
 **WIDMA ELEKTRONOWE UV – VIS**

800 – 400 nm	400 – 200 nm	> 200 nm
ZAKRES WIDZIALNY	BLISKI ULTRAFIOLET	DALEKI ULTRAFIOLET (PRÓŻNIOWY)
		<ul style="list-style-type: none"> ✓ optyka – kwarc ✓ rejestracja utrudniona poprzez obecność tlenu lub ozonu – pomiar w próżni

 **Prawo Lamberta-Beera**

$$\frac{I}{I_0} = T [100]$$

T - transmitancja

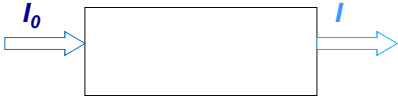
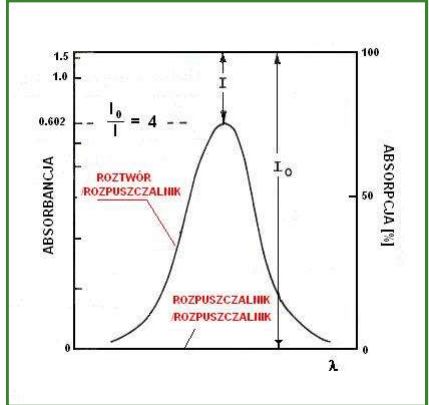
$$A = \log \frac{I_0}{I} = \varepsilon c l$$


A – absorbancja (ekstynkcja)
 ε – molowy współczynnik ekstynkcji
 c – stężenie cząsteczek absorbujących [mol/dm³]
 l – grubość warstwy [cm]

e – molowy współczynnik ekstynkcji jest charakterystyczny dla danego związku

↓

zależy od:
długości fali stosowanego rozpuszczalnika


 $I = \int \varepsilon(\nu) d\nu$

$\Psi_n \rightarrow \Psi_k$

$I = |\bar{d}_{nk}|^2$

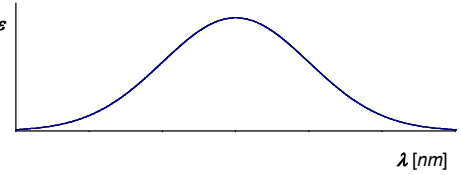
$\bar{d}_{nk} = \int \psi_n^* \hat{\mu} \psi_k d\nu = \int \psi_n^* (e\vec{r}) \psi_k d\nu$

$\hat{\mu} = \hat{\mu}_x + \hat{\mu}_y + \hat{\mu}_z = e(\hat{x} + \hat{y} + \hat{z})$

$(\bar{d}_{nk})_x = \int \psi_n^* \hat{x} \psi_k d\nu$

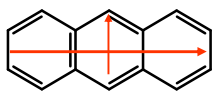
$(\bar{d}_{nk})_y = \int \psi_n^* \hat{y} \psi_k d\nu$


$(\bar{d}_{nk})_z = \int \psi_n^* \hat{z} \psi_k d\nu$

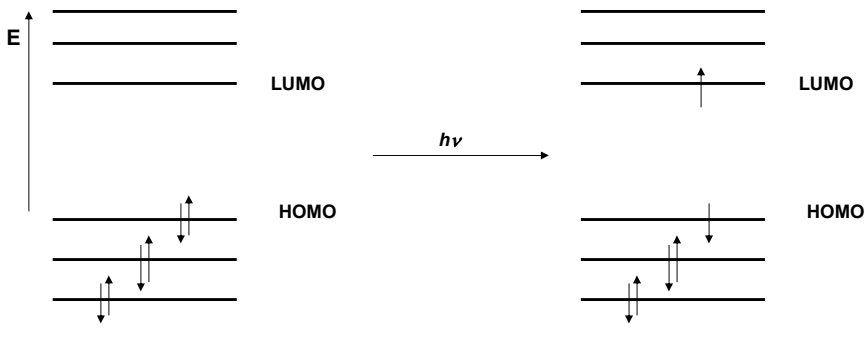


$\varepsilon < 10^3$ przejście wzbronione
 $\varepsilon > 10^3$ przejście dozwolone

POLARYZACJA PRZEJŚCIA







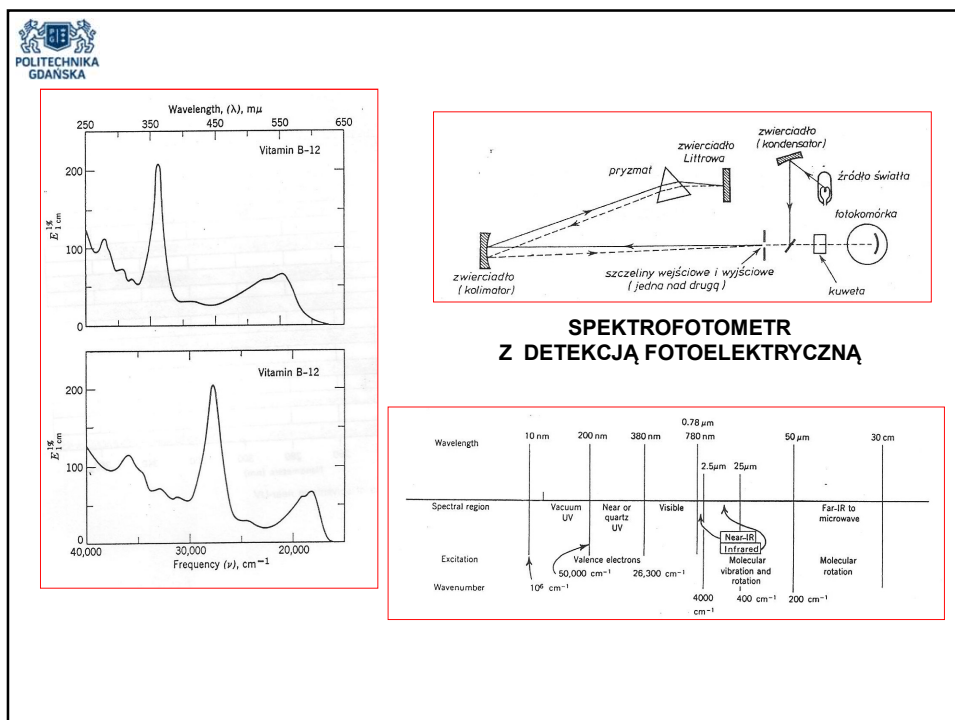
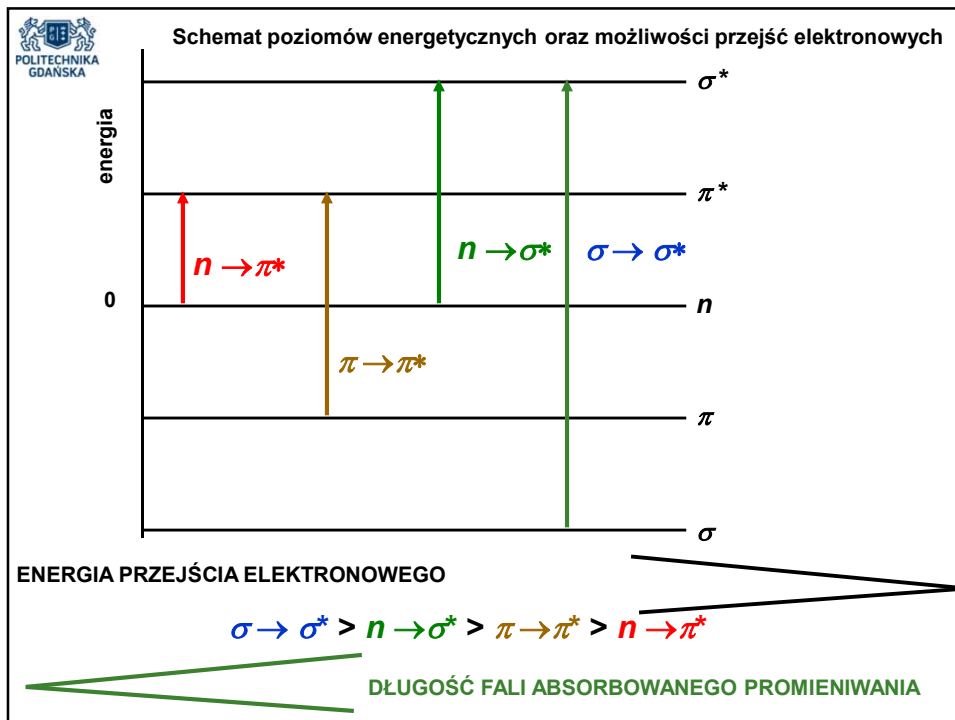
STAN PODSTAWOWY

