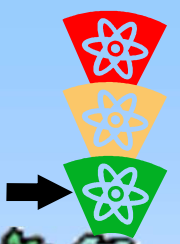


# Colorants (dyes and pigments)



# Dyes and pigments



## High VIS light absorption

### Dyes:

- high affinity to fibers, fastness (stability on fibers)
- dyes are applied from liquid solution

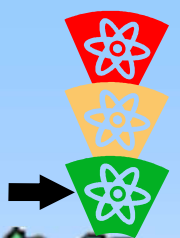


### Pigments (color pigments):

- Insoluble in water
- other properties similar as dyes, but without affinity to fibers



# Natural dyes



Natural dyes : Limited number of products

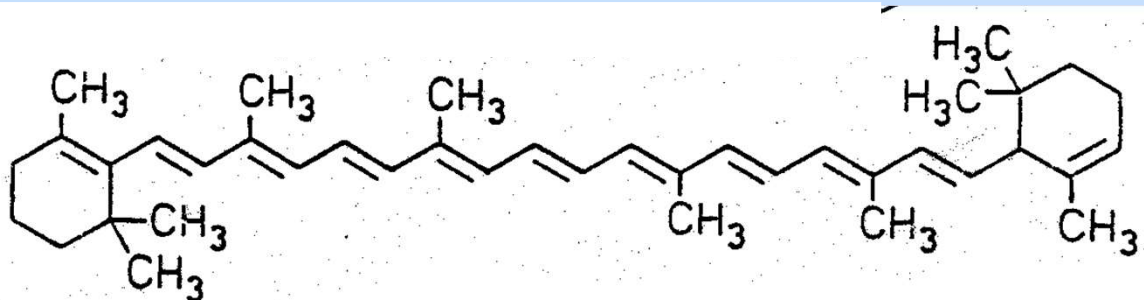
Non productive dyeing (low affinity to fibers)

No bright (brilliant) color

Low fastness

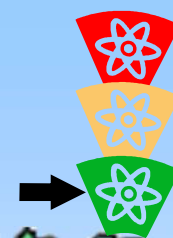
For light absorption is necessary system of conjugated double bond, in nature many different structures:

**$\beta$ -carotene (C.I.75130) - from carrot**





# Natural dyes



Useful structures:

## Indigo (C.I.75780)

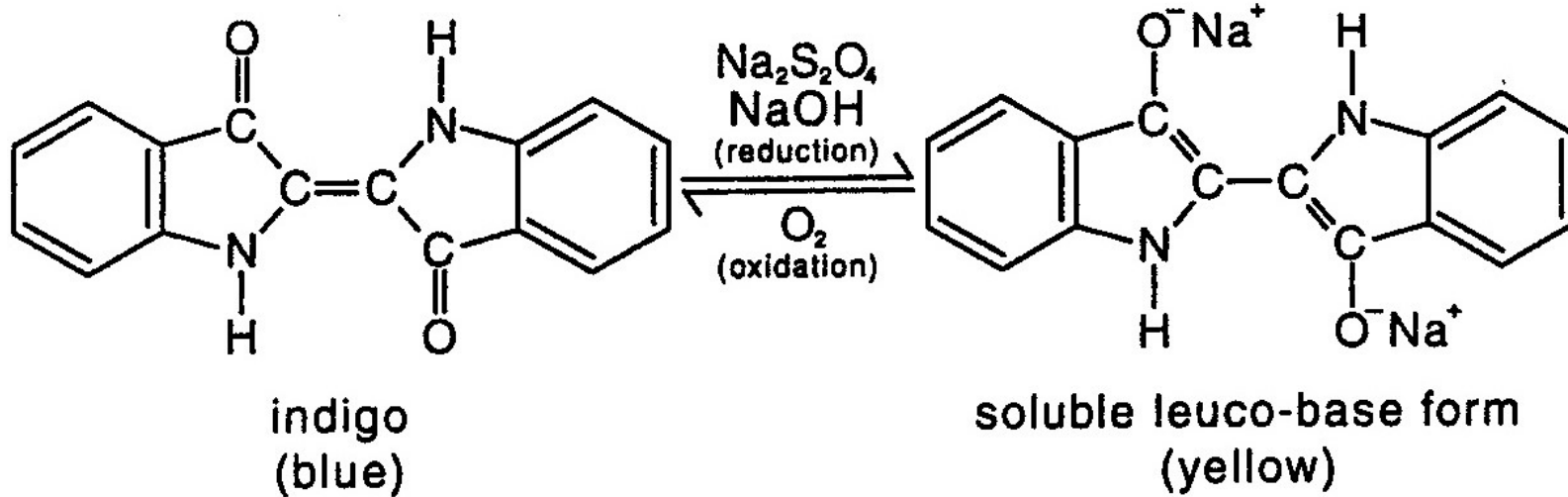
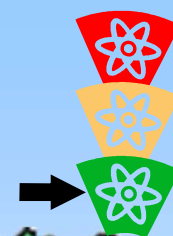
- from plants (*Indigofera tinctoria*)
- ideal fastness

indigo



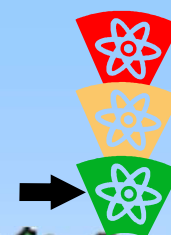


# Natural dyes



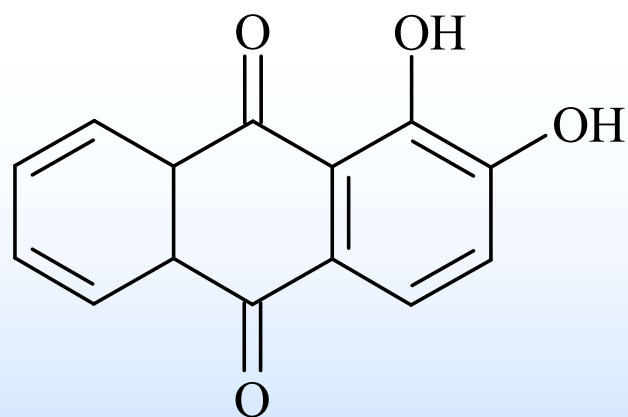


# Natural dyes

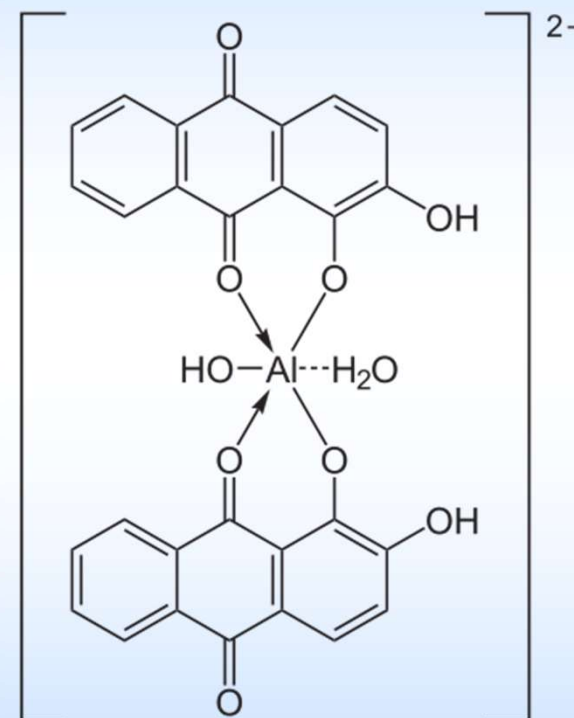


## Alizarin (C.I.75330)

- from plants (*Rubia tinctorium*)
- color pigments with metal ions (Mordant: Al, Fe, Cu...)



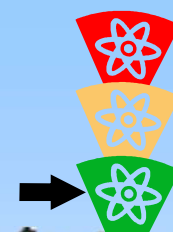
alizarin



Indigo + alizarin: aromatic, heterocyclic structures  
were chemically imitated



# History of Synthetic Dyes

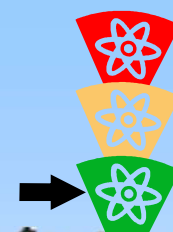


- Limited range of natural dyes - about 20-30 dyes
- Consequence of Industrial revolution was a high energy demand – resulted in piles of tars. They drew interested organic chemists
- First synthesized dye – Mauvein by William Henry Perkins in 1856.
- First attempts in dye production – copying nature.  
Synthesis of indigo was once regarded as a great achievement in organic synthesis

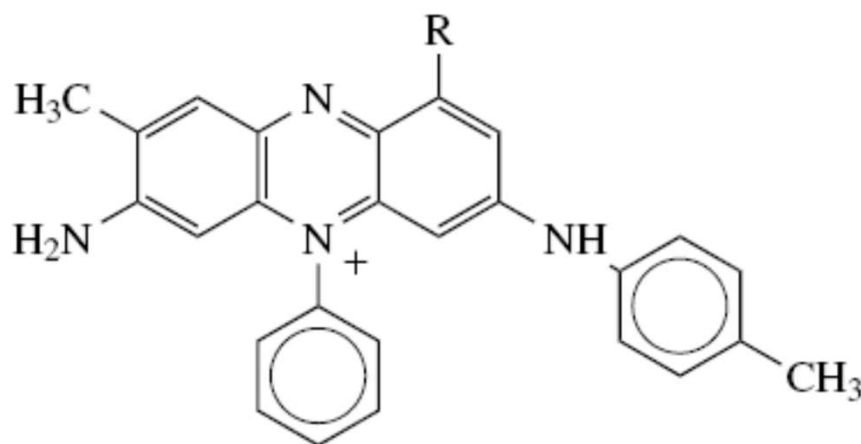
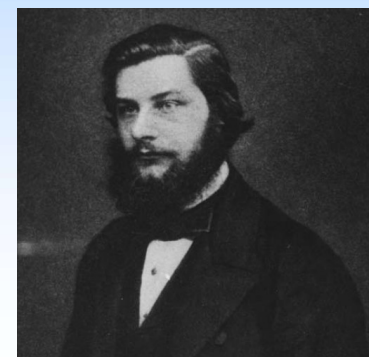




# History of Synthetic Dyes



**In 1856, William Henry Perkin, while experimenting with coal tar in hopes of finding an artificial quinine as a cure for malaria, discovered the first synthetic dyestuff which he called "Mauveine".**



mauveine

(Tyrian purple, aniline purple)

R = H

R = CH<sub>3</sub> (minor component)

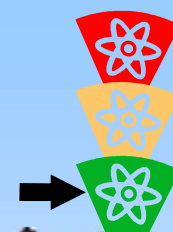
**By successive nitration**

**of benzene to nitrobenzene, with mixed sulfuric and nitric acids, reduction of the nitro compound**

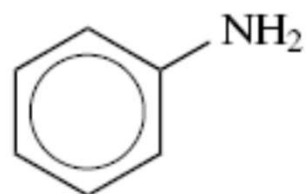
**to aniline, with iron and acid, and oxidation, the colorant was obtained.**



# Indigo - synthesis

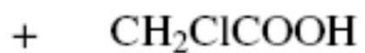


## Manufacture

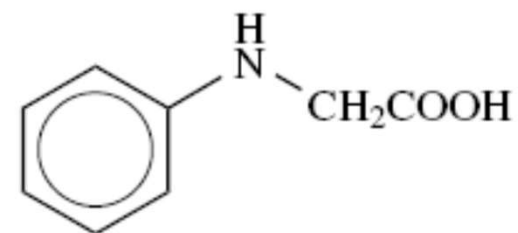


aniline

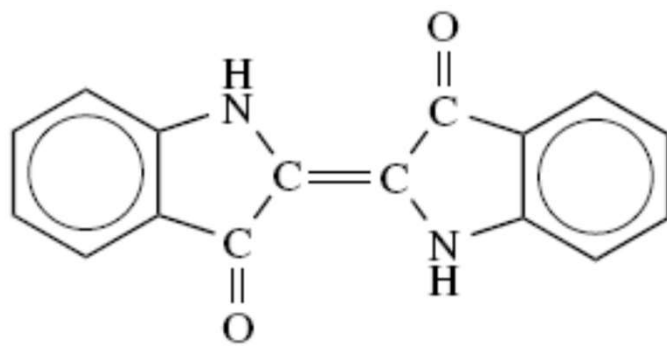
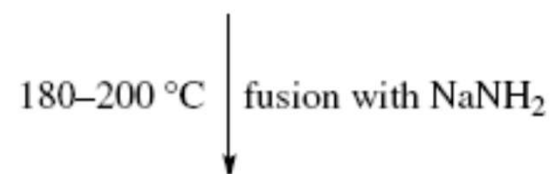
(1)



