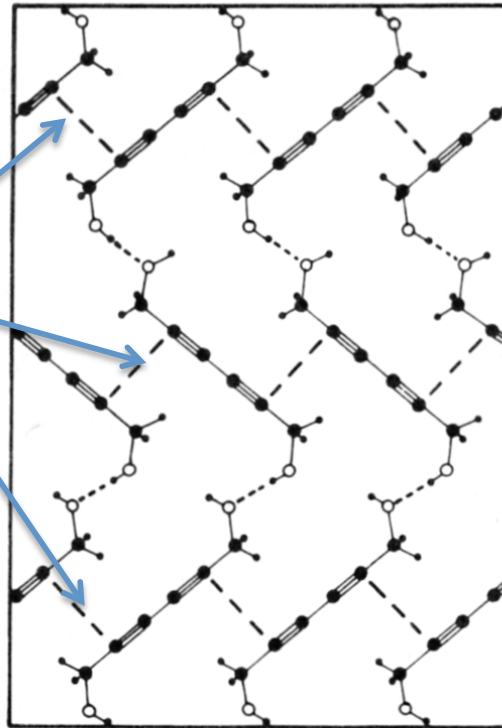


Solid state chemistry

ex.3) photo-polymerization

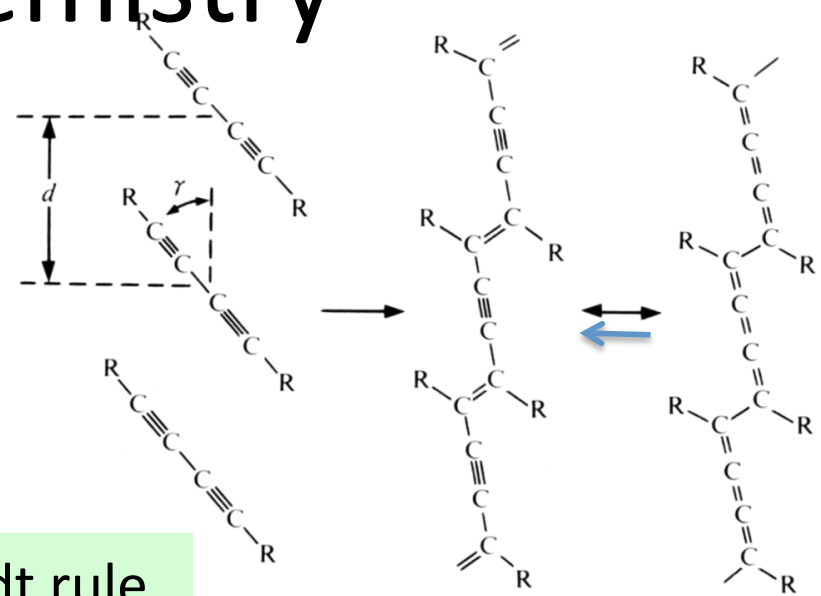
Crystal structure of diacetylenes

Reactive carbon atoms



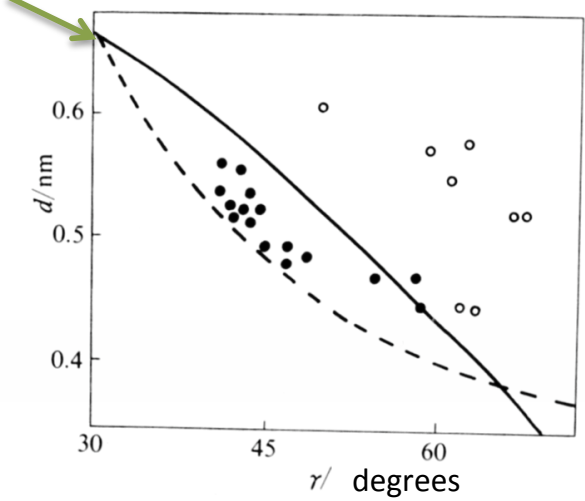
- = C
- = O
- = H
- = hydrogen bonds
- - - = C-C bonds to come

Hydrogen bonding helps molecular arrangement suitable for photo-polymerization



Schmidt rule boundary

reaction scheme



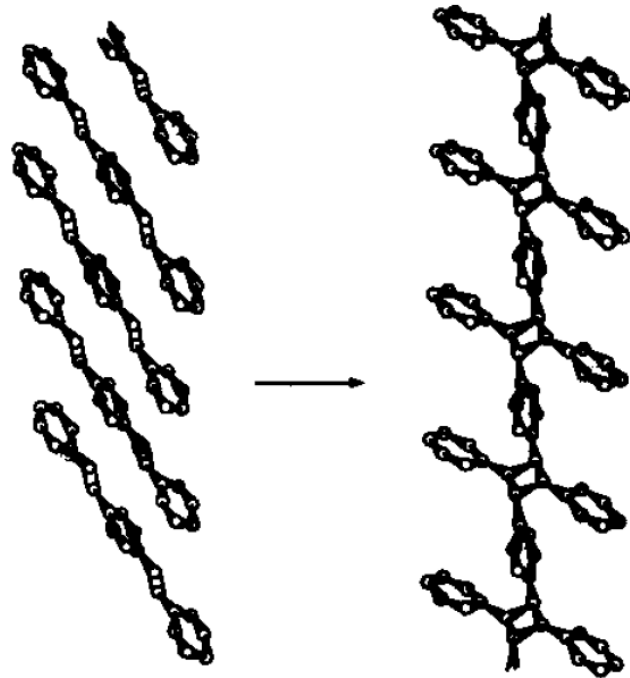
- = reactive
- = non-reactive

Reactivity – geometry relationship

“Molecular Crystals” by J.D.Wright

Solid state chemistry

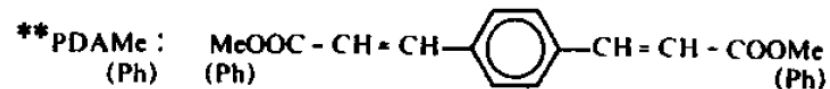
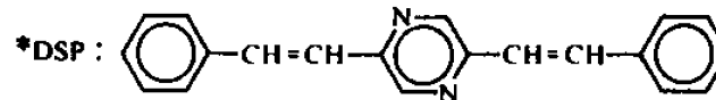
ex.3) photo-polymerization



α -phase distylylpyrazine (DSP)

Table. The cell parameters of reactive DSPs

化合物	空間群	a (α)	b (β)	c (/nm) (γ) ($^\circ$)	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	