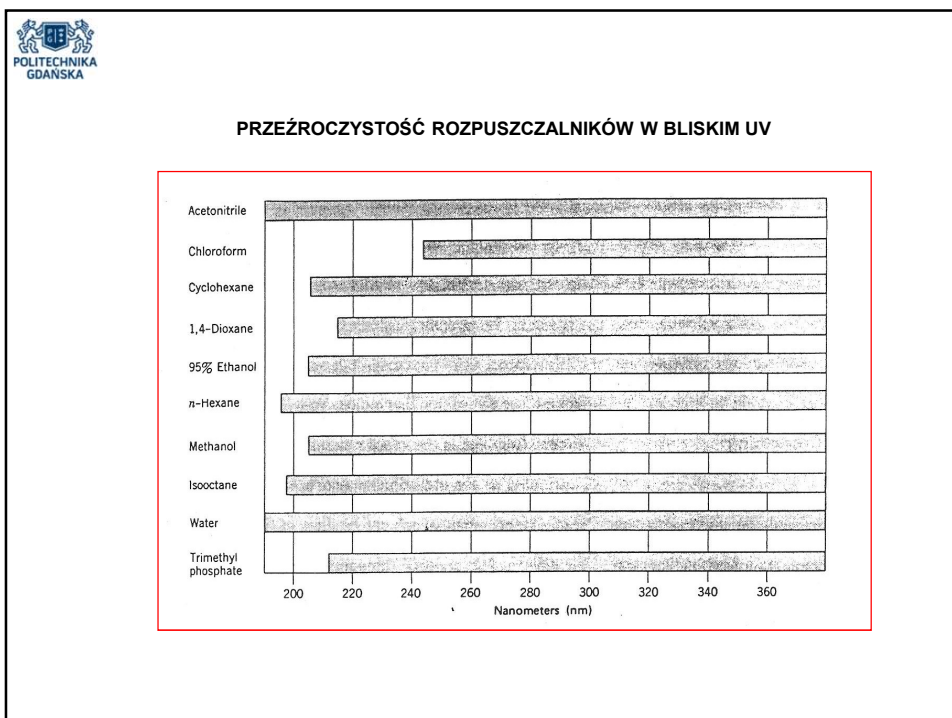
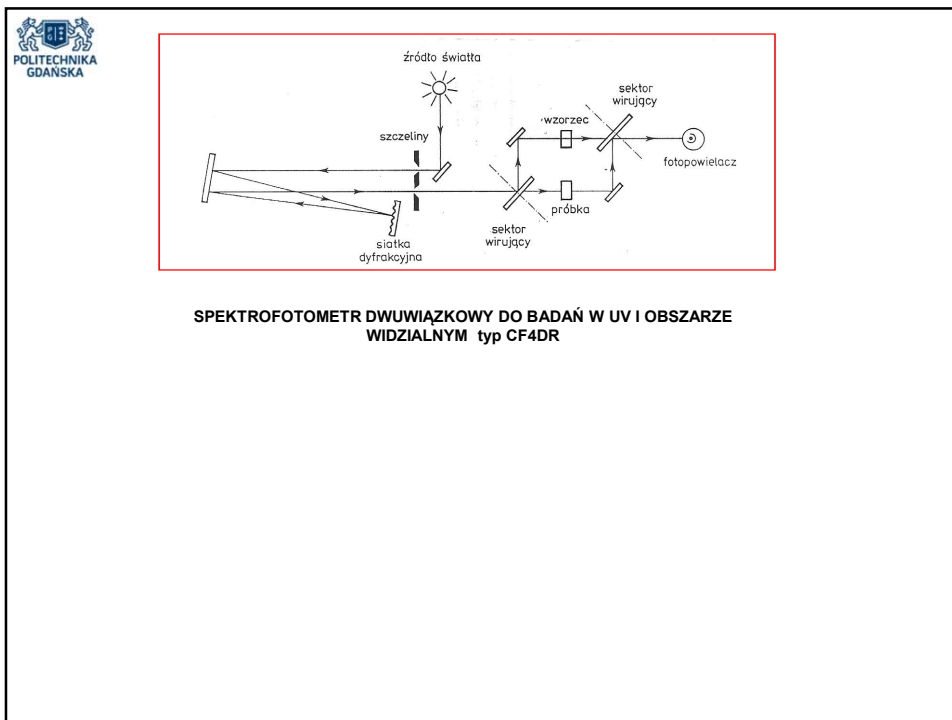
STAN WZBUDZONY