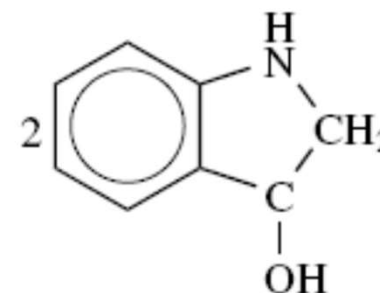
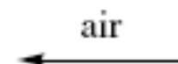
chloroacetic acid



*N*-phenylglycine



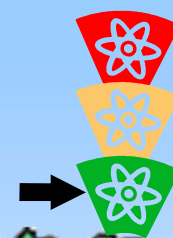
indigo



indoxyl



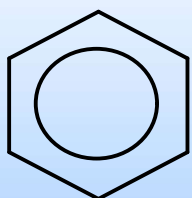
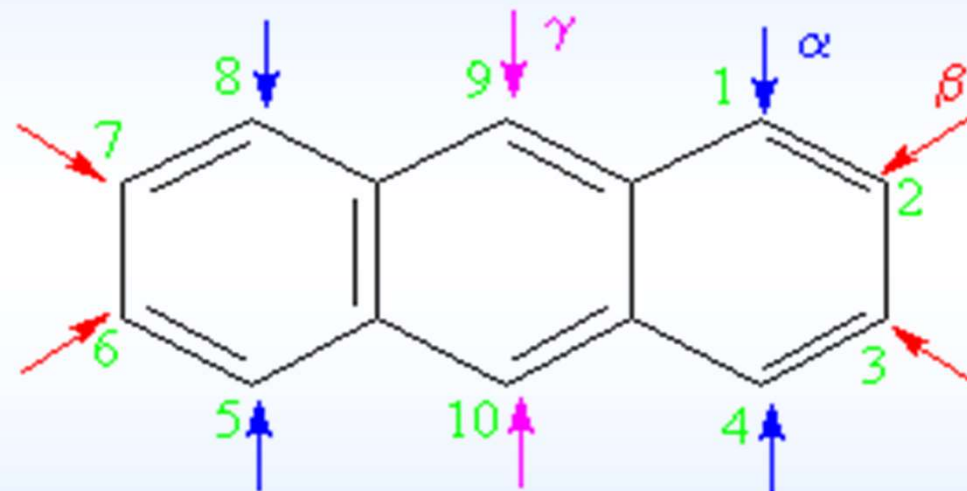
# Synthetic dyes



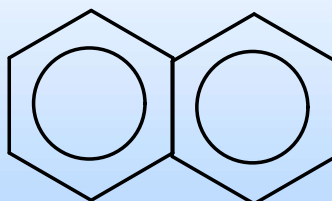
$10^5$  synthetic dyes were synthesized – practical application ( $10^3$ )

By the synthesis is important:

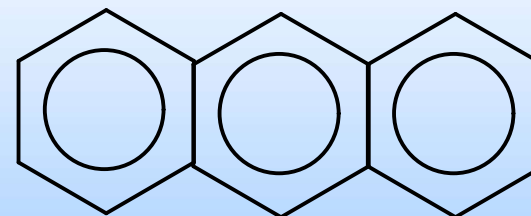
- light absorption coefficient
- toxicology
- brilliance
- fastness



Benzene



Naphthalene

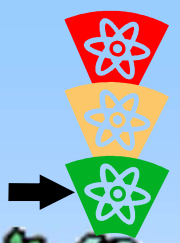


Anthracene

**system of conjugated double bonds = easy electron-transfer**

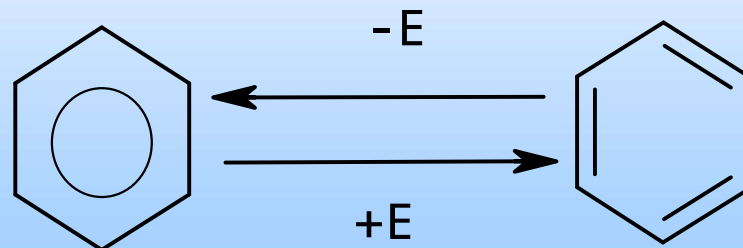


# Synthetic dyes



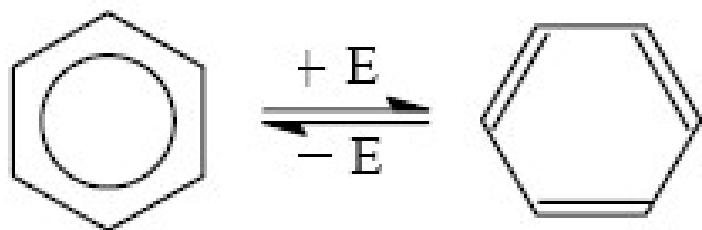
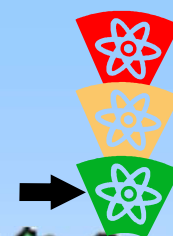
Light absorption in dyes:

Photon with right energy (wave length) is absorbed in dye structure, the dye is now excited (transferred to energy rich configuration) and immediately the dye emitted the energy in form of heat





# Synthetic dyes



**Benzene (colourless)**

$\lambda = 250 \text{ nm}$

**mesomery**

**Energetically  
poor state**

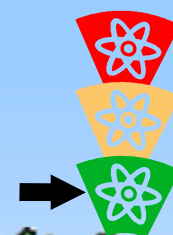
**Energetically  
rich state**

Picture on right site is sometimes used for description of standard state of benzene, real situation in normal conditions is on the left site.

Many chemical containing benzene cycle – this is basis of standard detection of organic chemical – light absorption at 250nm.



# Synthetic dyes



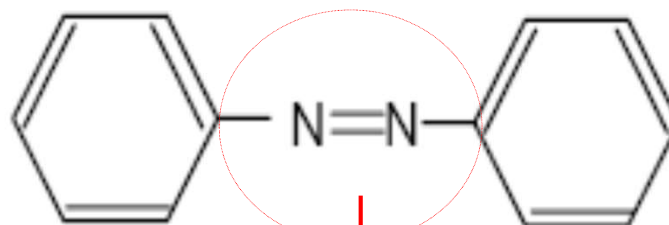
**Azo-group** can connect two benzenes

The structure is more complicated to benzene

This structure absorb photons with low energy (about 400 nm) – azobenzene is slightly yellow

**Azo benzene (yellowish)**

$\lambda = 400 \text{ nm.}$



**Chromophore**

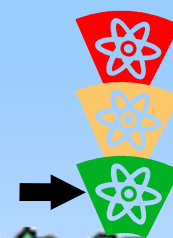
Dyes contained azo-group - azodyes

**Positive: brilliance of color**

**Negative: low fastness**



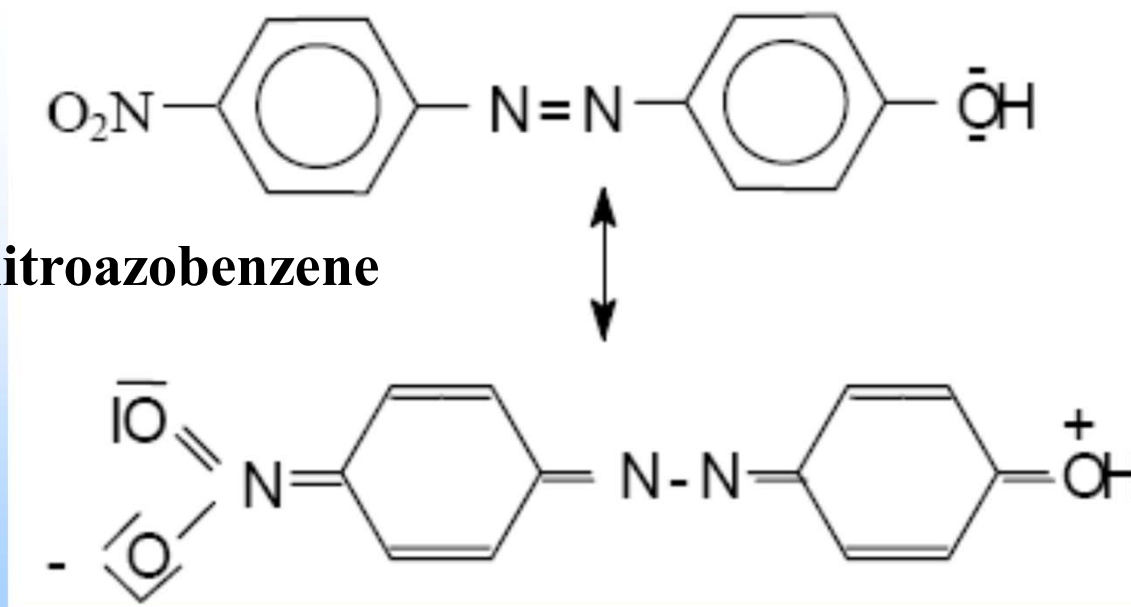
# Synthetic dyes



The shift of light absorption to the longer wavelengths is reached by additional suitable polarizing groups („auxochrome“) or atoms on the optimal places in molecule.

The generation of mesomeric structures with lower excitation energy  $\Delta E$  then enables the absorption of photons of lower energy  $\rightarrow$  **visible rays**

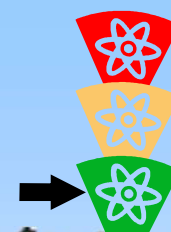
4-hydroxy -4-nitroazobenzene



The color compounds (which must not be applicable dye) is called **“CHROMOGENE”**

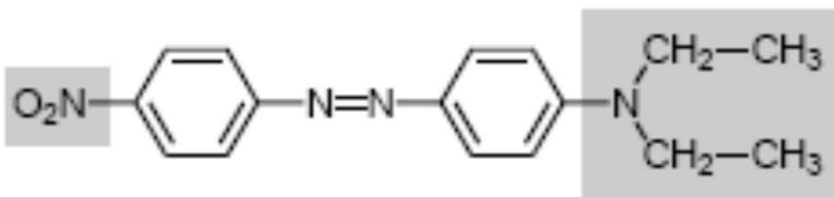


# Synthetic dyes

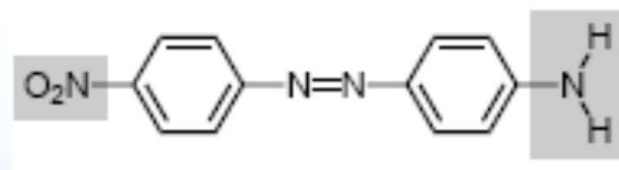


## Colour of some azo compounds

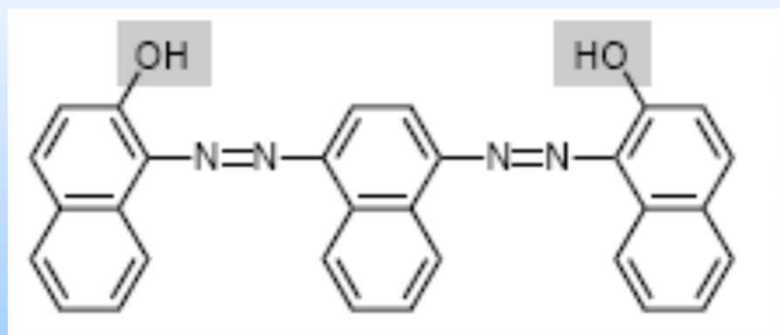
**Auxochrome** =



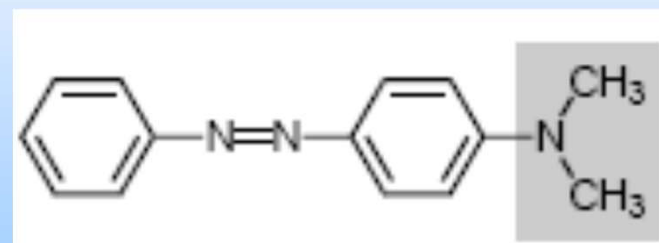
**Red**



**Yellow**



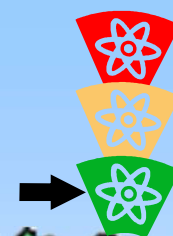
**Blue**



**Yellow-green**

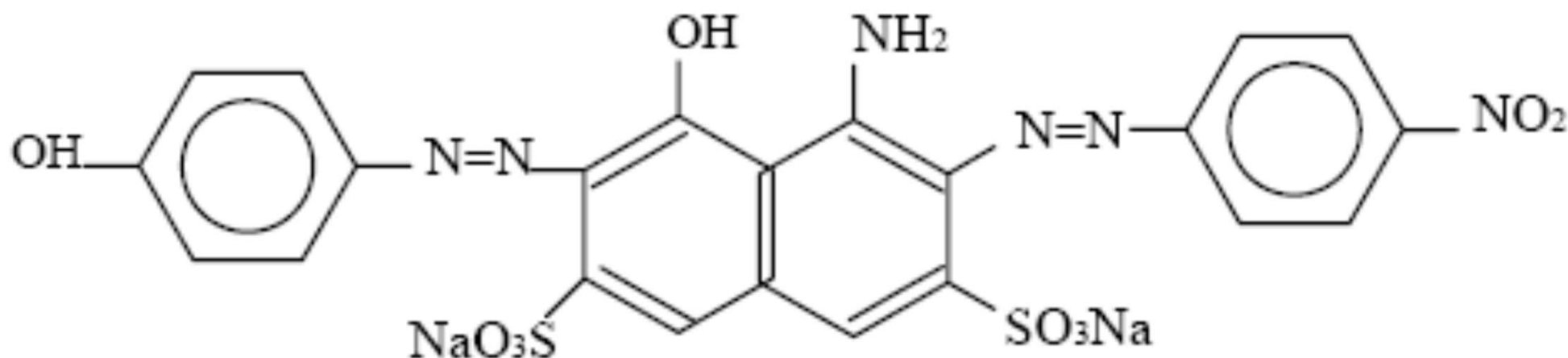


# Synthetic dyes



By the combination with further substituent-groups (and often with very important **sulpho-groups**) and 1 – 3 azo-groups connecting the benzene and naphthalene units obtained thousands of AZODYES with very different property