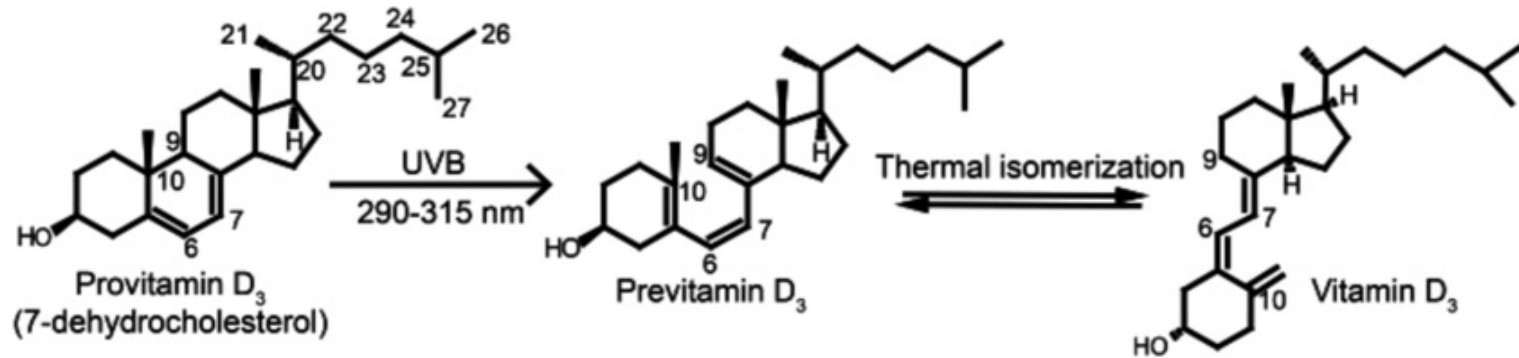
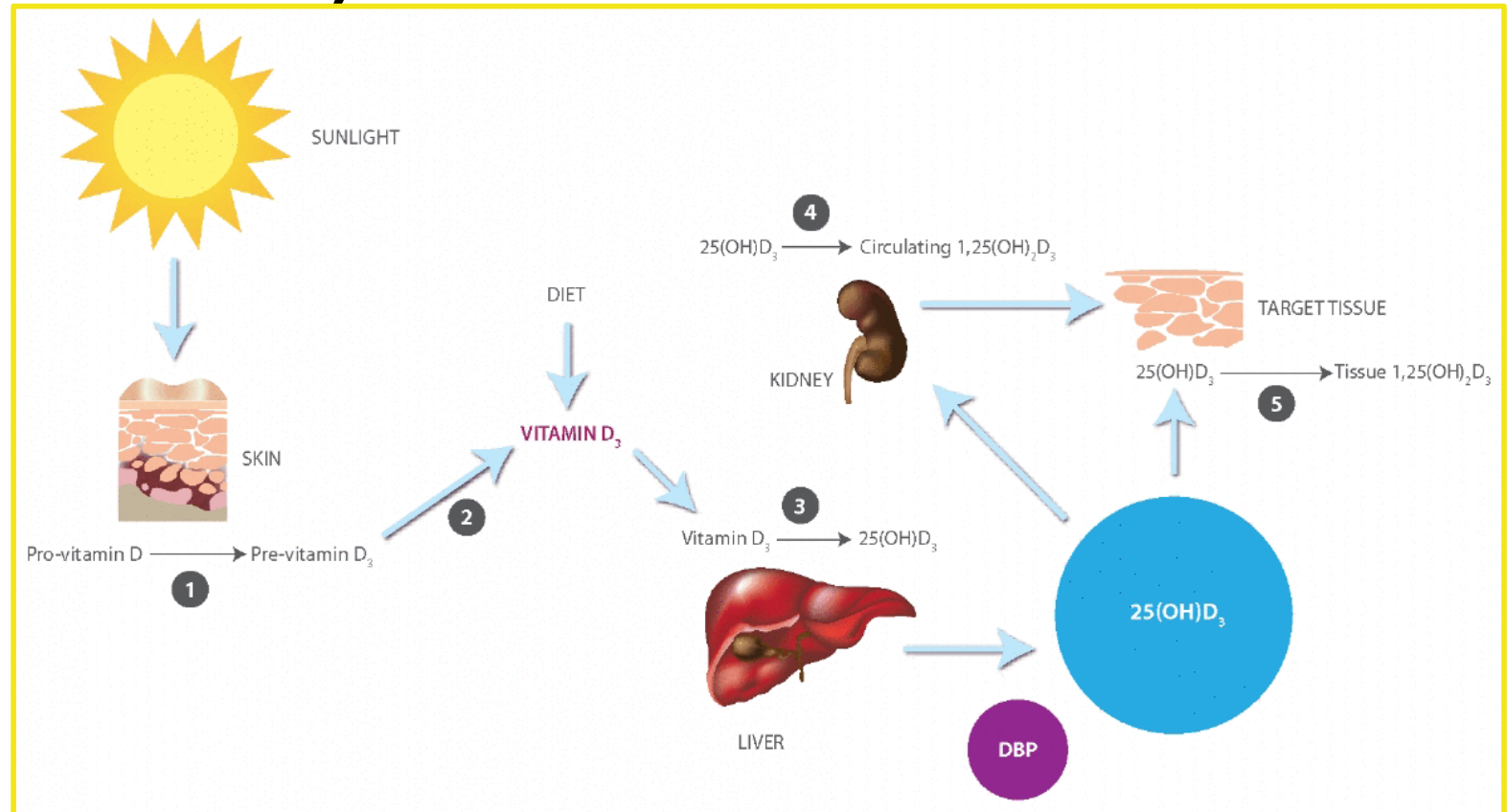


Explain why $2\pi + 2\pi$ cycloaddition reactions are allowed in photo-process and forbidden in thermal-process.

Solid state chemistry

ex.2) 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

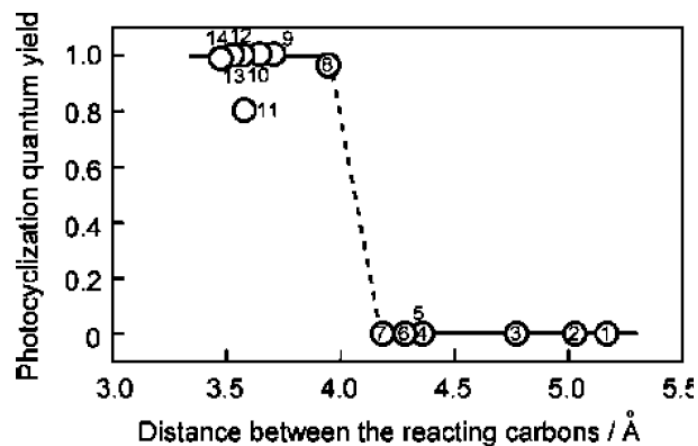


Schmidt rule (0.4 nm rule)

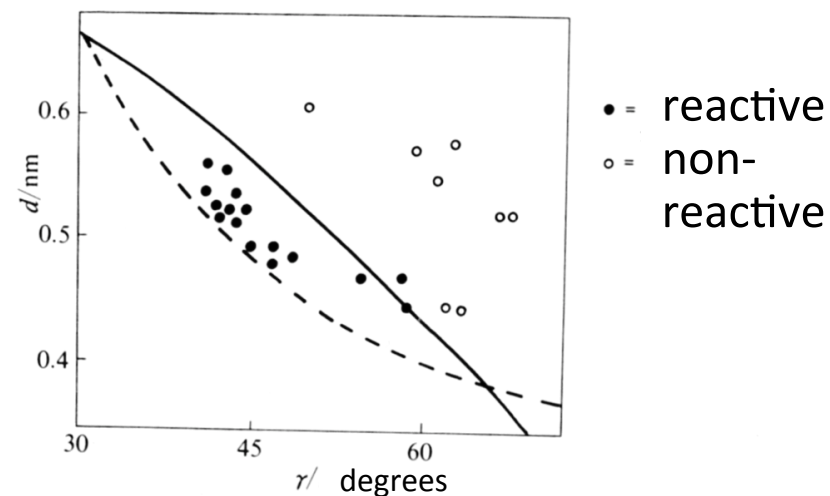
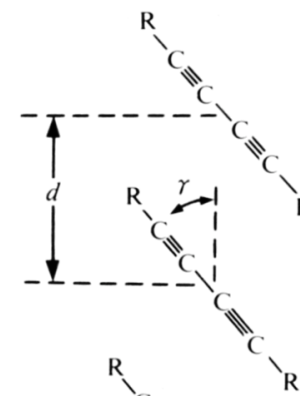
Photoreaction requires “parallel arrayed double bonds” and “the interatomic distance within 0.4 nm.”

G. M. J. Schmidt, *Pure Appl. Chem.* **1971**, 27, 647.

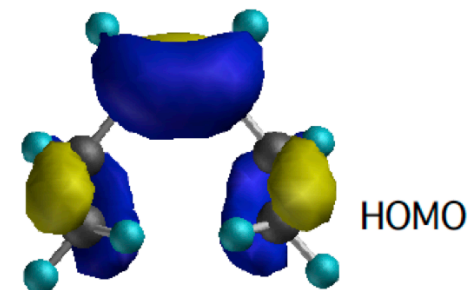
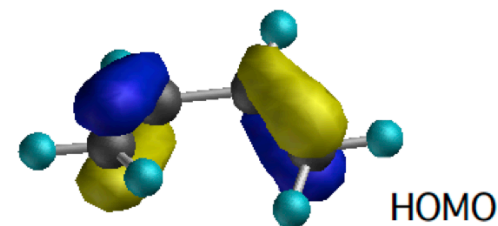
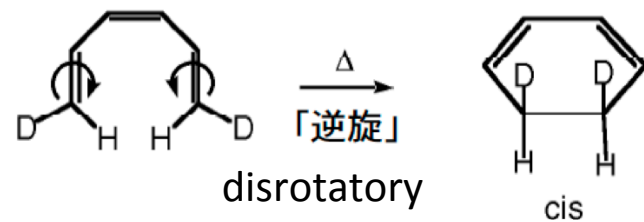
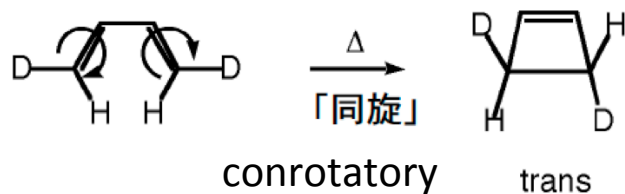
Diarylethenes
(intramolecular)