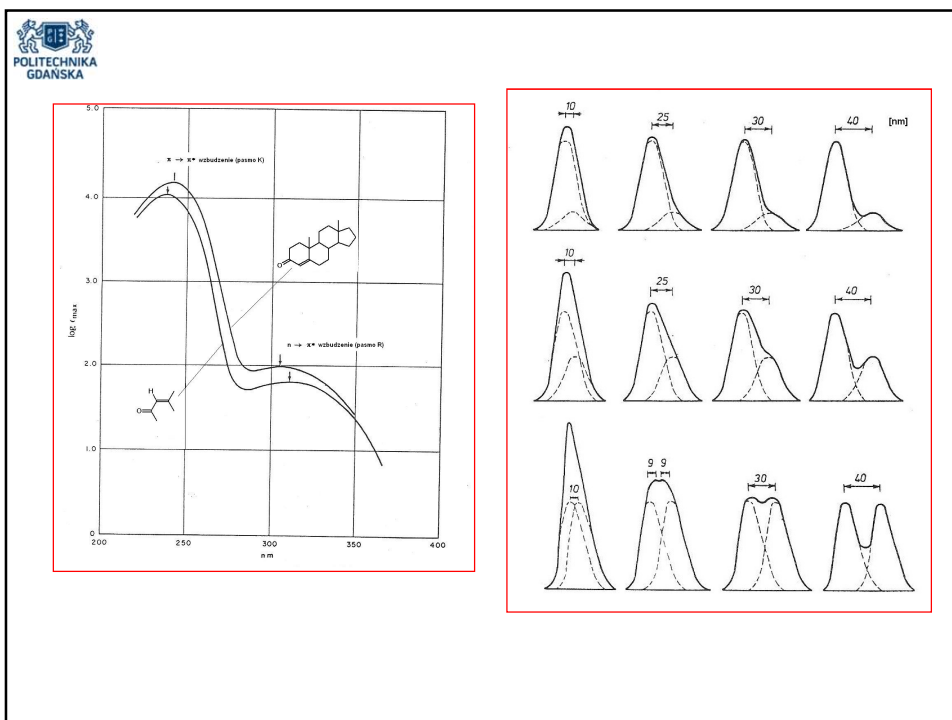
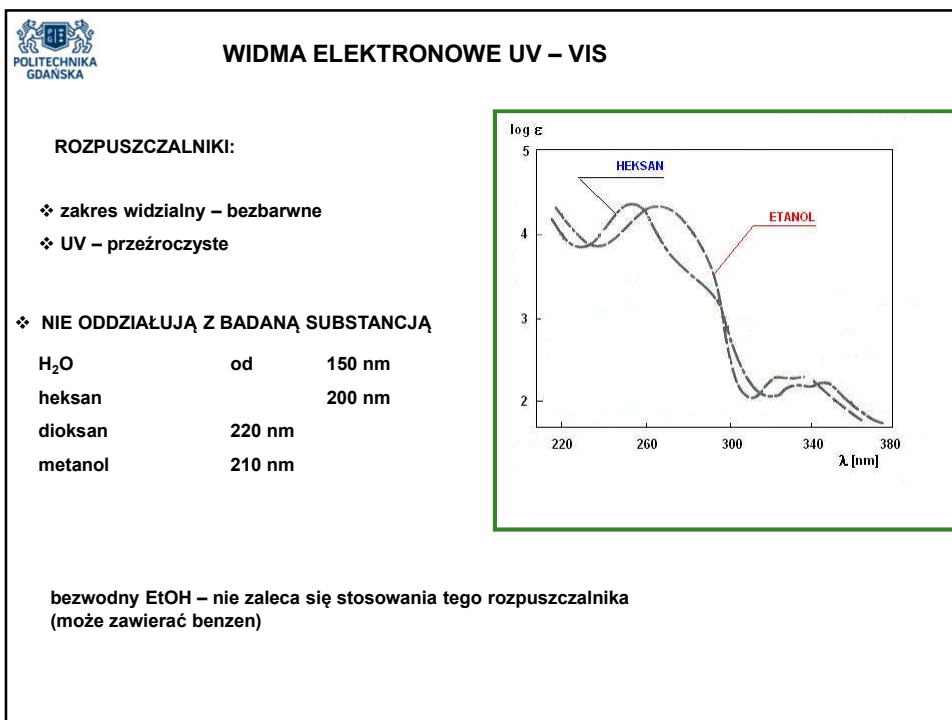
$\Delta E [kJ/mol] = 118\,825 / \lambda$

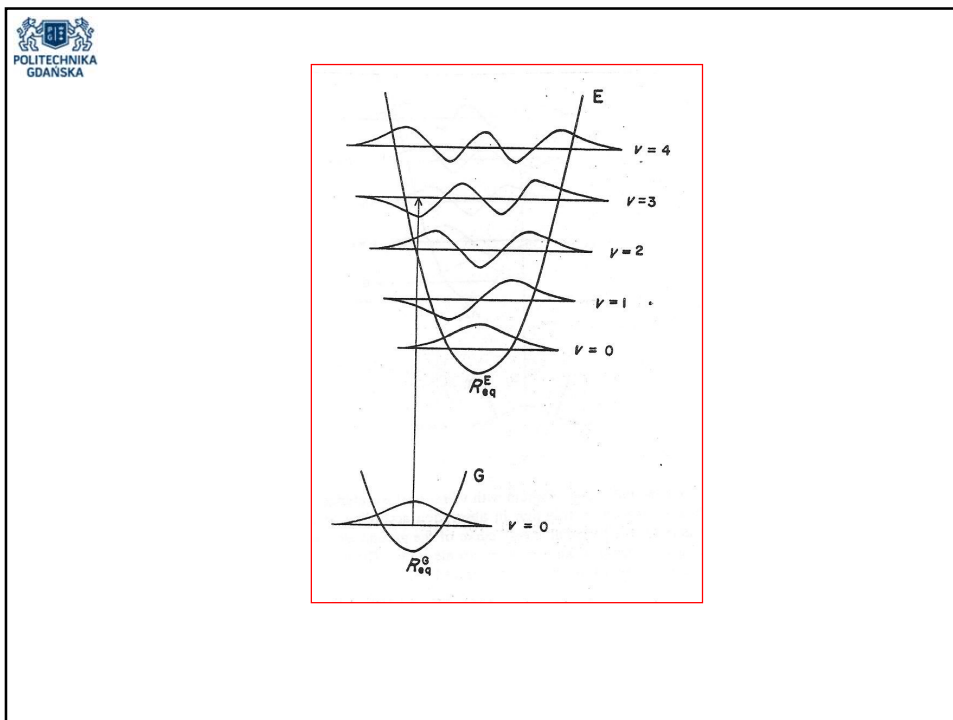
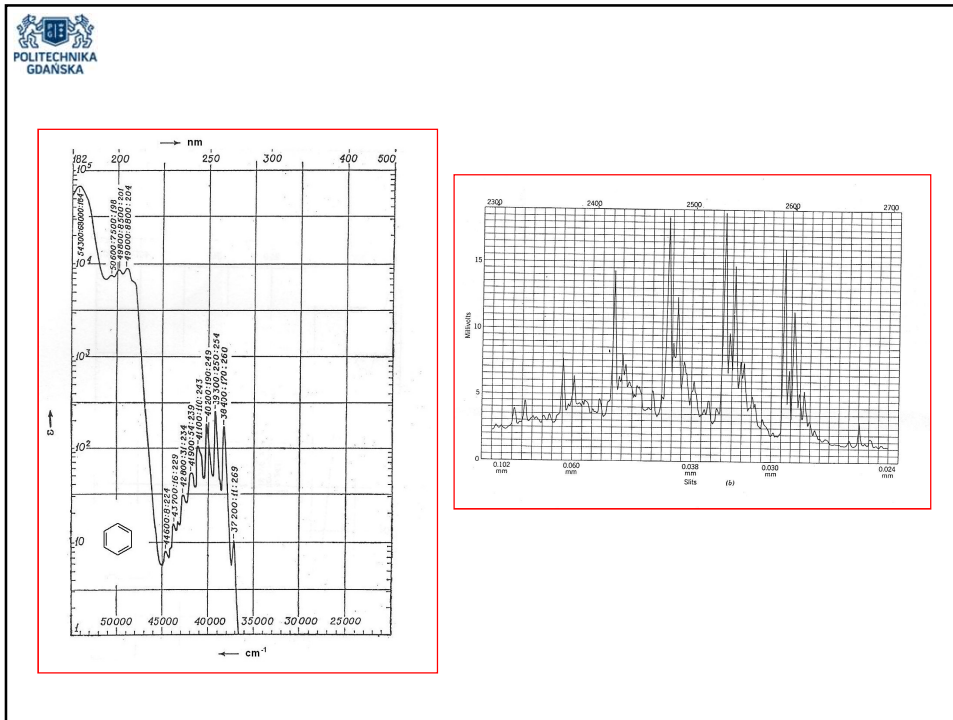
$\Delta E = h\nu$