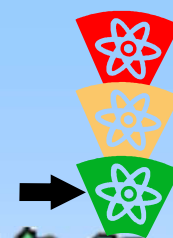
**Dark blue (Acid dye)**



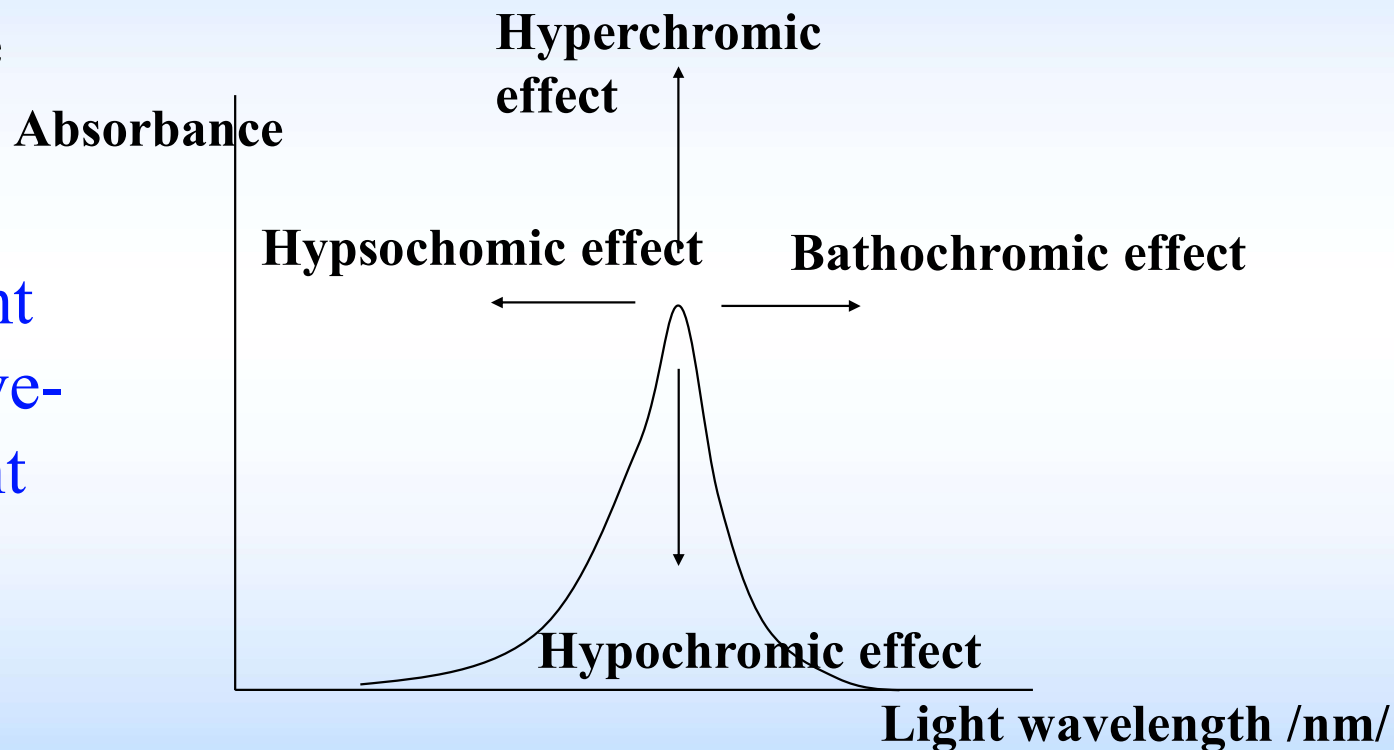




# Color changes of dye



By the mean of  
absorption spectra are  
the dye-structure  
changes studied  
(influences of different  
chemical groups in dye-  
molecule, enlargement  
of dye-molecule), the  
main effects :



Hyperchromic effect: increase in absorption (increase of color intensity)

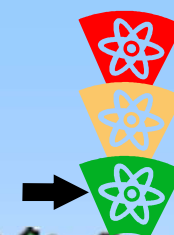
Hypochromic effect: decrease in absorption (decrease of color intensity)

Bathochromic effect: absorption- shift to longer wave lengths

Hypochromic effect: absorption-shift to shorter wave lengths



# Chemical groups of dyes



## Dyes of one chemical group (Classification by **chromophore**) :

produced from similar inputs and intermediate products  
have nearly the same fastnesses against photolytic and chemical influences

but can differ by coloristic properties, it depends on:

presence (in molecule) of specific groups:

**-SO<sub>3</sub>Na** (solubility in water),

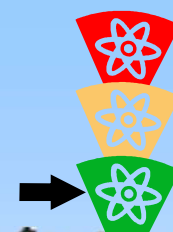
**chemical reactive groups** → possible reactions with fiber  
**size and shape of molecule** = physical interaction

In literature more than 20 chemical groups of dyes.

Here mentioned only the most important:

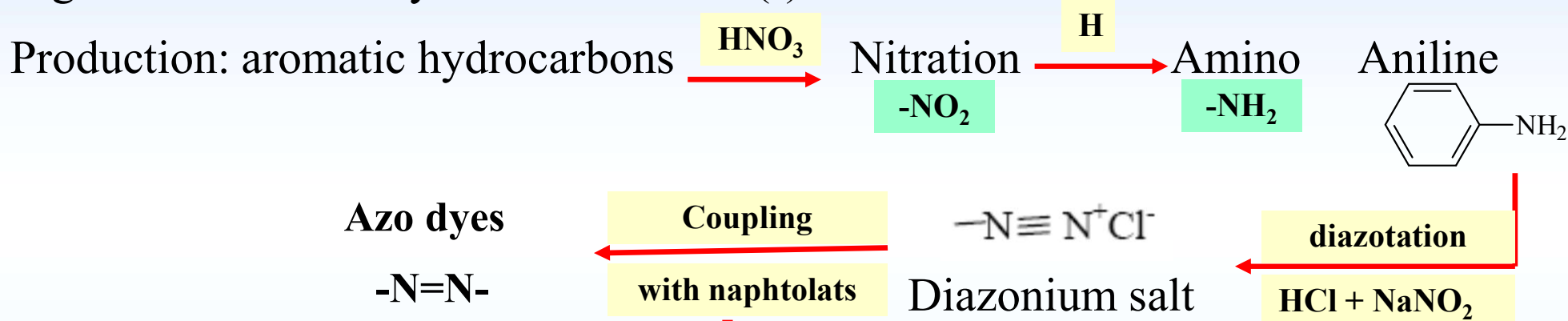


# Azo dyes

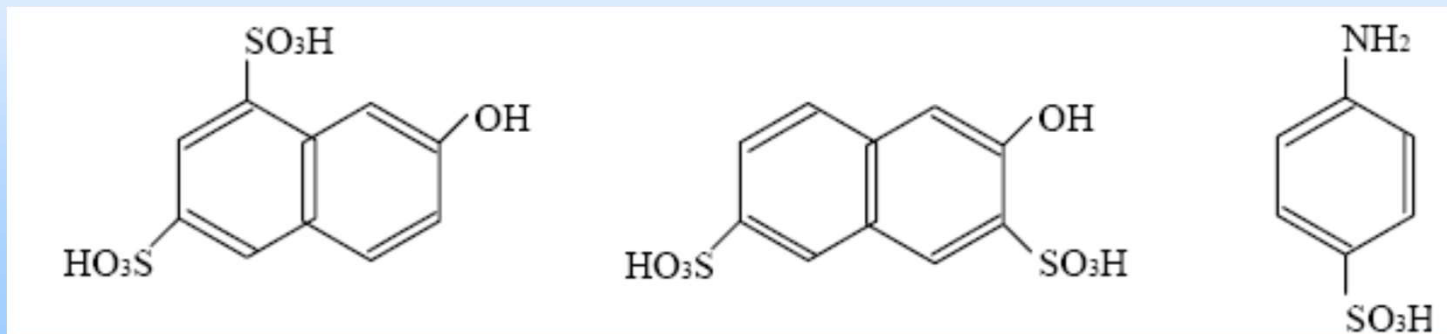


-N=N- (1-4 in molecule), over 1/2 all synthetic dyes !

Light fastness : only medium values (!)

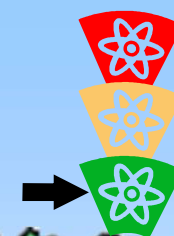


If the coupling component contain  $-\text{SO}_3\text{H}$  ( $\rightarrow$  dyes soluble in water)



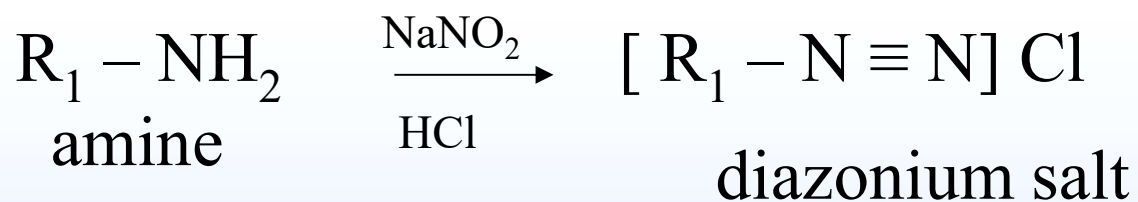


# Azo dyes

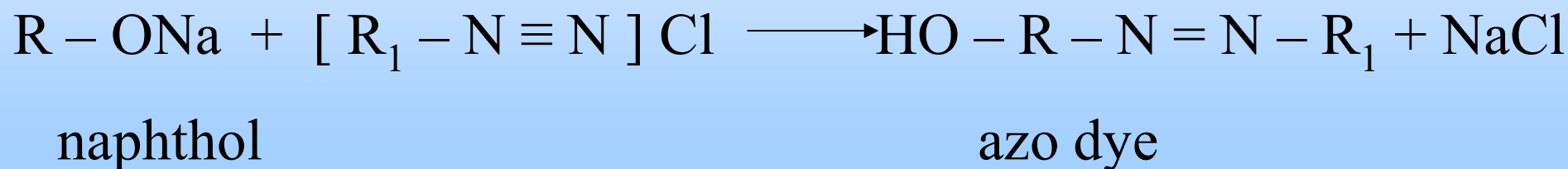


Azo dyes are made by diazotization of a primary aromatic amine followed by coupling of the resultant diazonium salt with an electron-rich nucleophile.