Diacetylenes
(intermolecular)



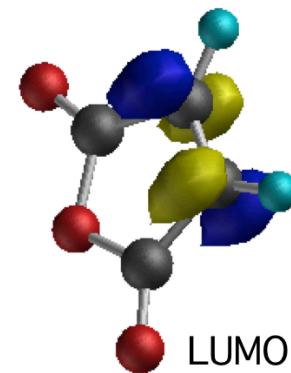
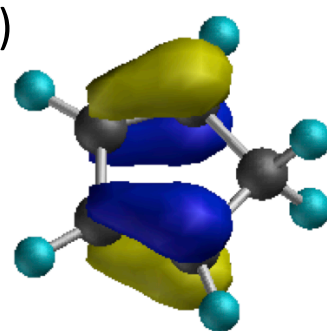
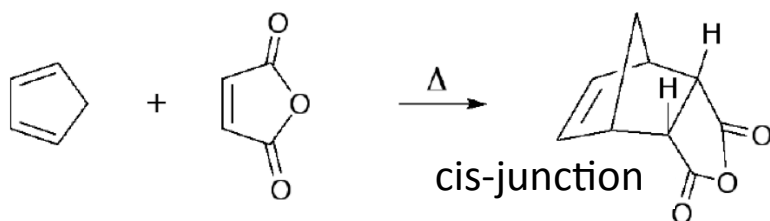
Pericyclic reactions (in polyenes)



Selectivity

number of π electrons	=	$4n$	therm. conrot.	photo. disrot.
		$4n+2$	therm. disrot.	photo. conrot.

Cycloaddition reactions (Diels-Alder reaction)



Selectivity for $i+j$ π electron systems

number of π electrons	=	$4n$	therm. forbidden	photo. allowed
		$4n+2$	therm. allowed	photo. forbidden

Motivation and stepwise goals:

Run a Hückel MO program in your PC.

Clarify the properties and reactivities of polyenes and aromatics.

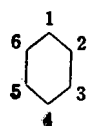
Explain the selectivity in pericyclic reactions and cycloadditions.

Predict properties of C₆₀ and related molecules.

How to make a secular equation (a case study on benzene)

3-1 永年方程式の作り方

いま、ベンゼンを例にとってその永年方程式を作ってみよう。各頂点にある炭素原子に左図のように1,2...6の番号をつける。すると理屈は一応あとまわしにして、次のような6個の斉1次連立方程式が書ける。



$$\left. \begin{aligned} c_1\lambda &= c_2 + c_6 \\ c_2\lambda &= c_1 + c_3 \\ c_3\lambda &= c_2 + c_4 \\ c_4\lambda &= c_3 + c_5 \\ c_5\lambda &= c_4 + c_6 \\ c_6\lambda &= c_1 + c_5 \end{aligned} \right\}$$

linear simultaneous equations based on the numbering of 2p_z AOs (χ_i).

(2.20)

c_i is a coefficient of χ_i in LCAO MO ϕ .

ここで c_1, c_2, \dots, c_6 は、ベンゼンの分子軌道 ϕ を各炭素原子の $2p\pi$ 原子軌道の1次結合で

$$\phi = c_1\chi_1 + c_2\chi_2 + \dots + c_6\chi_6 \quad (2.21)$$

と表わしたときの係数である。λについてはあとでその意味は明らかになるので、ここでは一応 $\lambda = (\epsilon - \alpha) / \beta$ という値であることをしるしておく。

(2.20) 式を書きおろす要領としては、たとえば1の原子については $c_1\lambda$ とし、これが隣の原子の原子軌道の係数の和に等しいとして $c_1\lambda = c_2 + c_6$ という式を作る。以下同様にして、隣の原子だけを考え他は無視すると、各原子について同じような式が作られるから、ベンゼンの場合(2.20)式が直ちに書きおろせることになる。

2節でも述べたように、LCAO MO 法においては1電子の有効ハミルトニアンを \mathbf{h} とすると、分子軌道 ϕ に対するエネルギー ϵ は

$$\epsilon = \frac{\int \phi \mathbf{h} \phi d\tau}{\int \phi \phi d\tau}$$

ϵ is an expected energy for ϕ .

(2.23)

で与えられ、この式中の ϕ に(2.21)式を代入すると

Substitute ϕ of (2.21) into (2.23).

without reason at this stage !

$$\varepsilon = \frac{(c_1^2\alpha_1 + c_2^2\alpha_2 + \dots + c_6^2\alpha_6) + 2(c_1c_2\beta_{12} + c_1c_3\beta_{13} + \dots)}{(c_1^2 + c_2^2 + \dots + c_6^2) + 2(c_1c_2S_{12} + c_1c_3S_{13} + \dots)} \quad (2.24)$$

となる。ただしここで $\alpha_r, \beta_{rs}, S_{rs}$ は

α : Coulomb integral

β : resonance integral

S : overlap integral

$$\left. \begin{aligned} \alpha_r &= \int \chi_r \mathbf{h} \chi_r d\tau \\ \beta_{rs} &= \int \chi_r \mathbf{h} \chi_s d\tau \\ S_{rs} &= \int \chi_r \chi_s d\tau. \end{aligned} \right\} \begin{matrix} \\ \\ (r=1,2,\dots,6) \\ (s=1,2,\dots,6) \end{matrix} \quad (2.25)$$

なる積分を表わし、それぞれクーロン積分、共鳴積分、重なり積分と呼ばれることは2節で説明したとおりである。なお、(2.24)式を導く際、各原子軌道関数は規格化されているとして

χ_i is normalized.

$$\int \chi_r \chi_r d\tau = S_{rr} = 1 \quad (2.26)$$

という条件を使い、また β_{rs} が β_{sr} に等しいことも用いている。またベンゼンの各炭素原子はすべて等価であるから、クーロン積分はすべて等しく、かつ炭素、炭素間の距離が皆等しいので共鳴積分も同じ値になることは容易に理解できる。すなわち、これらを今それぞれ α, β と置くと

Hückel approximation on α .

Hückel approximation on β .

$$\left. \begin{aligned} \alpha_1 &= \alpha_2 = \dots = \alpha_6 = \alpha \\ \beta_{12} &= \beta_{23} = \dots = \beta_{56} = \beta_{61} = \beta \end{aligned} \right\} \quad (2.27)$$

となる。この α, β はベンゼン分子についてのクーロン積分、共鳴積分と呼ばれるものである*。これらをパラメーターにしてエネルギーを表わすのは非常に簡単でしかも便利であり、この方法を π 電子の **Hückel 法** という。

さて、(2.24)式中の隣合わない原子軌道間の共鳴積分はかなり小さくなるので(距離が大きくなって)、ゼロと近似しても結果には大きな影響はないだろう。したがって

Hückel approximation on β #2.

$$\beta_{13} = \beta_{14} = \beta_{24} = \dots = 0 \quad (2.28)$$

とし、また重なり積分はすべて無視する。すなわち

Hückel approximation on S .

$$S_{12} = S_{13} = S_{14} = S_{23} = S_{24} = \dots = 0 \quad (2.29)$$

上のような近似を置くと、(2.24)式は

(2.24) is simplified as:

$$\varepsilon = \frac{(c_1^2 + c_2^2 + \dots + c_6^2)\alpha + 2(c_1c_2 + c_2c_3 + \dots)\beta}{c_1^2 + c_2^2 + \dots + c_6^2} \quad (2.30)$$

となつてかなり簡単な形になる。2節で述べたように、 ε が極小値をとるための条件は

Energy-minimizing conditions: $\frac{\partial \varepsilon}{\partial c_r} = 0 \quad (r=1, 2, \dots, 6) \quad (2.31)$

であるからこれより次の6個の式が得られる。

Combining (2.30) and (2.31) gives:

$$\left. \begin{aligned} c_1(\alpha - \varepsilon) + c_2\beta + c_6\beta &= 0 \\ c_1\beta + c_2(\alpha - \varepsilon) + c_3\beta &= 0 \\ c_2\beta + c_3(\alpha - \varepsilon) + c_4\beta &= 0 \\ c_3\beta + c_4(\alpha - \varepsilon) + c_5\beta &= 0 \\ c_4\beta + c_5(\alpha - \varepsilon) + c_6\beta &= 0 \\ c_1\beta + c_5\beta + c_6(\alpha - \varepsilon) &= 0 \end{aligned} \right\} \quad (2.32)$$