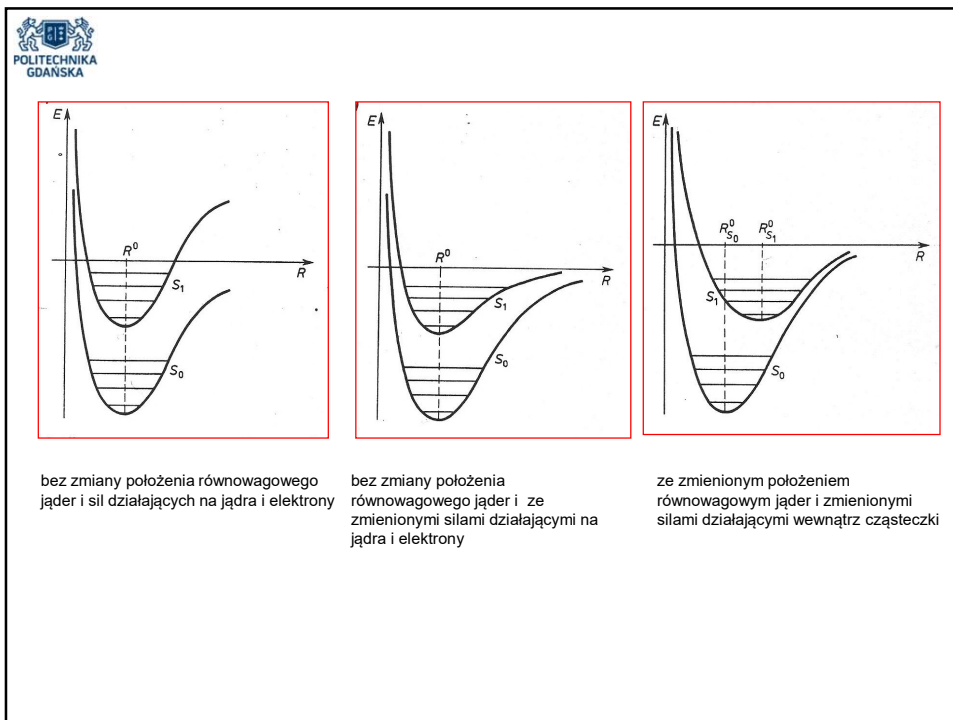
dla λ 200 – 700 nm 170 – 600 kJ/mol







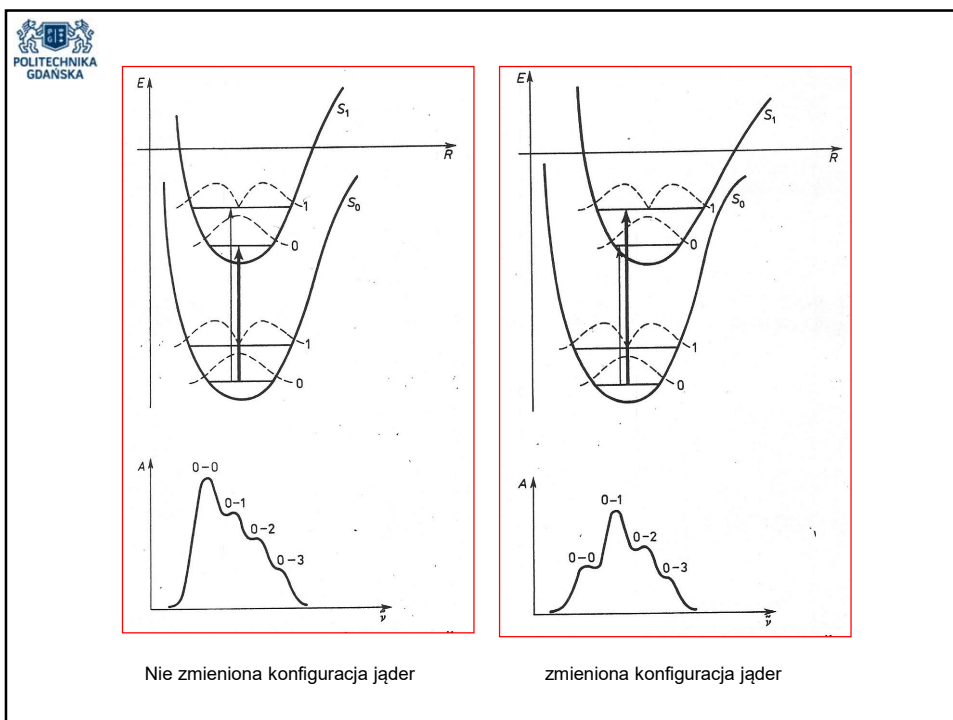




bez zmiany położenia równowagowego jąder i sił działających na jądra i elektrony

bez zmiany położenia równowagowego jąder i ze zmienionymi siłami działającymi na jądra i elektrony

ze zmienionym położeniem równowagowym jąder i zmienionymi siłami działającymi wewnątrz cząsteczki



Nie zmieniona konfiguracja jąder

zmieniona konfiguracja jąder


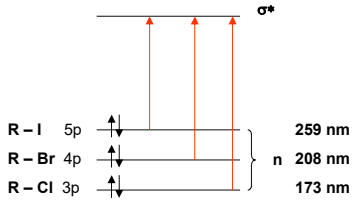
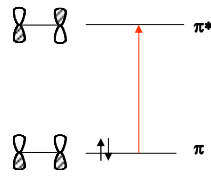
IZOLOWANE CHROMOFORY