## Diazotization

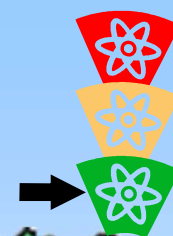


## Coupling



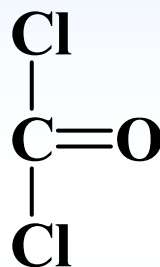


# Azo dyes

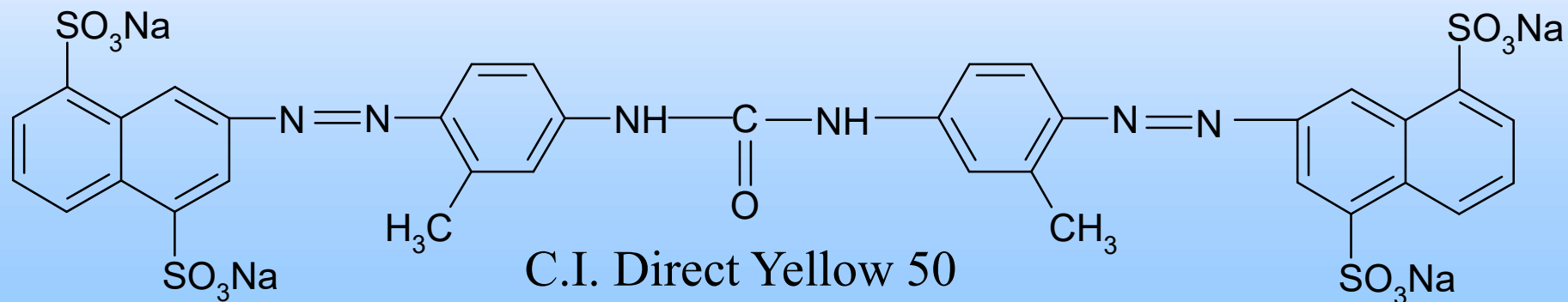


Other synthesis of azo-dyes with longer molecules are based on the reactions with phosgene

Phosgene

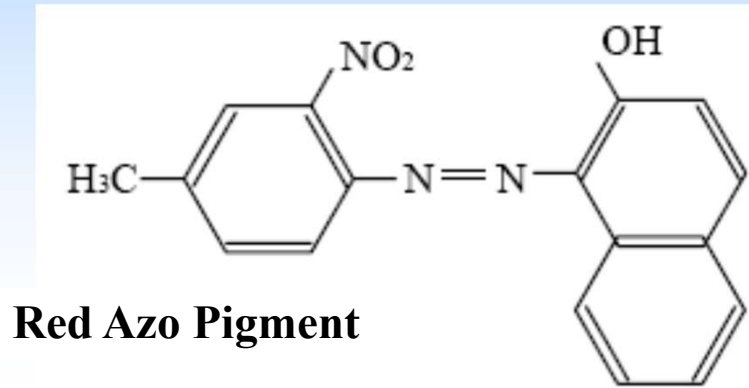


Simple “doubling” of 2 molecules of monoazodye ( $\rightarrow$  substantivity increased, color without change – conjugation interrupted !):

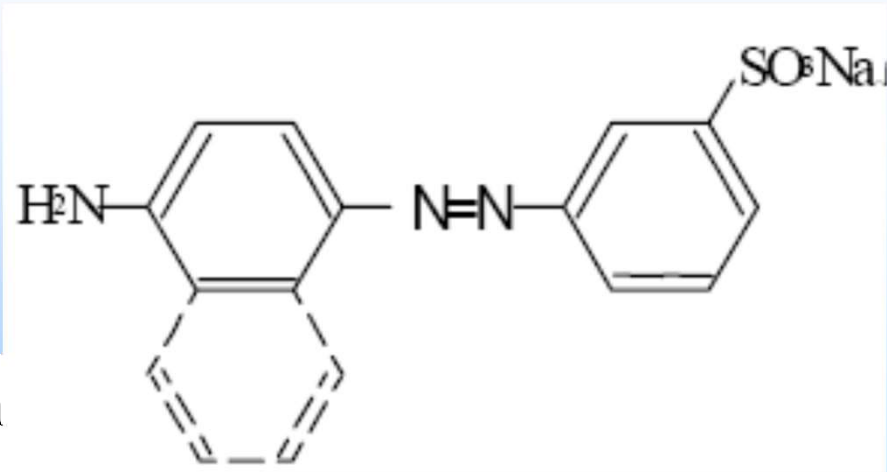


# Azo dyes

Organic azopigments (insoluble)



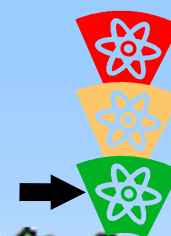
Analogous simple structures with 1 or 2 sulfo-groups (in form Na<sup>+</sup>)  
= **acid dyes** for wool and Polyamide



Acid yellow (or Orange with naphthalene ring)

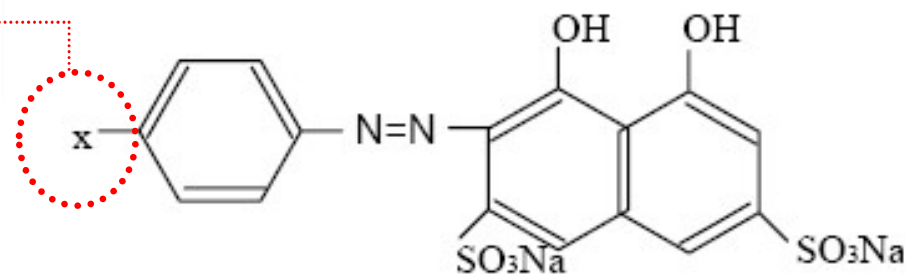


# Azo dyes



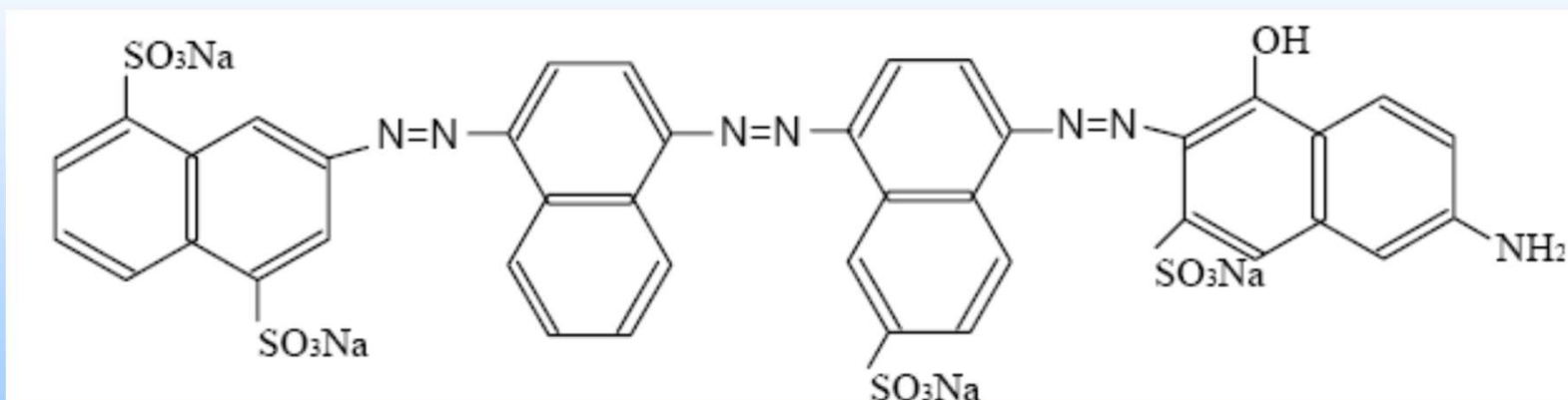
## Acid azodyes

X	Color	$\lambda_{\max}$
-H	Red	529.5
-NH <sub>2</sub>	Violet	579.5
-N(CH <sub>3</sub> ) <sub>2</sub>	Dark blue	590.0



By elongation of molecules → affinity for cellulose fiber (substantivity)

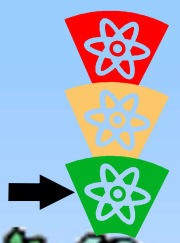
**Direct trisazo dye:**



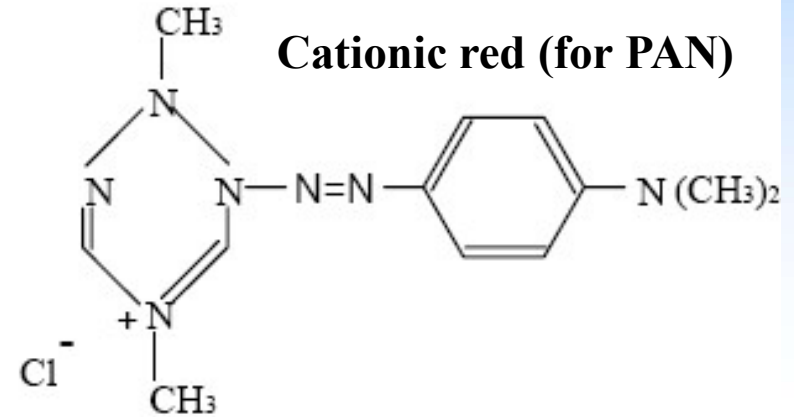
**Direct blue (with better light fastness)**



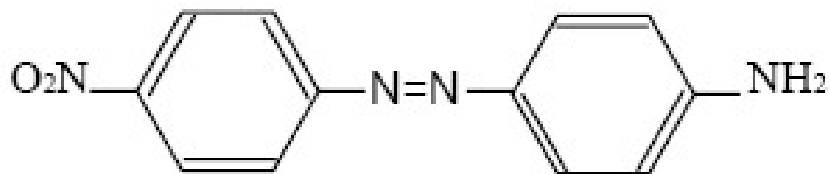
# Azo dyes



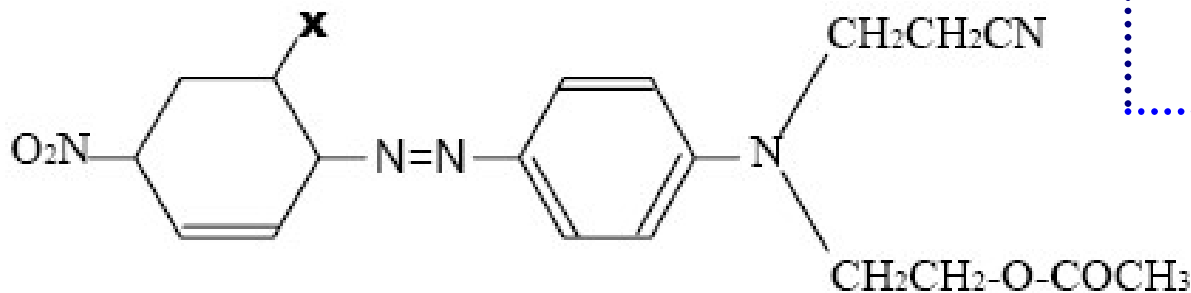
**Cationic dye:** Solubility of molecule obtainable also by the mean of positive charged group mostly quaternary N



similar to color pigments are **disperse dyes** (minimal solubility needed)



Disperse orange (for PAD)

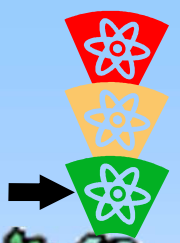


Disperse orange and red  
(x: Cl or CN) for PET fiber



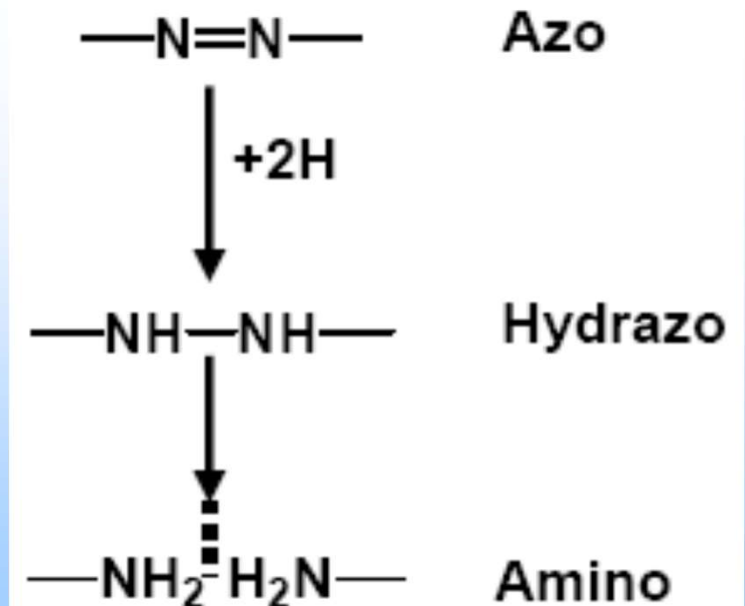


# Azo dyes



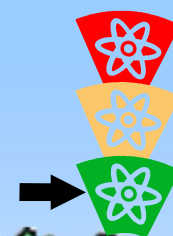
Typical simple **reduction** – destruction of azo groups → hydrazo compound (interrupted conjugation → decolorize!) → endphase – NH<sub>2</sub> **IRREVERSIBLE**

Supported by alkaline, by acids limited  
with temperature accelerated  
**ATTENTION** by dyeing!