これらの各式の両辺を β で割って移項すると

Rectifying (2.32) gives:

$$\left. \begin{aligned} c_2 + c_6 &= \frac{\varepsilon - \alpha}{\beta} c_1 \\ c_1 + c_3 &= \frac{\varepsilon - \alpha}{\beta} c_2 \\ c_2 + c_4 &= \frac{\varepsilon - \alpha}{\beta} c_3 \\ c_3 + c_5 &= \frac{\varepsilon - \alpha}{\beta} c_4 \\ c_4 + c_6 &= \frac{\varepsilon - \alpha}{\beta} c_5 \\ c_1 + c_5 &= \frac{\varepsilon - \alpha}{\beta} c_6 \end{aligned} \right\} \quad (2.33)$$

or in a matrix expression,

$$\begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{pmatrix} = \lambda \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{pmatrix}$$

となる。(2.33)式において $(\varepsilon - \alpha)/\beta$ を λ とおいたものが(2.20)式にほかならない。まえに天下り式にいきなり書きおろされた(2.20)式の意味が、これではっきりとわかっていただけただけのことと思う。またそのとき保留してあった λ の

The meaning of λ has been clarified as:

$$\varepsilon = \alpha + \lambda\beta \quad (2.34)$$

という形に書き表わしたときの β の係数になっていることがわかる。

米沢貞治郎、
「量子化学入門」
(化学同人)

Jacobi method (computer-friendly diagonalization)

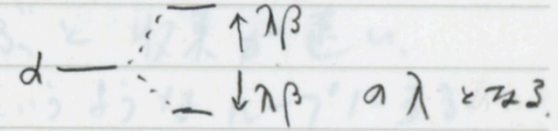
$$\begin{pmatrix} \alpha - E_1 & \beta \\ \beta & \alpha - E_1 \end{pmatrix} \begin{pmatrix} C_{11} \\ C_{12} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

eigenvalue (characteristic value) E#1

$$\begin{pmatrix} \alpha - E_2 & \beta \\ \beta & \alpha - E_2 \end{pmatrix} \begin{pmatrix} C_{21} \\ C_{22} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

eigenvalue (characteristic value) E#2

$$\lambda_i = (E_i - \alpha) / \beta \text{ is } \alpha' \text{ is } = \text{value of } \lambda$$



stabilization or destabilization scaled by λ_i with a unit of β .

$$\begin{pmatrix} -\lambda_1 \beta & \beta \\ \beta & -\lambda_1 \beta \end{pmatrix} \begin{pmatrix} C_{11} \\ C_{12} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\begin{pmatrix} -\lambda_1 & 1 \\ 1 & -\lambda_1 \end{pmatrix} \begin{pmatrix} C_{11} \\ C_{12} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\left[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \begin{pmatrix} -\lambda_1 & 0 \\ 0 & -\lambda_1 \end{pmatrix} \right] \begin{pmatrix} C_{11} \\ C_{12} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} C_{11} \\ C_{12} \end{pmatrix} = \lambda_1 \begin{pmatrix} C_{11} \\ C_{12} \end{pmatrix}$$

λ_1 is an eigenvalue of this matrix. The number of λ 's is 2.

$$\text{to } \lambda_2 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} C_{21} \\ C_{22} \end{pmatrix} = \lambda_2 \begin{pmatrix} C_{21} \\ C_{22} \end{pmatrix}$$

The above 2 equations are expressed as one.

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} C_{11} & C_{21} \\ C_{12} & C_{22} \end{pmatrix} = \begin{pmatrix} \lambda_1 C_{11} & \lambda_2 C_{21} \\ \lambda_1 C_{12} & \lambda_2 C_{22} \end{pmatrix}$$

$$= \begin{pmatrix} C_{11} & C_{21} \\ C_{12} & C_{22} \end{pmatrix} \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}$$

Jacobi method

$$\text{場合2} \quad \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} c_{11} & c_{21} \\ c_{12} & c_{22} \end{pmatrix} = \begin{pmatrix} c_{11} & c_{21} \\ c_{12} & c_{22} \end{pmatrix} \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}$$

$$\text{二カを} \quad \underline{HC = C\lambda} \quad \text{と書く}$$

二に 左から + = を掛けたら

もしうが 対角化できるから C^{-1} をかけたら

$$C^{-1}HC = C^{-1}C\lambda = \lambda$$

たとえば $C = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$ のとき ために $\frac{1}{\sqrt{2}}$

$$C^{-1}HC = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 2 & 0 \\ 0 & -2 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

おもしろい。つまり C^{-1} の選択は正しかった。

実際には $n \times n$ 行列の逆行列を解析的に書くのは
たか、対角行列の逆行列は行列を決めかける。

非対角項の n を $n-1$ まで行列を n まで
その累積を解ける。(ヤコビ法)

非対角項ターゲットは最も大きさを n と収束が速い。

非対角項 n が 0.00001 以下なら終了というルールがある。

Calculation of $\lambda (= C^{-1}HC)$ is the job for a computer to do. So, we have to learn only how to make H .

From the textbook of the third-year exercise class.

演習 計算化学

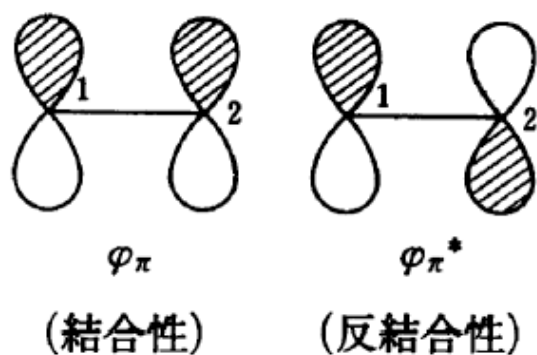
π MO of ethylene: $\text{CH}_2=\text{CH}_2$

エチレンの π と π^* の MO は、 χ_1, χ_2 をそれぞれの炭素の χ_{2pz} とすると、

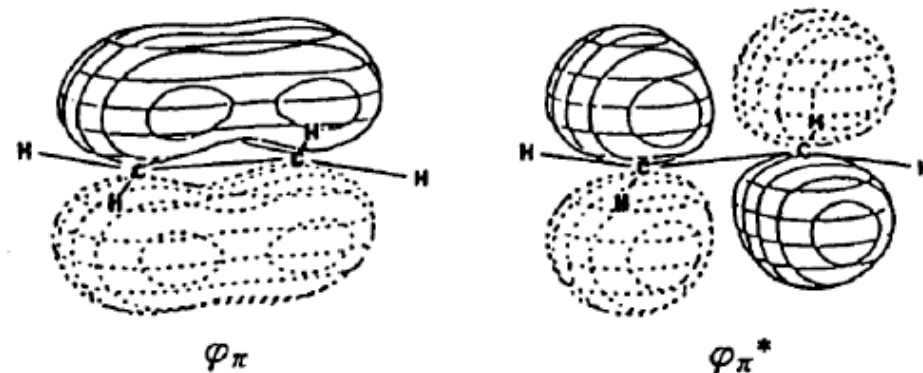
$$\varphi_2 = \varphi_{\pi^*} = 0.7071 \chi_1 - 0.7071 \chi_2$$

$$\varphi_1 = \varphi_{\pi} = 0.7071 \chi_1 + 0.7071 \chi_2$$

図 1 に、黒板に描くときの表現法と、コンピュータに描かせるときの等値曲面法を示した。



(a) 慣用的表現
handwriting way



(b) 等値曲面による表現
MO software way

図 1 エチレンの π, π^* 軌道

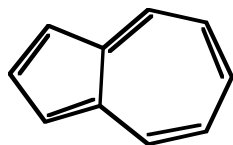
For a benzene input file;

```
benzene
  6      6
.00
1.00 .00
.00 1.00 .00
.00 .00 1.00 .00
.00 .00 .00 1.00 .00
1.00 .00 .00 .00 1.00 .00
```

説明 : Title (memo.)
The number of AOs; the number of electrons
A triangle (half) matrix, in which
in a diagonal, put 0.
in a neighboring position, put 1.
otherwise, put 0.