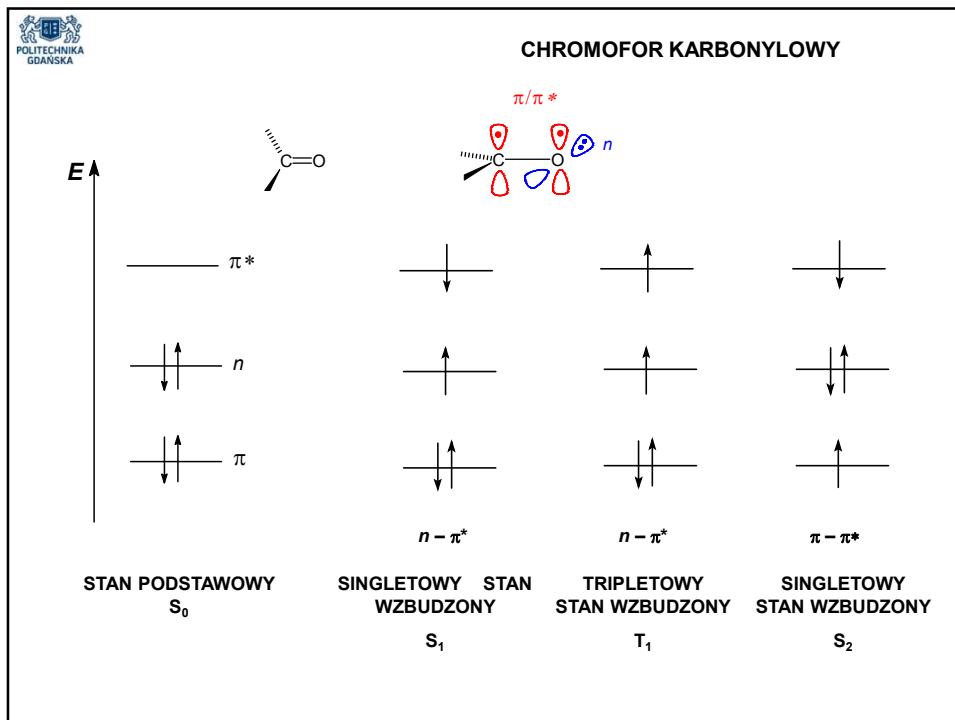
Chromophoric Group	System	Example	λ_{\max} (nm)	ϵ_{\max}	Transition	Solvent
Ethylenic	RCH=CHR	Ethylene	165	15,000	$\pi \rightarrow \pi^*$	Vapor
			193	10,000	$\pi \rightarrow \pi^*$	
Acetylenic	R-C \equiv C-R	Acetylene	173	6,000	$\pi \rightarrow \pi^*$	Vapor
Carbonyl	RR ₂ C=O	Acetone	188	900	$\pi \rightarrow \pi^*$	n-Hexane
			279	15	$n \rightarrow \pi^*$	
Carbonyl	RHC=O	Acetaldehyde	290	16	$n \rightarrow \pi^*$	Heptane
Carboxyl	RCOOH	Acetic acid	204	60	$n \rightarrow \pi^*$	Water
Amido	RCONH ₂	Acetamide	<208		$n \rightarrow \pi^*$	
Azomethine	>C=N-	Acetoxime	190	5,000	$\pi \rightarrow \pi^*$	Water
Nitrile	-C \equiv N	Acetonitrile	<160		$\pi \rightarrow \pi^*$	
Azo	-N=N-	Azomethane	347	4.5	$n \rightarrow \pi^*$	Dioxane
Nitroso	-N=O	Nitrosobutane	300	100	$n \rightarrow \pi^*$	Ether
			665	20		
Nitrate	-ONO ₂	Ethyl nitrate	270	12	$n \rightarrow \pi^*$	Dioxane
Nitro		Nitromethane	271	18.6	$n \rightarrow \pi^*$	Alcohol
			346.5 ^a			
Nitrite		Amyl nitrite	218.5	1,120	$\pi \rightarrow \pi^*$	Petroleum ether
			346.5 ^a		$n \rightarrow \pi^*$	
Sulfoxide		Cyclohexyl methyl sulfoxide	270	1,500		Alcohol
Sulfone		Dimethyl sulfone	<.80			

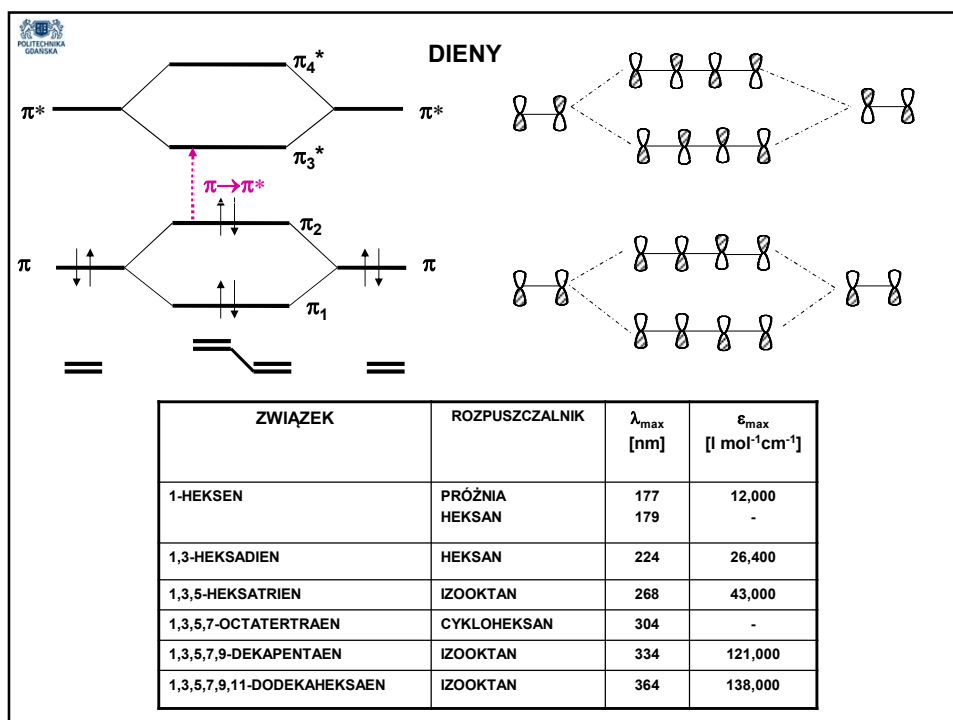
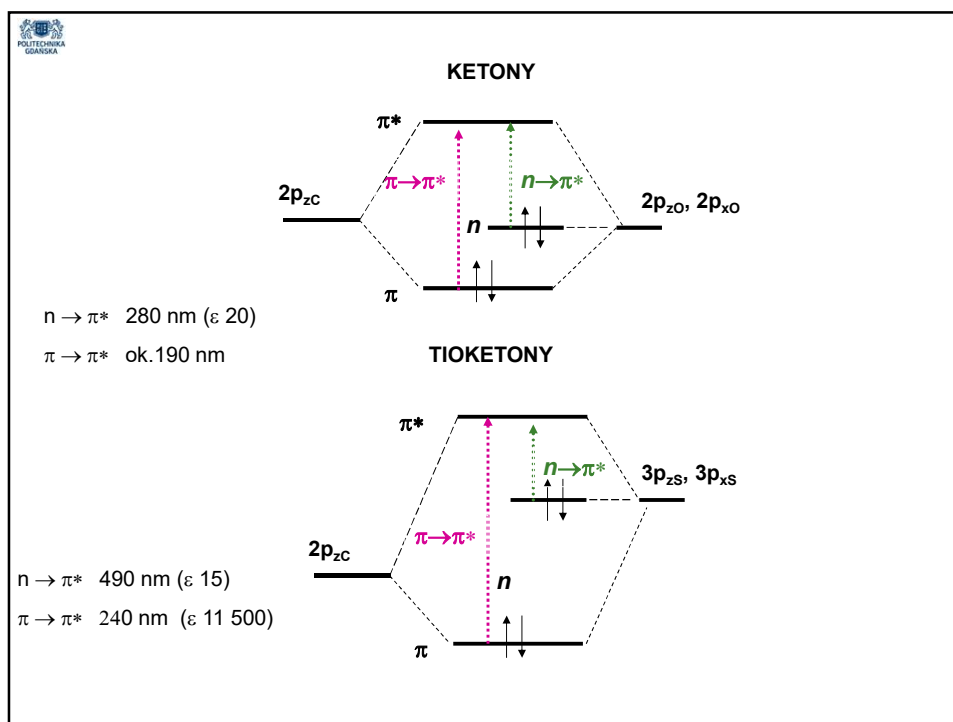
^aMost intense peak of fine structure group.