# Anthraquinone dyes

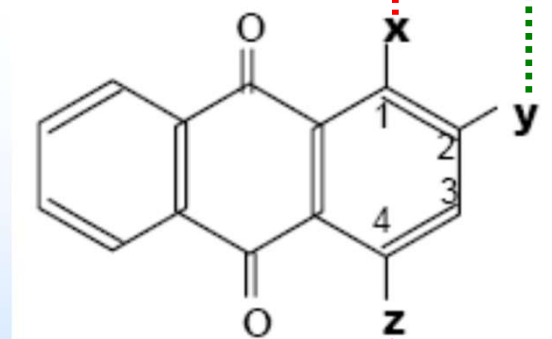


Derivates of anthraquinone = chromophore,

2. greatest dyes-group

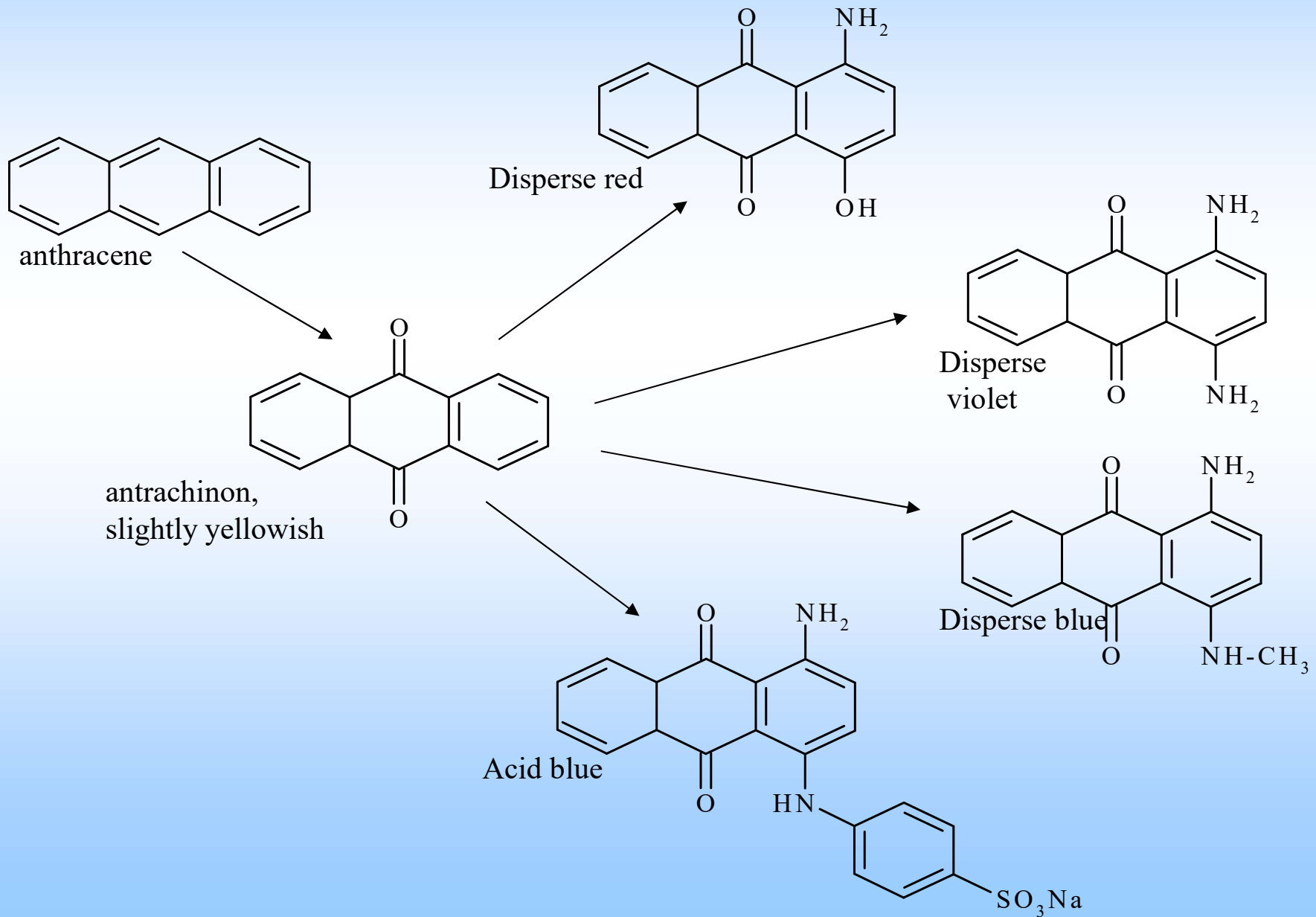
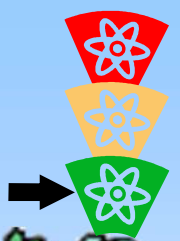
## Disperse anthaquinone dyes

x	y	z	Color
-NH <sub>2</sub>	-CH <sub>3</sub>	-H	orange
-NH <sub>2</sub>	-H	-OH	red
-NH.CH <sub>3</sub>	-H	-NH.C <sub>6</sub> H <sub>5</sub>	blue



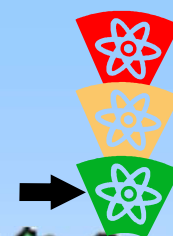
By addition of one or two sulpho-groups in this (and similar) structures → Important **acid anthraquinone dyes** (mostly **blue** and **green**)

# Anthraquinone dyes

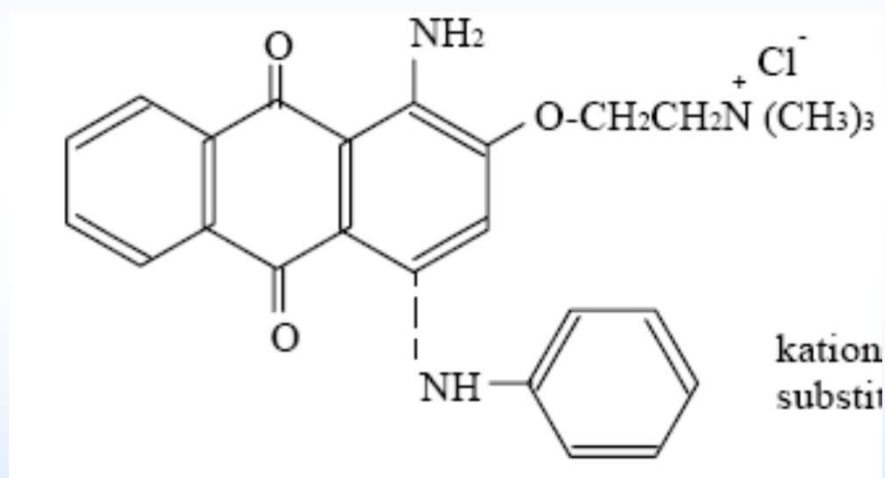




# Anthraquinone dyes



By addition of cationic group to anthraquinone chromophore →  
Cationic dyes for PAN fiber

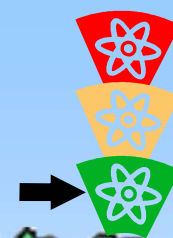


Cationic pink

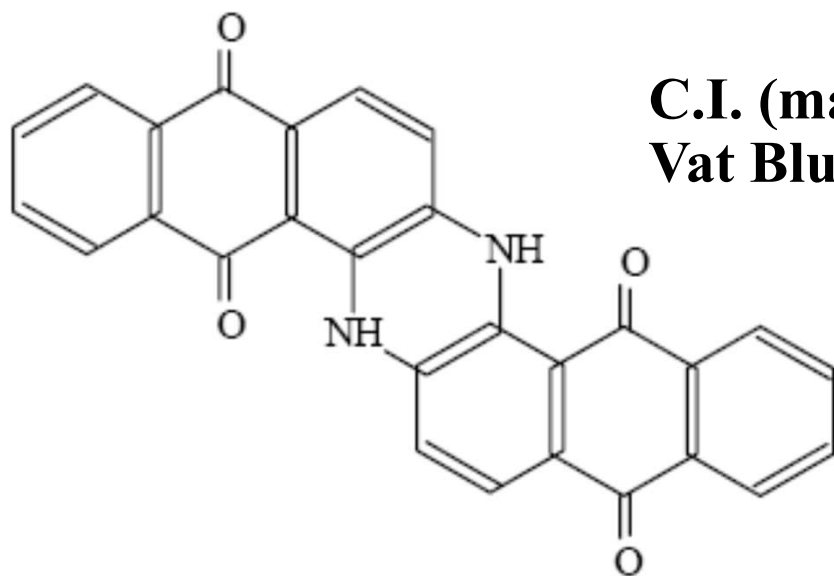
If in position 4 is substituted (according the figure) → shade shifted to longer waves (bathochromy) → blue



# Anthraquinone dyes



Important are the anthraquinone **vat dyes**. From 1-aminoanthraquinone was synthesized (1901) **indanthrene**, up to the present day the primary vat dye. Indanthrene is also widely used as pigment with excellent light fastness



**C.I. (marking after Color Index)  
Vat Blue 4 and Pigment Blue 60**

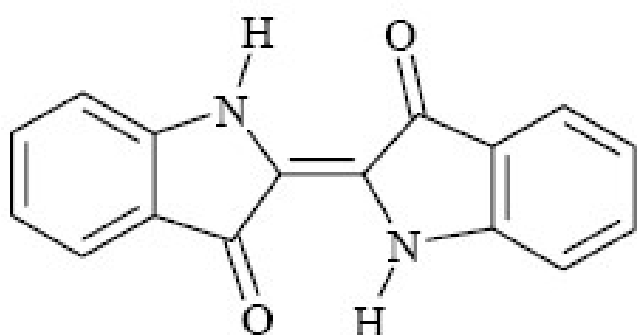
Important: the derivatives of indanthrene – (the **chloro-derivatives** ~ improved fastness against chlorine and peroxide bathes → possible bleaching of cotton woven articles with colored effects – dyed in yarn



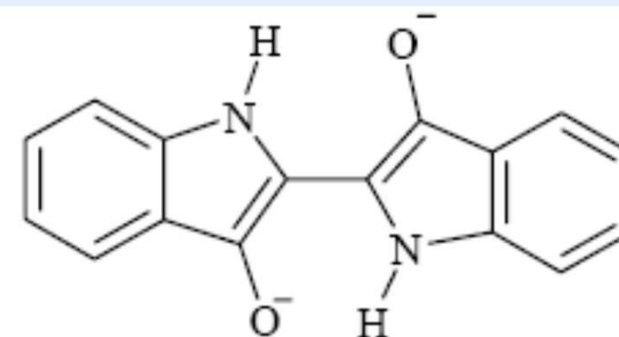
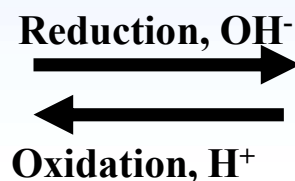
# Indigoid and thioindigoid dyes



Derivates of **indigo** - produced already from 1870 by multistep-synthesis



Dark blue



Dull yellow vat

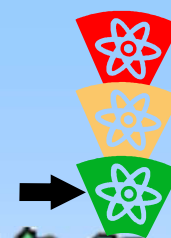
Meaningful are chloro-, bromo- and methyl derivatives of indigo- are more resistant against chlorine solution

**Thioindigo** is sulphur analogy: -S- instead of -NH- groups.

Derivatives of thioindigo (namely Br-derivatives) are important **red, violet, orange, brown** vat dyes.



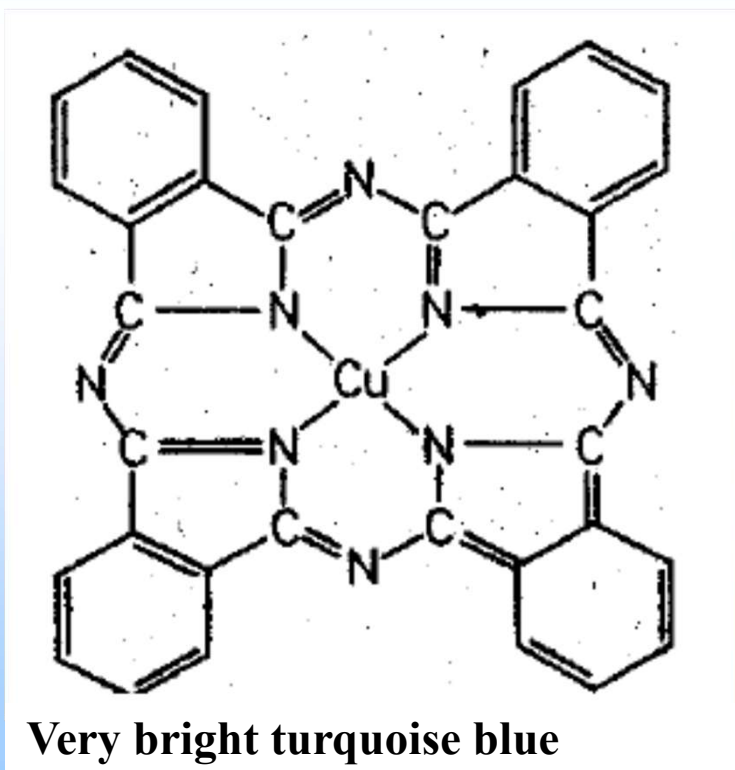
# Phthalocyanin dyes



Very brilliant and lightfast pigment turquoise blues and greens

Produced from derivatives of **phthalic acid**

By couple-bounded **Cu** or **Co** atom and substituents on the basic structure (**Cu-phthalocyanine**):

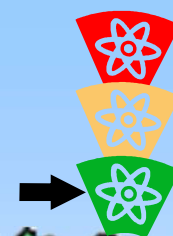


By **sulphonation** is obtained the **direct turquoise** (very brilliant and light fast; substantivity is low).