Try

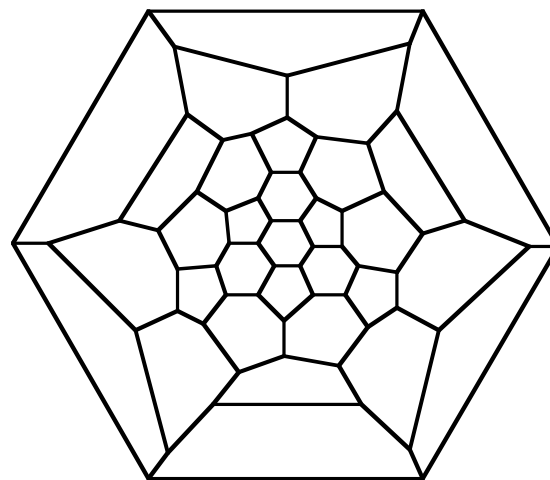
ethylene, 1,3-butadiene, 1,3,5-hexatriene, naphthalene,
anthracene, azulene, pyrene, benzyl radical/cation/anion,
fullerene[60], fullerene[70] etc.



Azulene



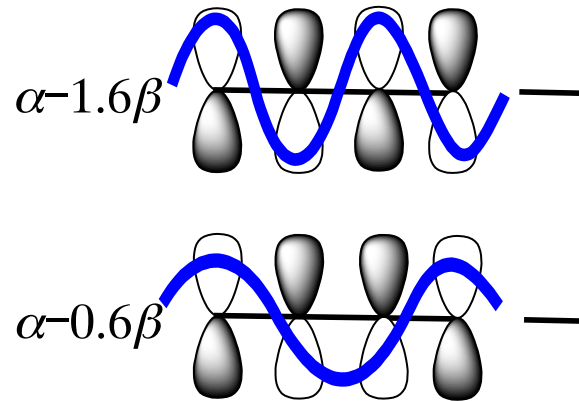
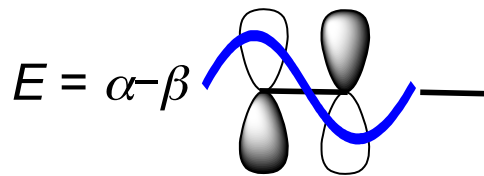
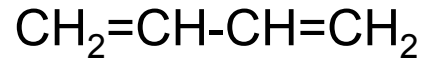
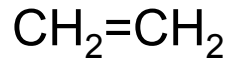
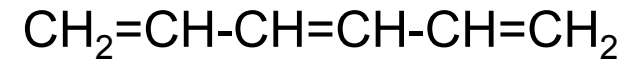
C60



C60 Schlegel diagram

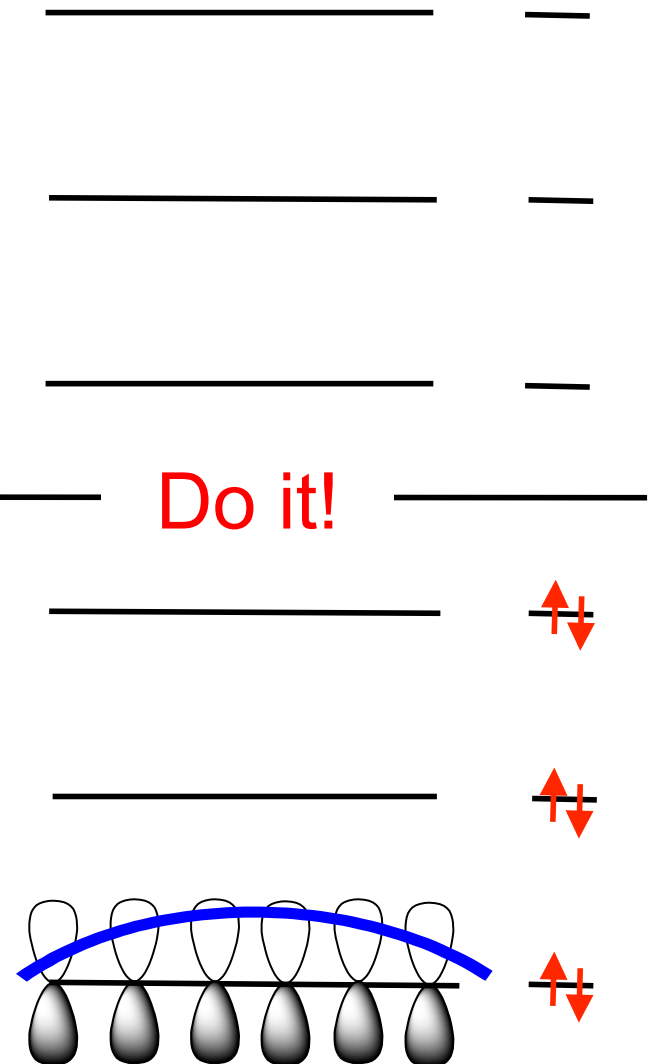
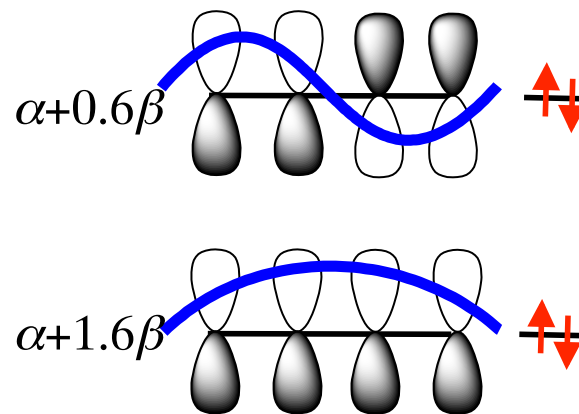
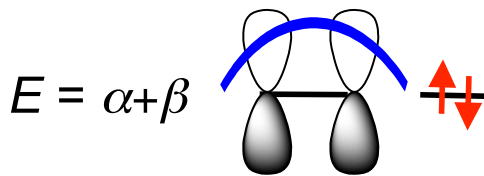
Homework:
HMO of C60.

Hückel MO on Linear Polyenes



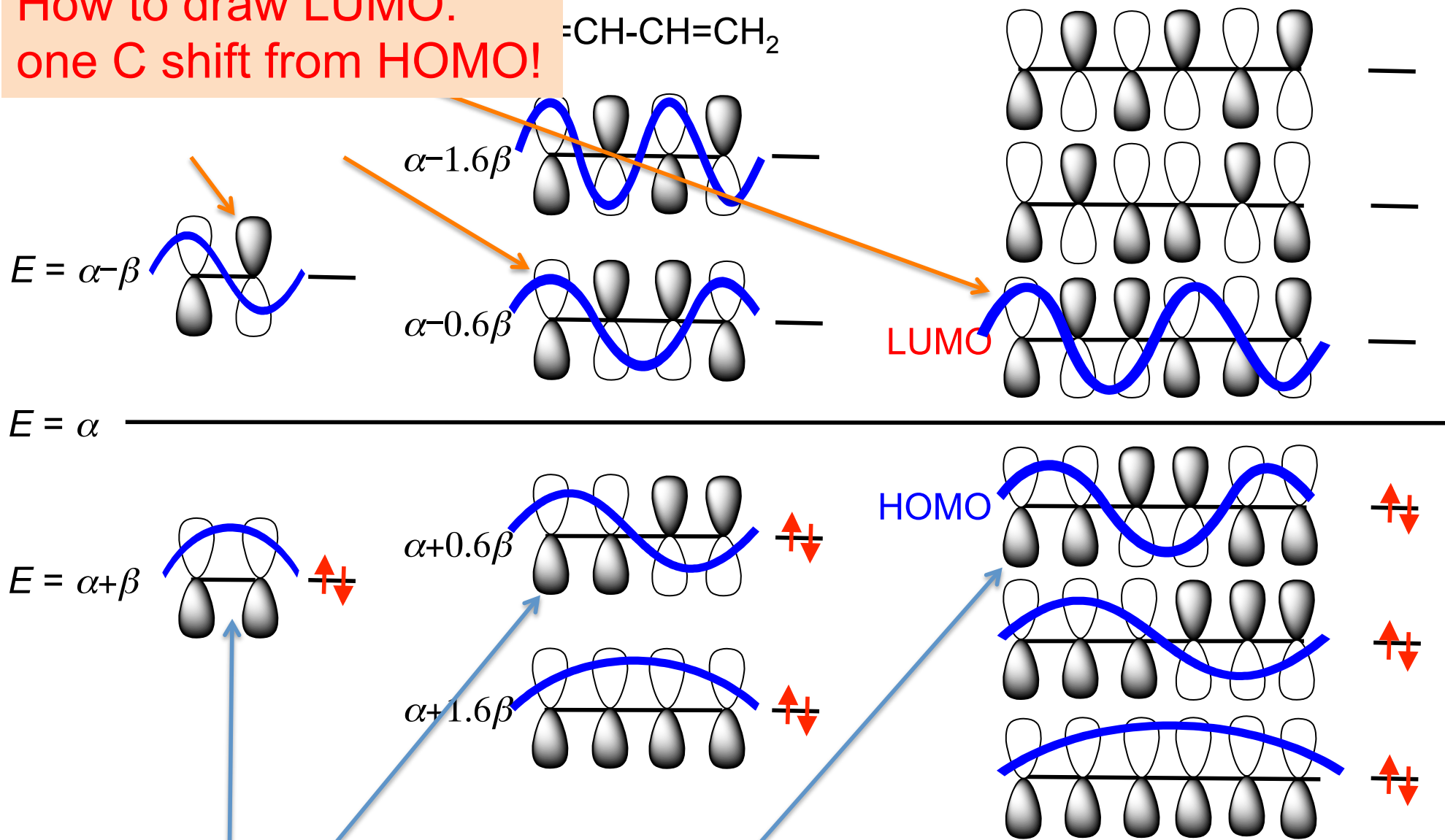
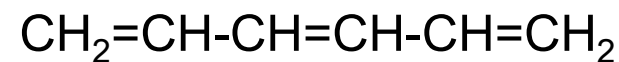
$E = \alpha$