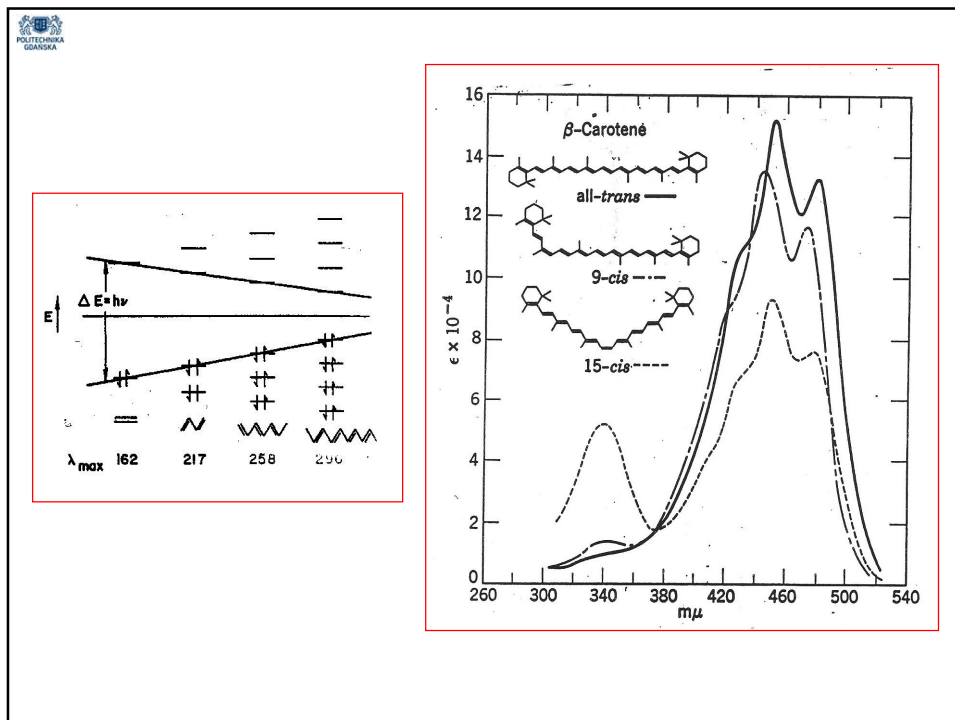
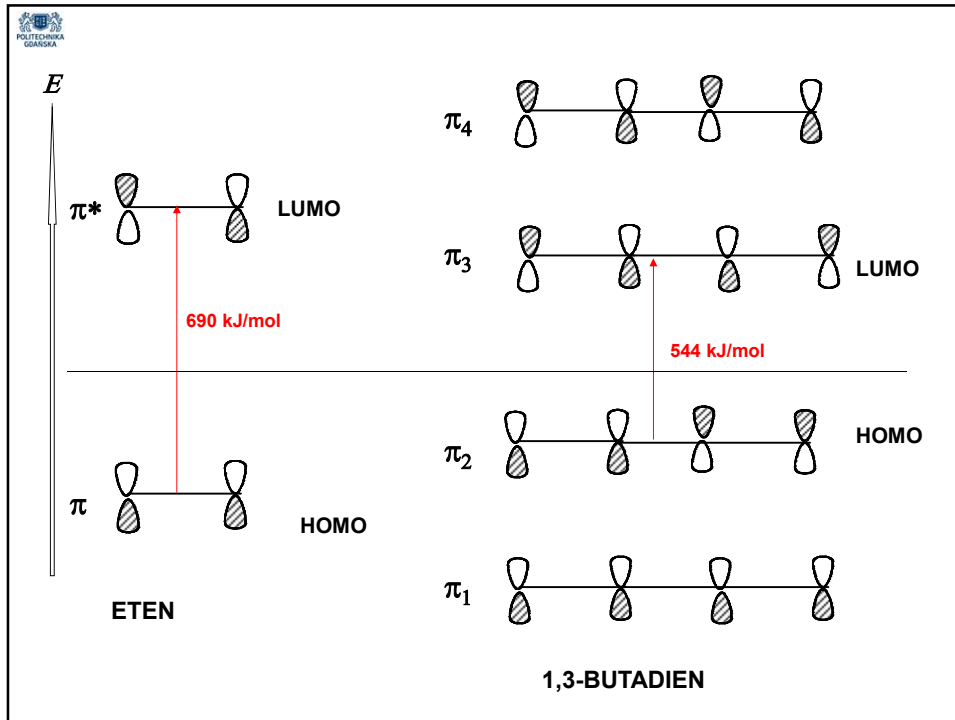
PASMA ABSORPCJI WYBRANYCH PROSTYCH CHROMOFORÓW