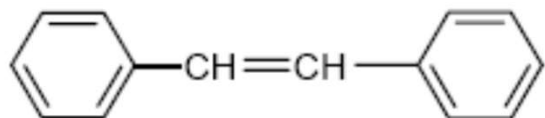
On phthalocyanin skeleton should be also add the **reactive group** → **reactive bright blue**



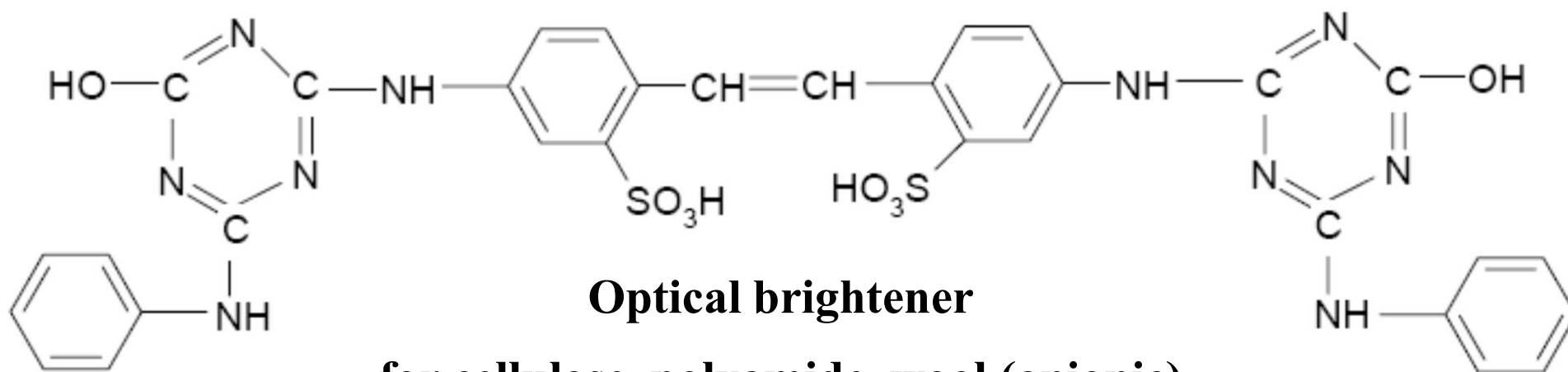
# Stilbene dyes



Some yellow or orange of direct and disperse dyes, and optical brighteners are based on stilbene ( $\lambda_{\max}$  295 nm.)



**chromophore**

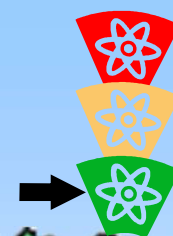


**Optical brightener**  
**for cellulose, polyamide, wool (anionic)**

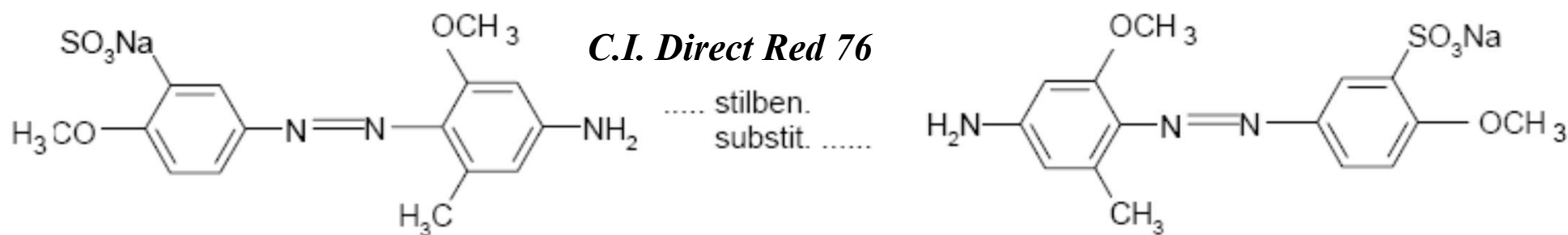




# Stilbene dyes



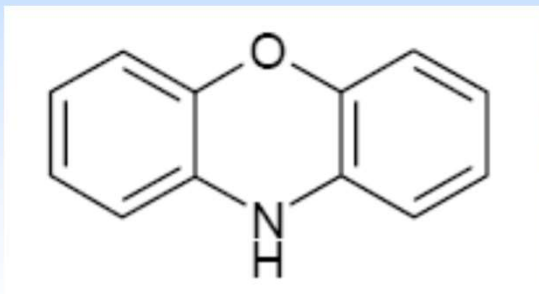
Stilbene is often used for “doubling” of 2 molecule monoazo dyes:



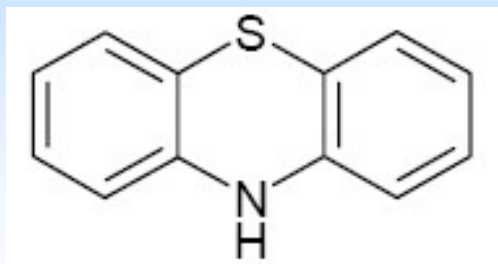
Stilbene is stable against reduction → this dye not “white discharged” (only azo groups decomposed)



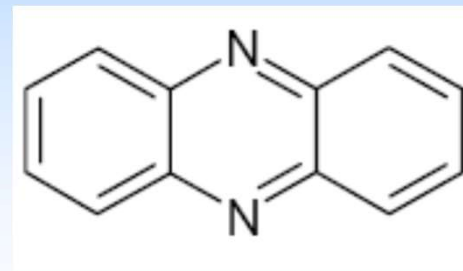
# Oxazin, Fenothiazine, fenazin dyes



Fenoxazin

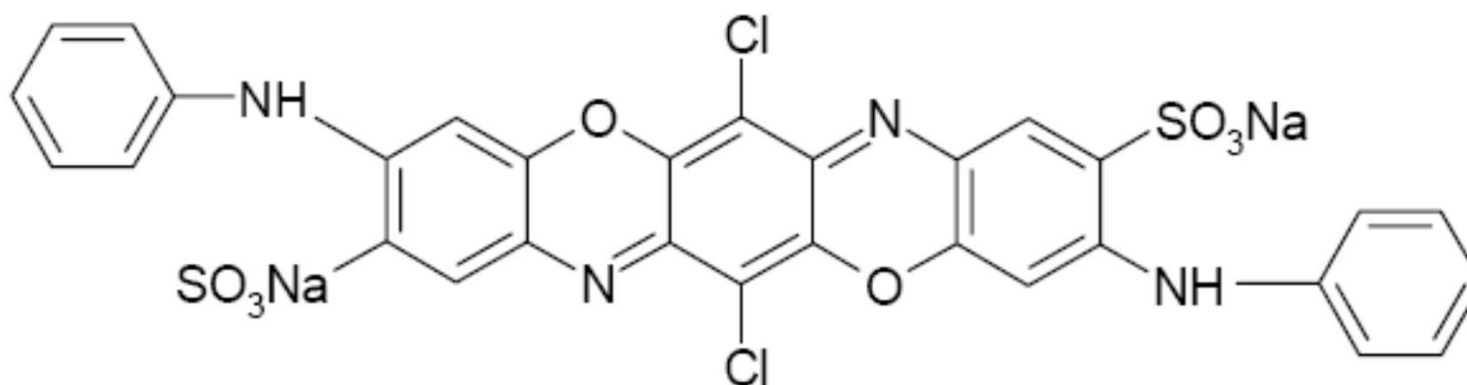


Fenothiazin

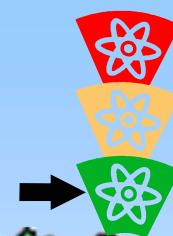


Fenazin

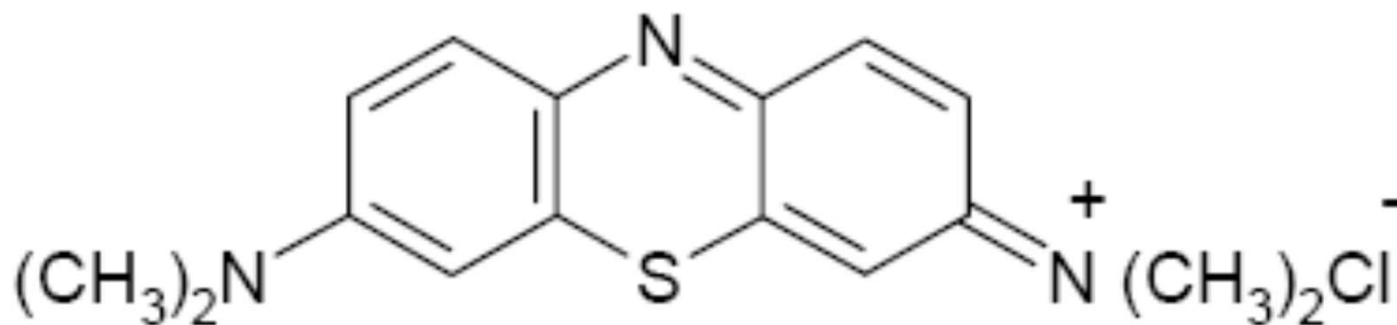
Greater meaning: direct dioxazin dyes (good substantivity and light fastness):



*C.I. Direct Blue 106* (very bright, the world-wide used direct blue)



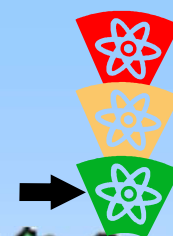
**Thiazine dye is e.g. the METHYLENE BLUE-C anionic dye, known also by testing of cellulose fiber (dyes the oxycellulose, cause: -COOH)**