Do it!

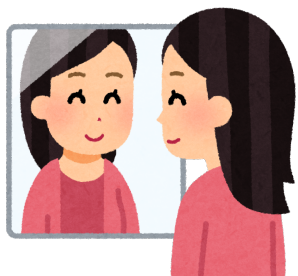


Hückel MO on Linear Polyenes

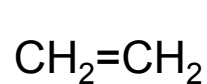
How to draw LUMO:
one C shift from HOMO!



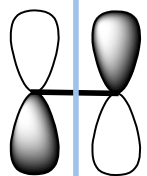
How to draw HOMO: Pairing!



Symmetry analysis of HMO on polyenes

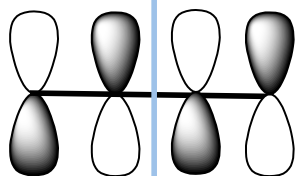
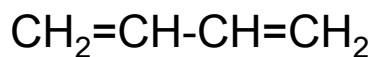


mirror

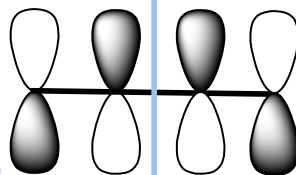


A

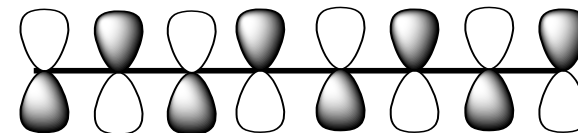
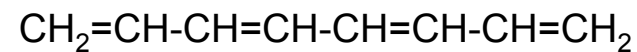
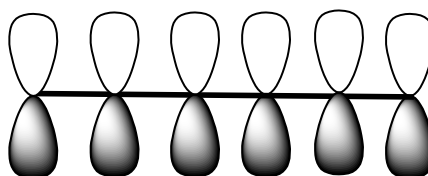
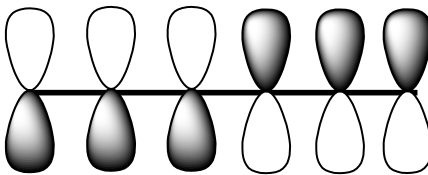
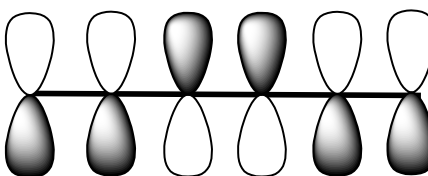
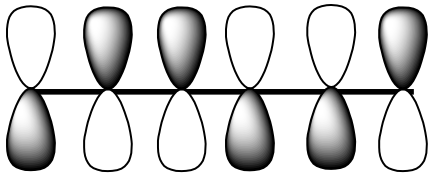
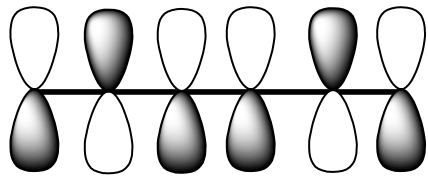
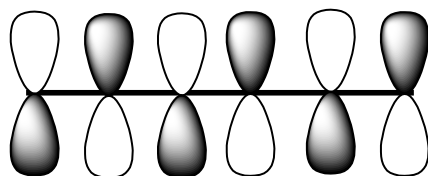
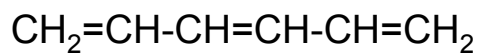
antisymmetric



A

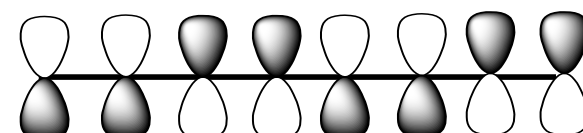
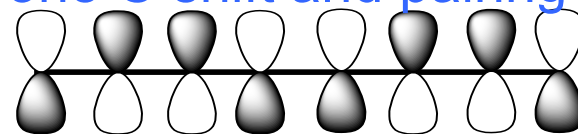