Chromofor	Molekuła	Długość fali maksimum pasma λ_{\max} [nm]	Dziesiętny molowy współczynnik absorpcji w maksimum ϵ_{\max} [dm ³ ·mol ⁻¹ ·cm ⁻¹]
przejścia $n \rightarrow \sigma^*$			
-Cl	CH ₃ Cl	173	200
-Br	CH ₃ Br	204	200
-I	CH ₃ I	259	3 600
-O-	H ₂ O	167	7 000
-N	CH ₃ OH	184	150
	CH ₃ -CO-CH ₃	188	1 900
	CH ₃ NH ₂	215	600
	(CH ₃) ₃ N	227	900
przejścia $\pi \rightarrow \pi^*$			
C=C	H ₂ C=CH ₂	165	10 000
	RCH=CH ₂	175	12 600
	R ₂ C=CH ₂	187	8 000
	cykloheksen	183	7 600
	C \equiv C	HC \equiv CH	173
C=C=C	RC \equiv CH	187	450
	RC \equiv CR	191	850
	C ₂ H ₅ CH=C=CH ₂	225	500
przejścia $n \rightarrow \pi^*$			
C=O	CH ₃ CHO	294	12
	CH ₃ -CO-CH ₃	279	14
N=N	CH ₃ N=NCH ₃	340	4.5
N=O	t-C ₄ H ₉ NO	665	20

 CHROMOFORY		
ALKANY	$\sigma \rightarrow \sigma^*$	przejrzyste w bliskim UV
ROH ROR' RSH RSR' RNH ₂ , R ₂ NH, R ₃ N	$n \rightarrow \sigma^*$	
R-X X = F, Cl, Br, I	$n \rightarrow \sigma^*$	
ALKENY	$\pi \rightarrow \pi^*$	












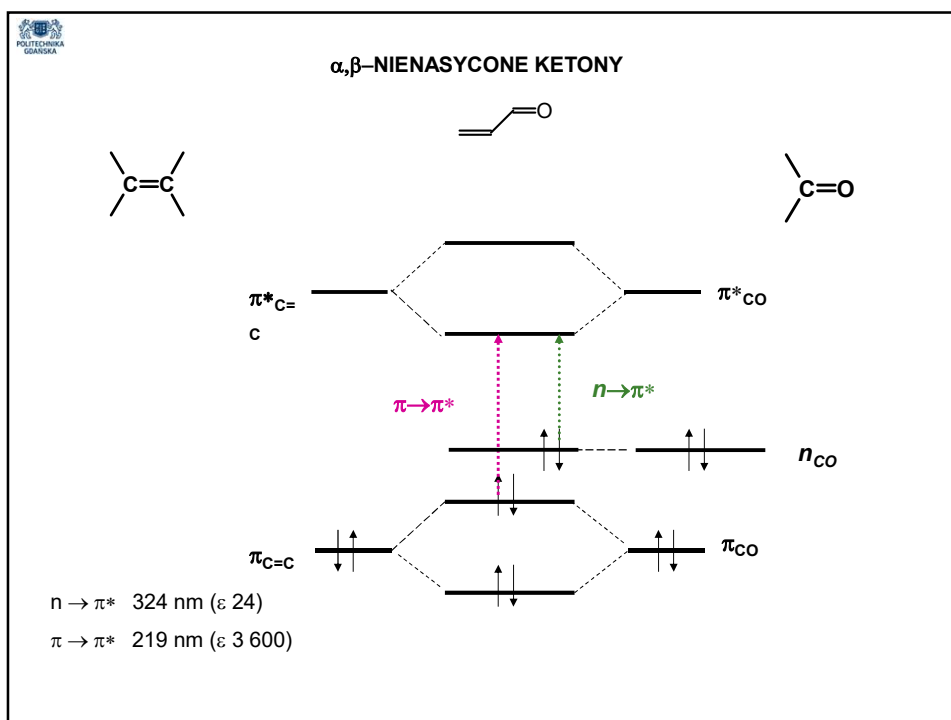


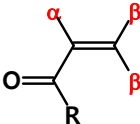
DIENY STEROLOWE I POLIENY

Group	Increment, m μ
Parent heteroannular diene	214
Parent homoannular diene	253
Double bond extending conjugation	30
Alkyl substituent or ring residue	5
Exocyclic double bond	5
Groups OAc or OR on diene system	0

WIDMA DIENÓW I TRIENÓW STEROLOWYCH

Compound	Observed		Calculated	
	λ_{max} , m μ	ϵ_{max}	λ_{max} , m μ	ϵ_{max}
(1) 	282	11,900	$253 + 4(5) + 2(5) = 283$	
(2) 	234	20,000	$214 + 3(5) + 5 = 234$	
(3)* 	245	...	$214 + 4(5) + 2(5) = 244$	
(4) 	324	11,800	$253 + 30 + 5(5) + 3(5) = 323$	
(5) 	306	14,500	$253 + 30 + 3(5) + 5 = 303$	
(6) 	315	19,800	$253 + 30 + 4(5) + 2(5) = 313$	
(7) 	355	19,700	$253 + 2(30) + 5(5) + 3(5) = 353$	




















LOKALIZACJA PASMA V ← N W α,β -NIENASYCONYCH KETONACH

Alkyl Substitution	Most Probable λ_{\max} m μ	
None	215	
α or β	225	
α,β or β,β	No exocyclic bond	235
	One exocyclic bond	240
α,β,β	No exocyclic bond	247
	One exocyclic bond	252

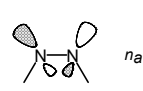
LOKALIZACJA PASMA V ← N w α,β -NIENASYCONYCH KETONACH W EtOH

ZWIĄZEK	PODSTAWNIKI	λ_{\max} , m μ		
		Calc.	Obs.	ϵ_{\max}
	α	225	221	6,450
	α	225	220	7,900
	β	225	224	9,750
	β,β	235	235	14,000
	α,β	235	233.5	...
	α,β,β	247	249	...
	β,β, exo	240	240	...
	$\alpha,\beta,\beta, \text{exo, exo}$	257	257.5	...
	α,β, exo	240	241	4,700
	$\alpha,\beta,\beta, \text{exo, exo}$	257	259	10,790


ZWIĄZEK	PODSTAWNIKI	λ_{\max} , m μ		
		Calc.	Obs.	ϵ_{\max}
	$\alpha,\beta,\beta, \text{exo}$	252	254	9,550
	α,β	235*	239	13,000
	α,β	235	233	13,000
	α,β,β	247	253	10,010
	α,β,β	247	249	6,890

ZWIĄZKI AZOWE

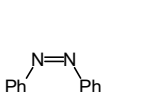
syn



n_a

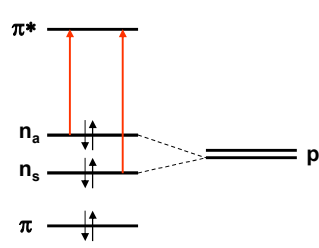


n_s



Ph N=N Ph

$n \rightarrow \pi^*$ 433 nm (ϵ 1520)
 $\pi \rightarrow \pi^*$ 281 nm (ϵ 5 260)