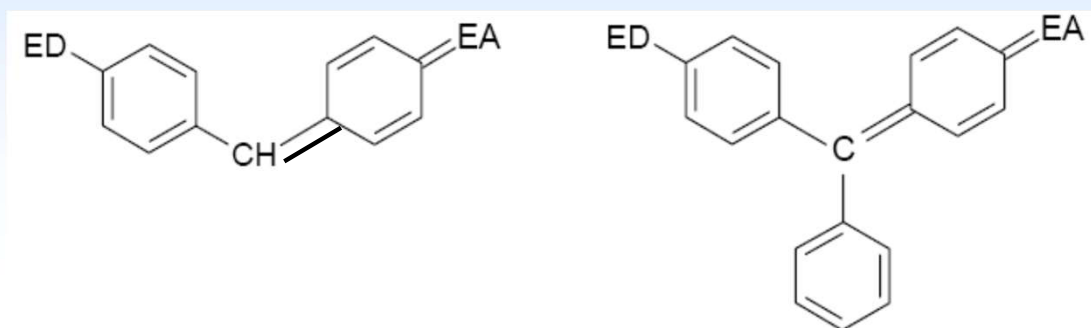
*C.I. Basic Blue 9*



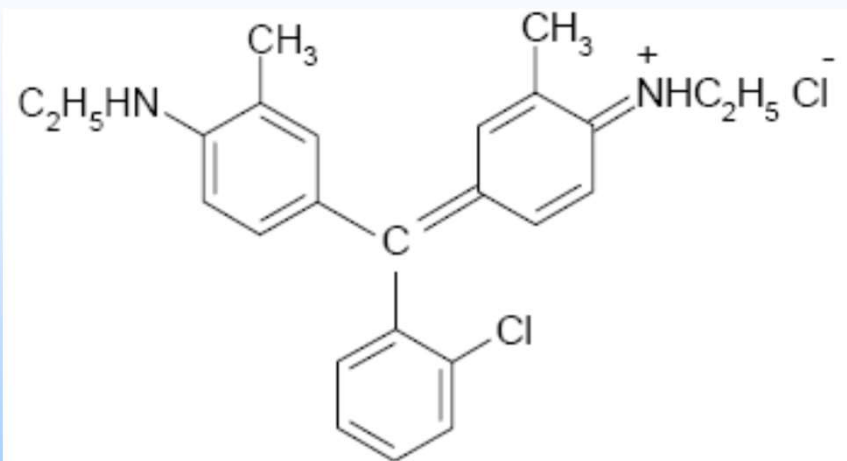
# Arylmethan dyes



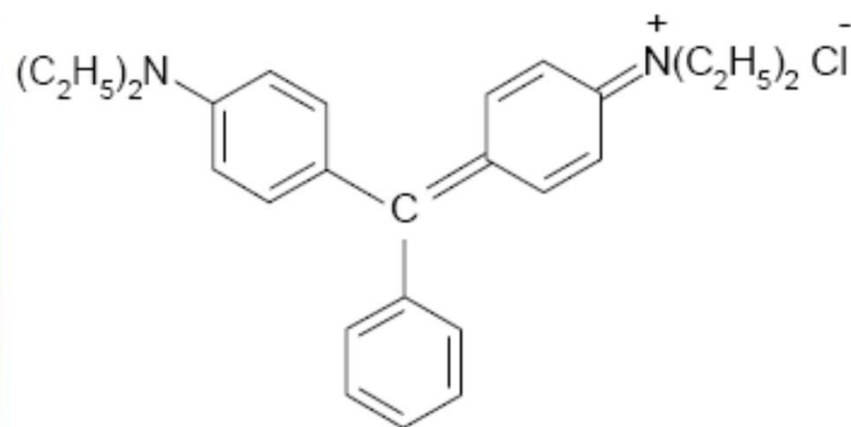
Derivatives of **triphenyl methane** or (less common) biphenyl methane generally (ED.....electron donor, EA....electron acceptor):



In last time decreasing meaning. Some cationic dyes for acrylics:



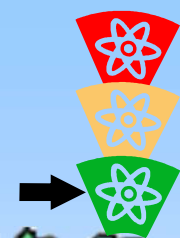
*C.I. Basic Blue 5*



*C.I. Basic Green 1*



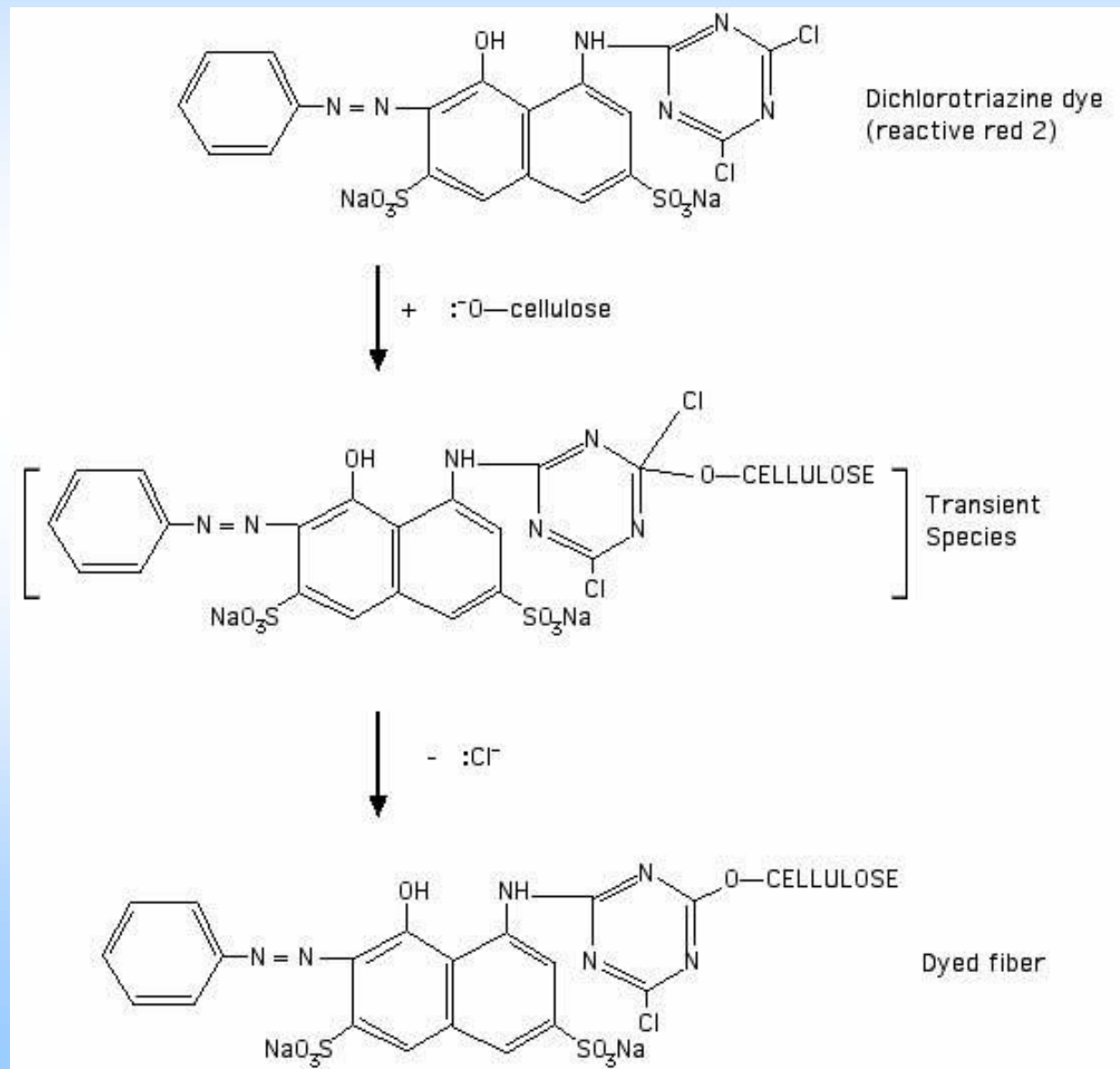
# Special dyes



## Dyes with reactive systems

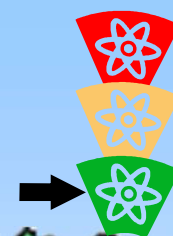
In dye structure is a group with high reactivity, which can bond the dye to fiber macromolecule by a covalent bond (wet fastness)

- „reactive dyes“

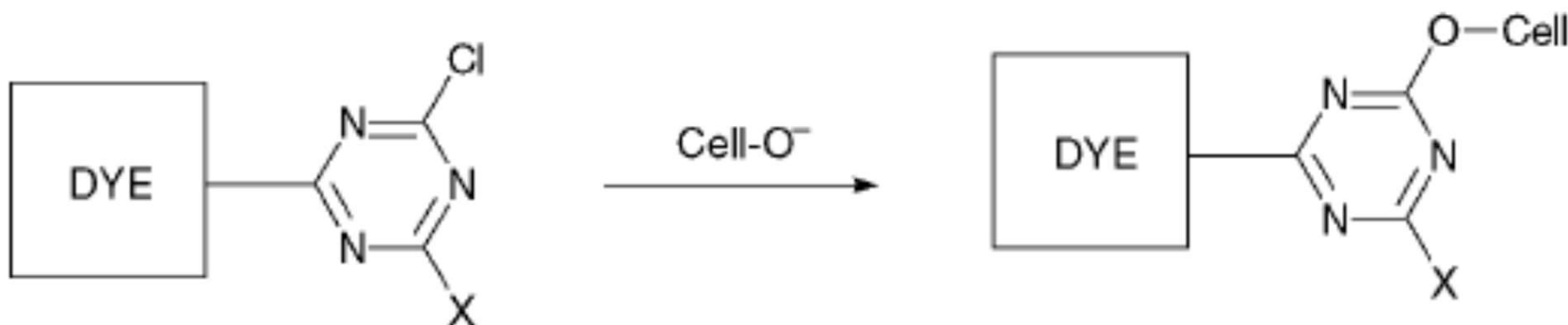




# REACTIVE DYES



**Reactive dyes - one of the most important application class of dyes for cellulosic fibres**

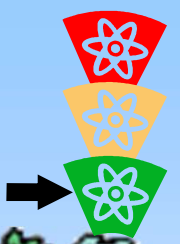


Procion (1,3,5-triazinyl) reactive dye

Covalently-bonded dye



# REACTIVE DYES



## Advantages

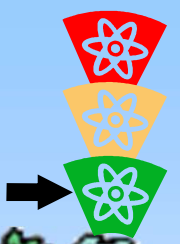
- **Full Colour Gamut**
- **Brilliant, bright colours**
- **Covalent fixation → high WashFastness (WF)**
- **Varying reactivities**

(various temperatures including low energy- cold dyeing)

- **Various methods of application**
- **Inexpensive to apply**



# REACTIVE DYES



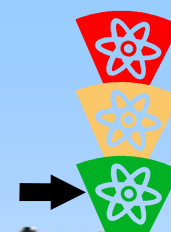
## Disadvantages

- **Incomplete fixation (problem with hydrolysis)**
- **Need for wash-off (for high WF)**
- **Need for high concentrations of salt**
- **High pH**
- **Some dyes are “AOX” – potentially harmful to the environment**



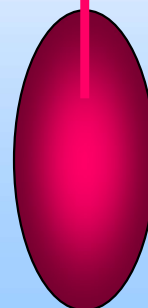
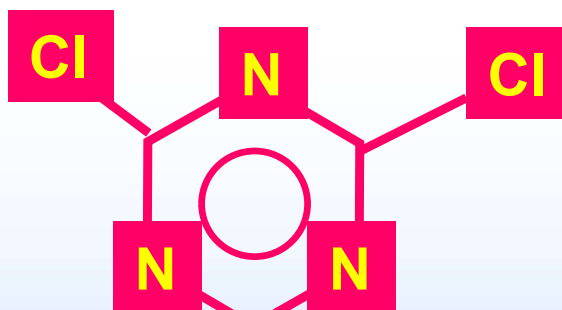
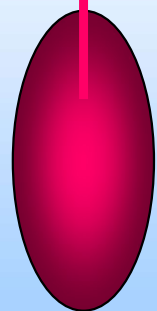


## Dichloro-s-triazine reactive group



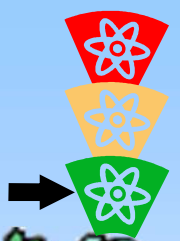
The reactive groups is usually a halogenated heterocyclic group

Reactive group



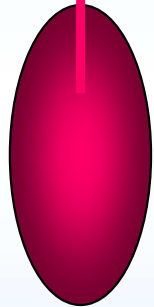
Nucleophilic substitution

# Vinylsulphone dyes



Reactive  
group

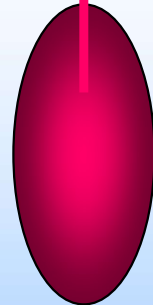
The reactive group is usually  
the vinylsulphone group



Sulphone (SO<sub>2</sub>)



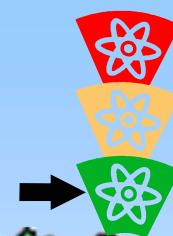
Vinyl (CH = CH<sub>2</sub>)



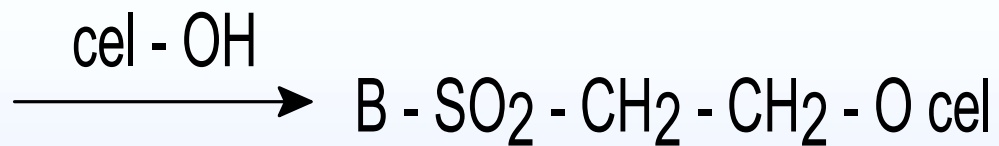
Nucleophilic  
addition



# REACTIVE DYES



## Vinylsulphone dyes





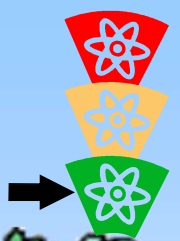
# REACTIVE DYES - SUMMARY



- **Dominant dye class for cotton**
- **Importance of nature and number of reactive groups**  
( → covalent fixation)
- **Different types/chemistries**  
→ many different application methods
- **Problem of dye hydrolysis**
- **Potential impact on environment**