S

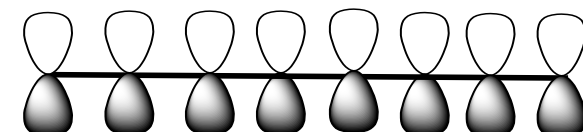


all antibonding

one C shift and pairing

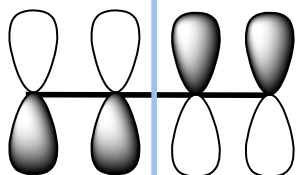


pairing

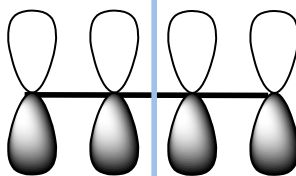


all bonding

鏡
S
symmetric



A



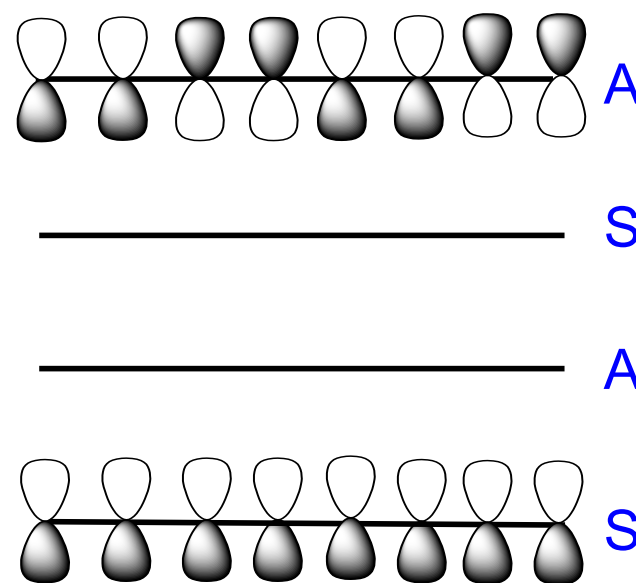
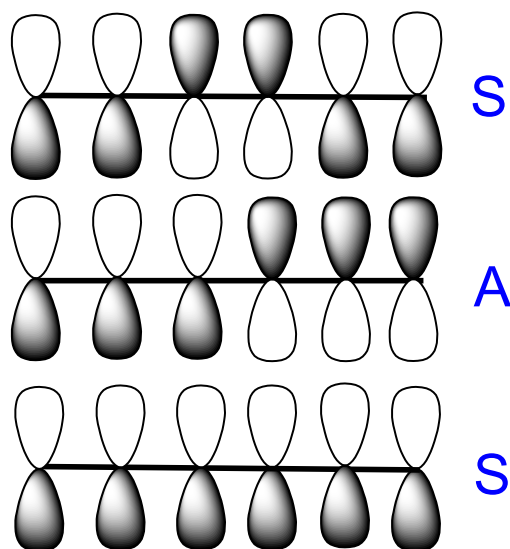
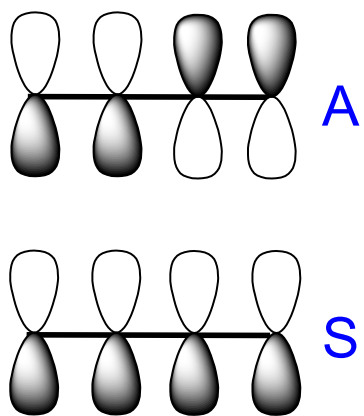
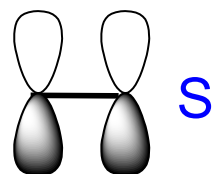
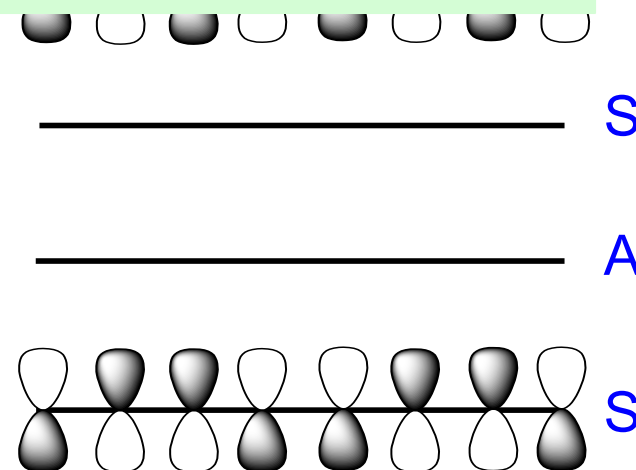
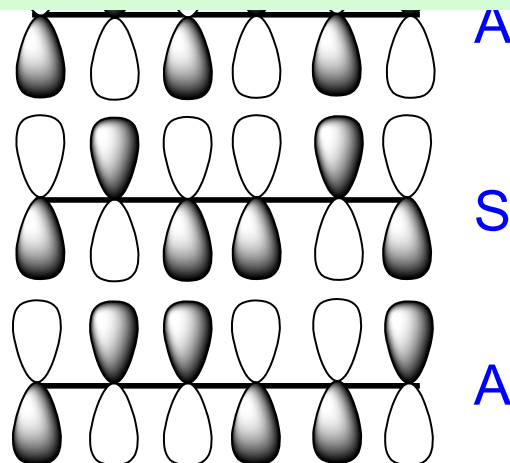
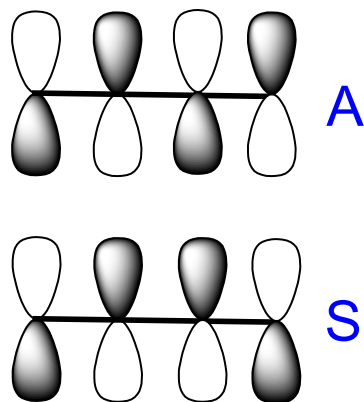
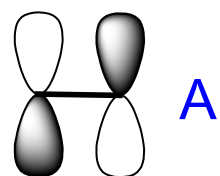
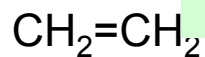
S

Think of S-A regularity.

Symmetry analysis of HMO on polyenes

S-A alternation from bottom to top.

HOMO S-A and LUMO A-S alternation as increasing C.



2

A

S

A

S

A

S

A

S

Hückel MO general solution: Frost-Musulin's method

Cyclic polyenes

$$\epsilon_j = \alpha + 2\beta \cos \frac{2\pi j}{n}$$

$$\psi_j = \sum_{\mu=1}^n C_{j\mu} \phi_{\mu}$$

$$C_{j\mu} = \sqrt{\frac{1}{n}} \exp[i2\pi j\mu/n]$$

$$j = 0, \pm 1, \pm 2, \dots, \pm \frac{n}{2}$$

$$i = \sqrt{-1}$$

Linear polyenes

$$H\psi_j = \epsilon_j H_j$$

$$\psi_j = \sum_{\mu=1}^n C_{j\mu} \phi_{\mu}$$

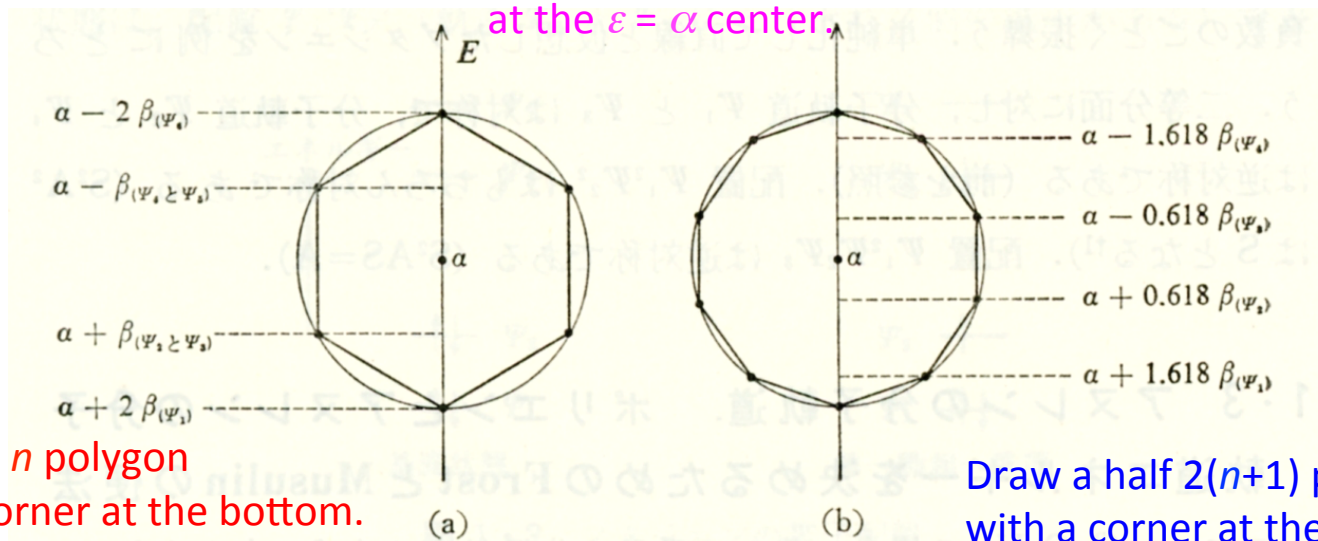
$$\epsilon_j = \alpha + 2\beta \cos \frac{j\pi}{n+1}$$

$$C_{j\mu} = \sqrt{\frac{2}{n+1}} \sin \frac{j\mu\pi}{n+1}$$

$$j = 1, 2, 3, \dots, n$$

Draw an $r = 2\beta$ circle
at the $\epsilon = \alpha$ center.

(大学院有機化学上、
講談社サイエンティフィック)



Draw an n polygon
with a corner at the bottom.

Draw a half $2(n+1)$ polygon
with a corner at the bottom

図 1・5 Frost と Musulin の方法によるベンゼンとブタジエンの分子軌道のエネルギー図

(Woodward-Hoffman rule、
N.T. Anh、東京化学同人)

A typical output file from molecular-orbital calculation softwares.

orbital energy and LCAO coeff.

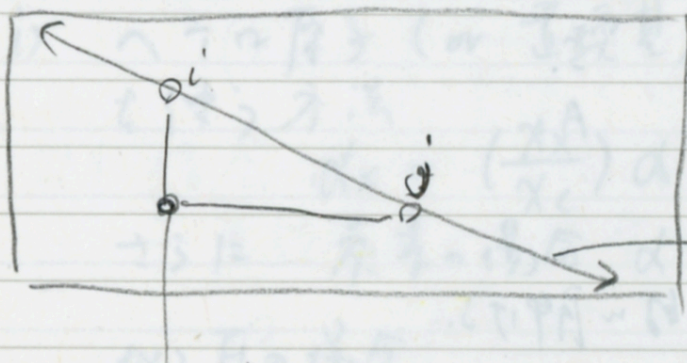
λ_1	λ_2	...
C_{11}		
C_{12}		
C_{13}		
\vdots		

Eigenvalue

Coefficients for the i^{th} eigenvalue

The sum of C_{ij}^2 equals to unity.

bond order and electron density



electron density, g_r

The π bond order between atoms i and j .

P_{rs}

To get "a chemical bond order", add 1 due to the σ bond.

$$P_{rs} = 2 \sum_{i}^{\text{occ}} C_{ri} C_{si}$$

$$g_r = 2 \sum_{i}^{\text{occ}} C_{ri}^2$$

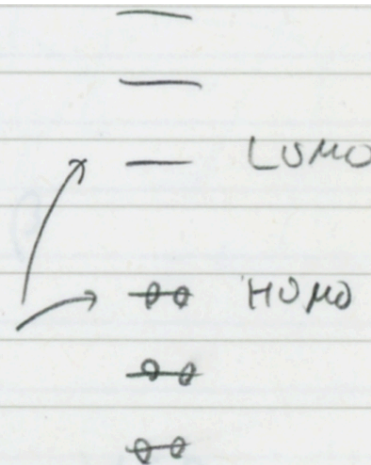
Calculated from the same loop.

Reaction coefficients for electrophilic, nucleophilic, and radical reactions.

$$f_r^{(E)} = 2 (C_r^{\text{HOMO}})^2$$

$$f_r^{(N)} = 2 (C_r^{\text{LUMO}})^2$$

$$f_r^{(R)} = (C_r^{\text{HOMO}})^2 + (C_r^{\text{LUMO}})^2$$



Only the frontier orbitals regulate reactivity.

As for radicals,

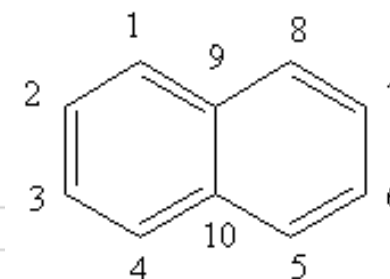
spin density ρ_r

No spin direction (α , β) in the Hückel level. The number of electron is 1 in SOMO.

$$\rho_r = (C_r^{\text{SOMO}})^2$$

Selectivity of reactions of naphthalene

Hückel results



ORBITAL ENERGIES, OCCUPANCIES, AND LCAO COEFFICIENTS									
2.3028	1.6180	1.3028	1.0000	0.6180	-0.6180	-1.0000	-1.3028	-1.6180	-2.3028
2	2	2	2	2	0	0	0	0	0
-0.3006	0.2629	0.3996	0.0000	-0.4253	0.4253	0.0000	-0.3996	-0.2629	0.3006
-0.2307	0.4253	0.1735	0.4082	-0.2629	-0.2629	-0.4082	0.1735	0.4253	-0.2307
-0.2307	0.4253	-0.1735	0.4082	0.2629	-0.2629	0.4082	0.1735	-0.4253	0.2307
-0.3006	0.2629	-0.3996	0.0000	0.4253	0.4253	0.0000	-0.3996	0.2629	-0.3006
-0.3006	-0.2629	-0.3996	0.0000	-0.4253	-0.4253	0.0000	-0.3996	-0.2629	-0.3006
-0.2307	-0.4253	-0.1735	0.4082	-0.2629	0.2629	0.4082	0.1735	0.4253	0.2307
-0.2307	-0.4253	0.1735	0.4082	0.2629	0.2629	-0.4082	0.1735	-0.4253	-0.2307
-0.3006	-0.2629	0.3996	0.0000	0.4253	-0.4253	0.0000	-0.3996	0.2629	0.3006
-0.4614	0.0000	0.3470	-0.4082	0.0000	0.0000	0.4082	0.3470	0.0000	-0.4614
-0.4614	0.0000	-0.3470	-0.4082	0.0000	0.0000	-0.4082	0.3470	0.0000	0.4614

PI BOND ORDER AND ELECTRON DENSITY									
1.0000	0.7246	0.0000	-0.3623	0.0849	0.0000	-0.1699	0.0000	0.5547	0.0000
0.7246	1.0000	0.6032	0.0000	0.0000	0.1560	0.0000	-0.1699	0.0000	-0.2409
0.0000	0.6032	1.0000	0.7246	-0.1699	0.0000	0.1560	0.0000	-0.2409	0.0000
-0.3623	0.0000	0.7246	1.0000	0.0000	-0.1699	0.0000	0.0849	0.0000	0.5547
0.0849	0.0000	-0.1699	0.0000	1.0000	0.7246	0.0000	-0.3623	0.0000	0.5547
0.0000	0.1560	0.0000	-0.1699	0.7246	1.0000	0.6032	0.0000	-0.2409	0.0000
-0.1699	0.0000	0.1560	0.0000	0.0000	0.6032	1.0000	0.7246	0.0000	-0.2409
0.0000	-0.1699	0.0000	0.0849	-0.3623	0.0000	0.7246	1.0000	0.5547	0.0000
0.5547	0.0000	-0.2409	0.0000	0.0000	-0.2409	0.0000	0.5547	1.0000	0.5182
0.0000	-0.2409	0.0000	0.5547	0.5547	0.0000	-0.2409	0.0000	0.5182	1.0000

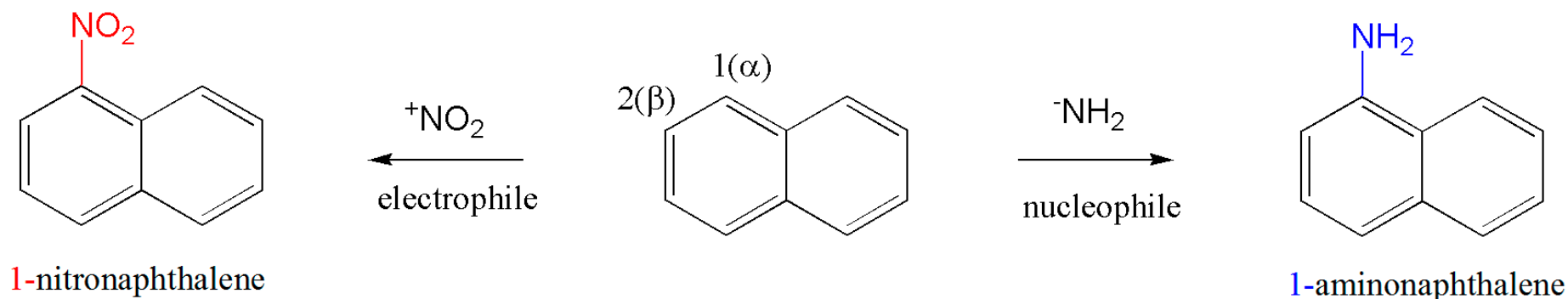
ρ_{π} is shown in a diagonal element.

All unity!

Reactions occur between a nucleophile and an electrophile.



In a naphthalene molecule, every carbon atom carries a completely neutral charge, because $\rho_{\pi} = 1$ appears at every carbon.

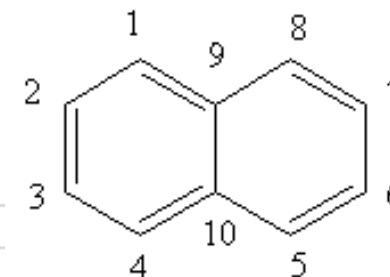


Both electrophilic and nucleophilic reagents are ready to bond at the 1-(α -) position of naphthalene.

Charge is NOT a reason for the selectivity.

Selectivity of reactions of naphthalene

Hückel results



ORBITAL ENERGIES, OCCUPANCIES, AND LCAO COEFFICIENTS

Energy	Occupancy	LCAO Coefficients																			
2.3028	2	0.3618	0.3618	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	
1.6180	2	0.3618	0.3618	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
1.3028	2	0.3618	0.3618	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
1.0000	2	0.3618	0.3618	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.6180	2	0.3618	0.3618	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
-0.0180	0	0.3618	0.3618	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
-1.0000	0	0.3618	0.3618	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
-1.3028	0	0.3618	0.3618	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
-1.6180	0	0.3618	0.3618	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
-2.3028	0	0.3618	0.3618	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

FR(E) and FR(N) are highlighted in red and blue boxes respectively. Red arrows point to the HOMO (0.6180) and LUMO (-0.0180) orbitals. Blue arrows point to the HOMO (0.6180) and LUMO (-0.0180) orbitals.

Frontier electron density (orbital density)

“Look at the frontier (HOMO and LUMO) only.”

Electrophilic reaction coefficient (when a reagent is electrophilic)

$$fr^E_1 = 2C_{1(\text{HOMO})}^2$$

Nucleophilic reaction coefficient (when a reagent is nucleophilic)

$$fr^N_1 = 2C_{1(\text{LUMO})}^2$$

【from Fukui's work】