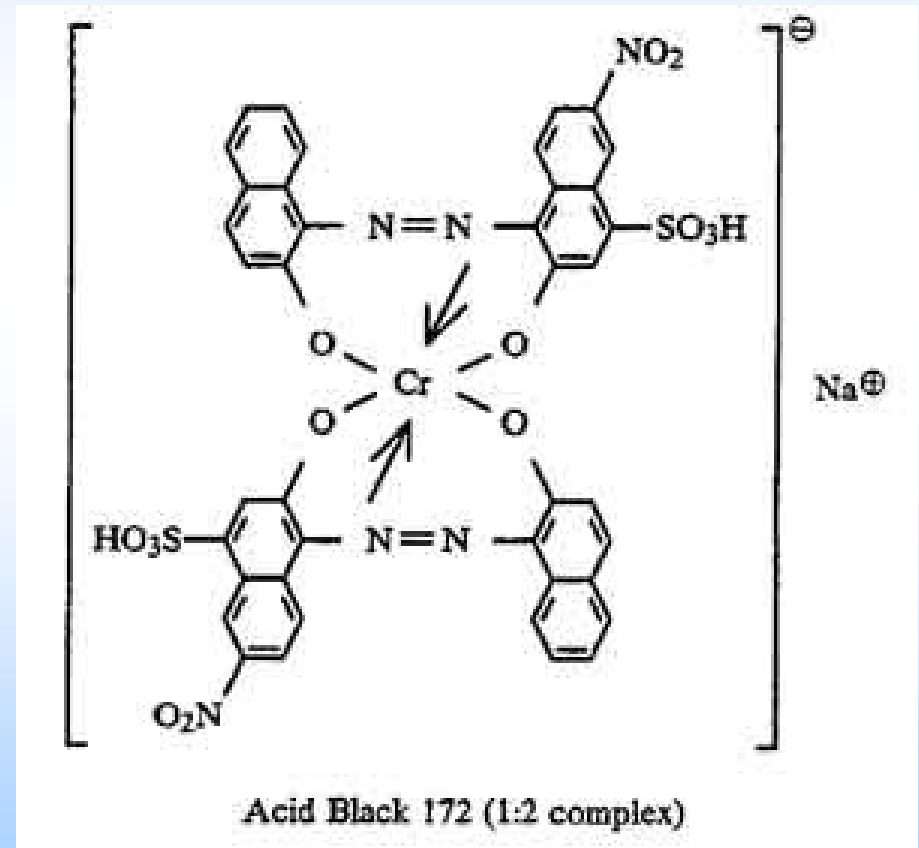
# Special dyes



## Complex dyes

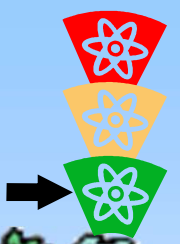
Creation of complex bonds  
between dye and fiber  
macromolecule is connected with  
improve of fastness

The color of complexed dye is  
darker but not so brilliant





# Sensitive dyes

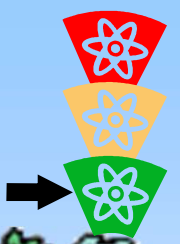


Dyes reacting according the imputes – ideal for testing and special effects:

- **pH** (pH indicators)
- **Photochromic or Phototropic** (color induced by illumination, reversible, color les chemical was illuminated and changes the color)
- **Thermotropic** (color changes based on temperature)
- **Piezochromic** – changes of color by mechanical forces, reversible by time or by solving of crystals
- **Tribochromic** - changes of color by mechanical forces, irreversible
- **Solvatochromic** - changes of color in different solvents



# Luminescence



**Photoluminescence** – high energy photon absorption and low energy photon emission (the energy difference was changed to heat, Stokes-law)

## **Luminescence:**

**fluorescence** (emission is immediately after absorption)

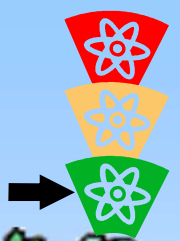
**phosphorescence** (emission after longer time).

Difference: in electron configurations in molecules, ... electron spin changes)

Special kind of fluorescence: **optical brighteners**  
(**UV light absorption, VIS light emission**)

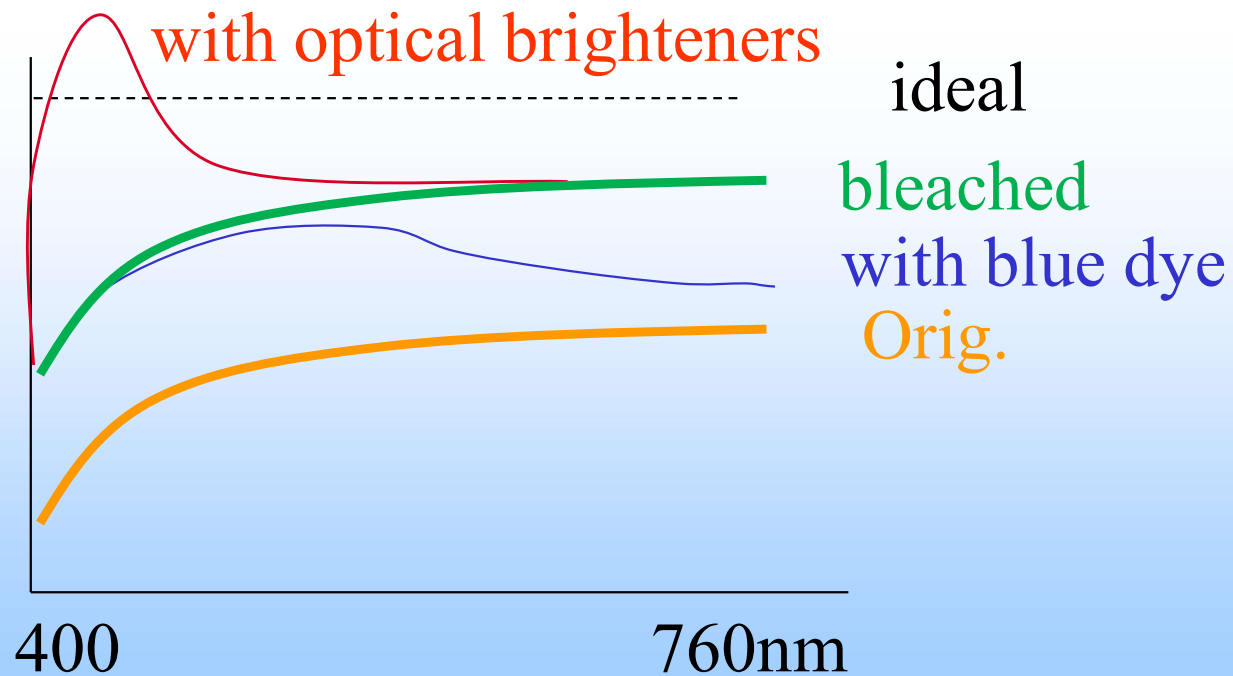


# Optical brighteners



Rough cotton – yellowish (light absorption at 400-450 nm), natural pigments,

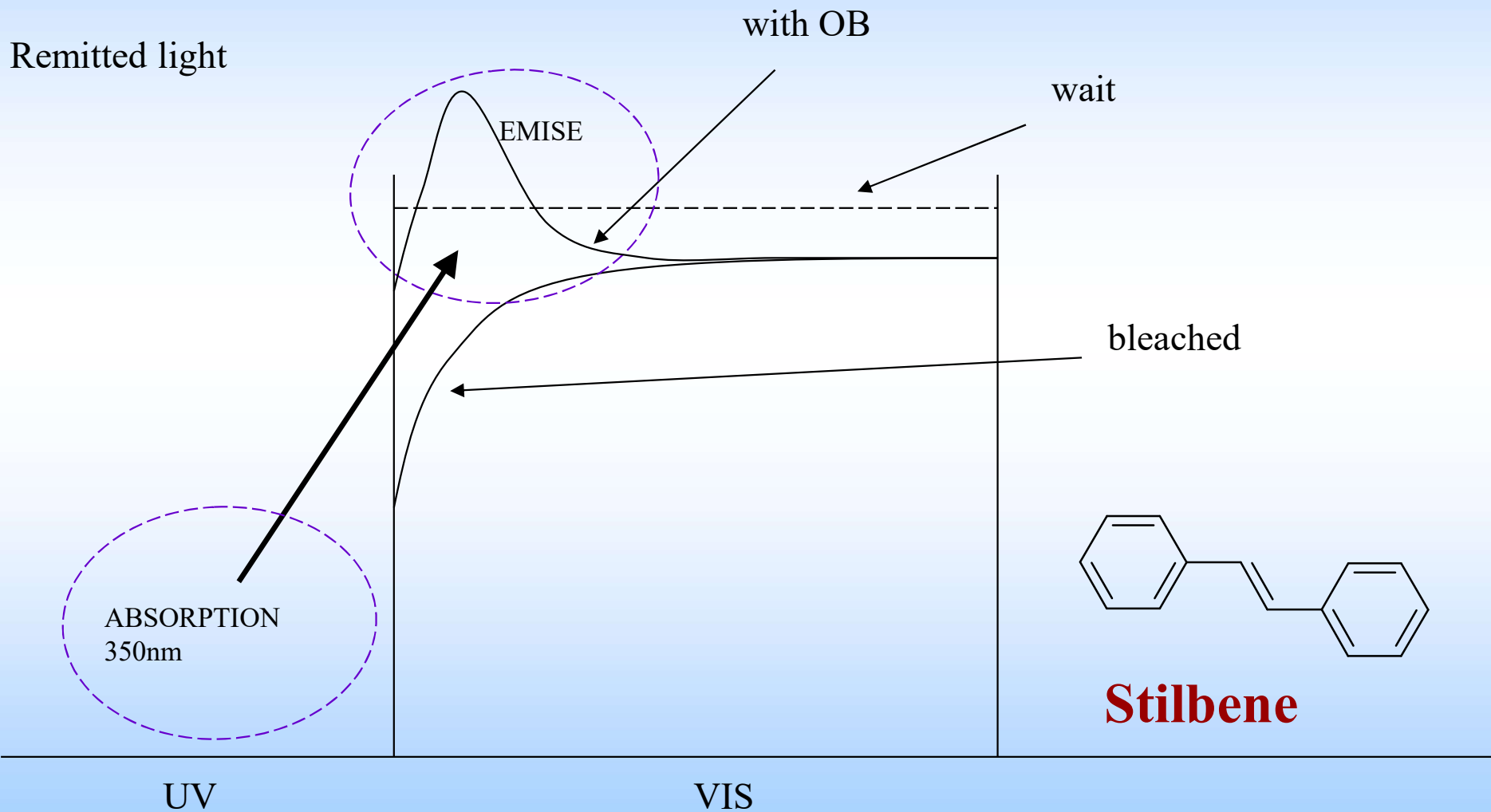
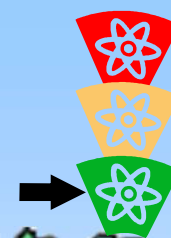
Common solving: bleaching, application of optical brighteners or blue dyes







# Optical brighteners





# CLASSIFICATION OF COLORANTS

Classification of dyes and pigments:

- by chemical structure  
( azo dyes, antraquinone dyes, etc. )
  
- by use  
( reactive dyes, disperse dyes, pigments, etc.)

# CLASSIFICATION OF COLORANTS



Classification of dyes and pigments by use (example):

- direct dyes
- sulfur dyes
- vat dyes
- reactive dyes
- acid dyes
- disperse dyes
- pigments

# CLASSIFICATION OF COLORANTS



Class	Chemical types	Method of application
DIRECT	azo, anthraquinone	applied from neutral or slightly alkaline baths containing additional electrolyte
VAT	anthraquinone, indigoids	water-insoluble dyes solubilized by reducing with sodium dithionite, then exhausted on fiber and reoxidized

# CLASSIFICATION OF COLORANTS



Class	Chemical types	Method of application
REACTIVE	azo, anthraquinone	active site on dye reacts with functional group on fiber to bind dye covalently under influence  of heat and pH (alkaline)
DISPERSE	azo, anthraquinone, benzodifuranone	fine aqueous dispersions often applied by high temperature/pressure



# CLASSIFICATION OF COLORANTS



Class	Chemical types	Method of application
ACID	azo, anthraquinone	usually from neutral to acidic dyebaths
BASIC	azo, anthraquinone, cyanine	applied from acidic dyebaths



# COLOUR INDEX CLASSIFICATION



Dyes are named either by their commercial trade name or by their Colour Index (C.I.) name.

The C.I. ( *Colour Index* ) name for a dye is derived from the application class to which the dye belongs:

( C.I. GENERIC NAME )

E.g. C.I. Generic Name: C.I. Pigment Yellow 1

C.I. Disperse Red 60

C.I. Constitution number

E.g. C.I. 11680