π^*

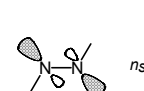
n_a

n_s

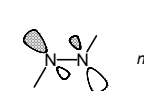
π

p_N

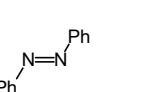
anti



n_s



n_a



Ph N=N Ph

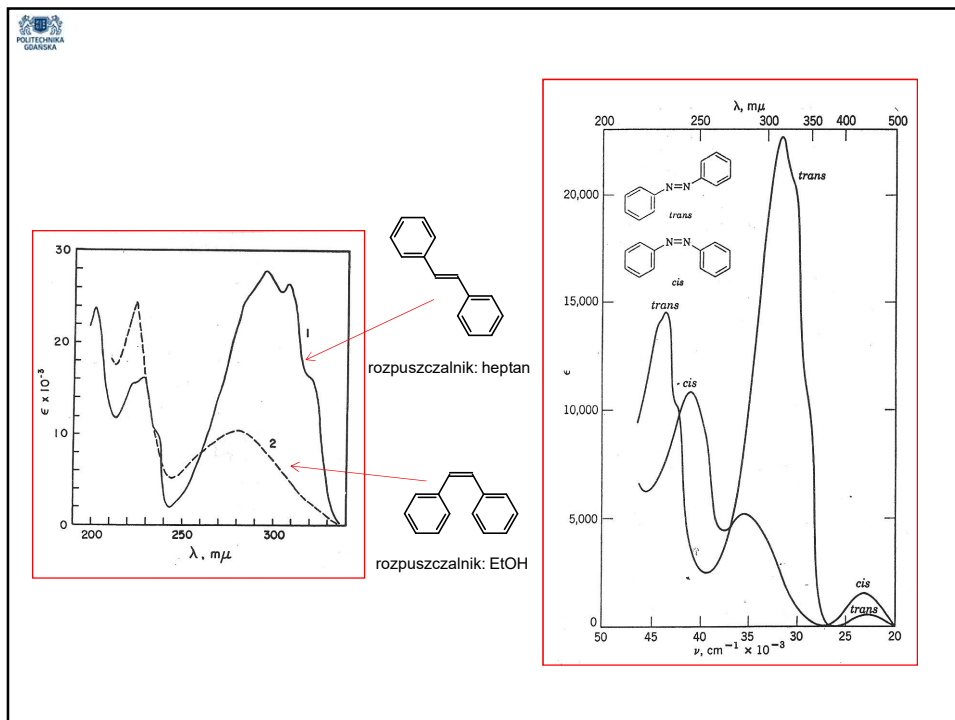
$n \rightarrow \pi^*$ 443 nm (ϵ 560)
 $\pi \rightarrow \pi^*$ 320 nm (ϵ 21 300)

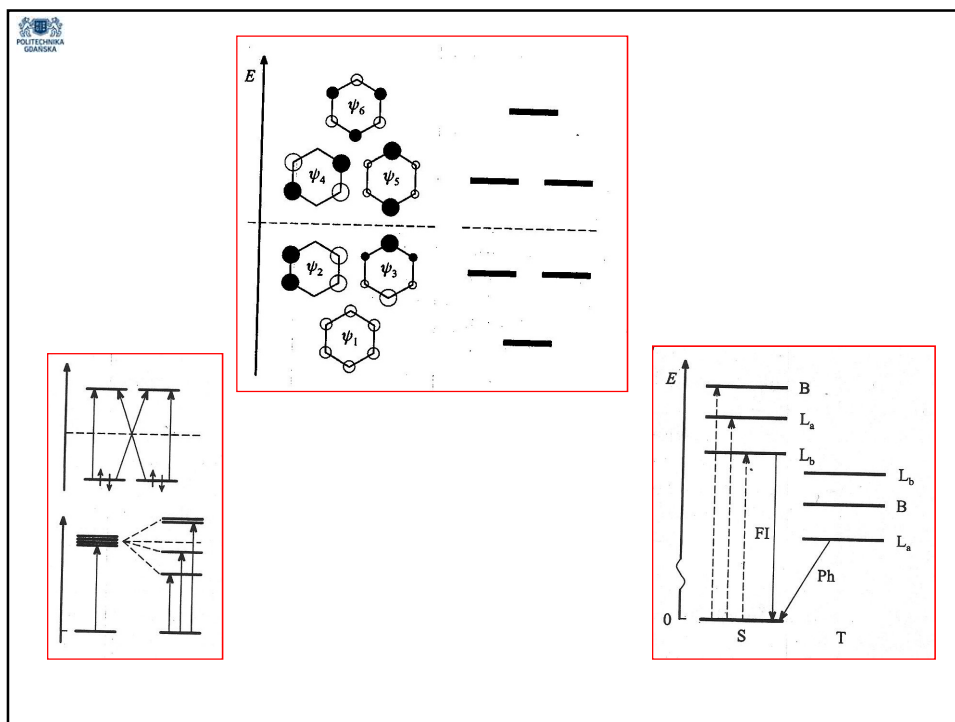
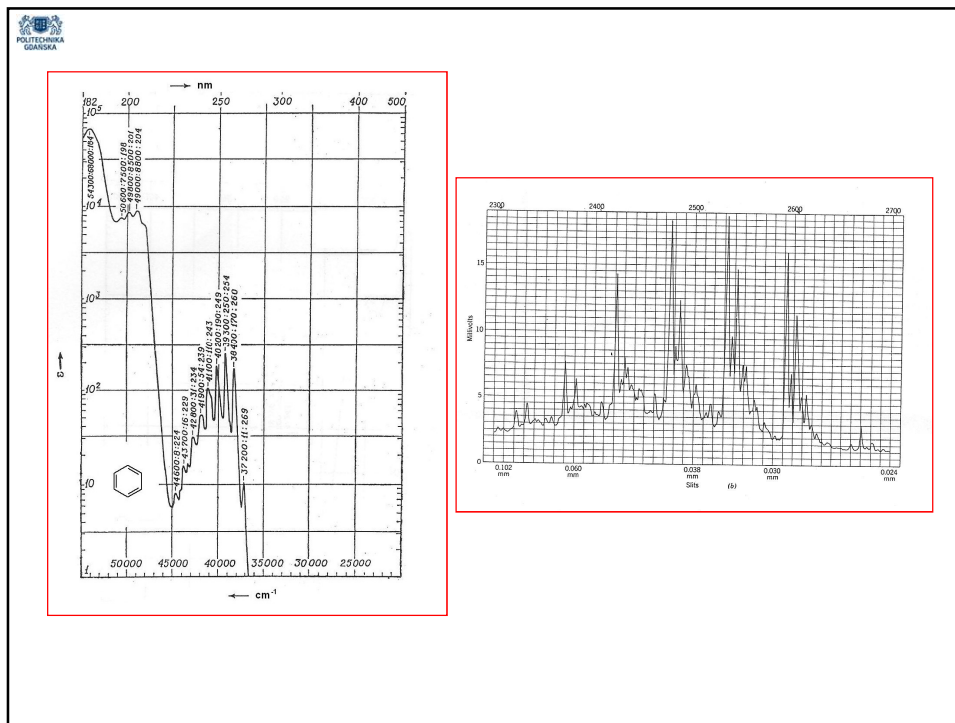
CF3-N=N-CF3

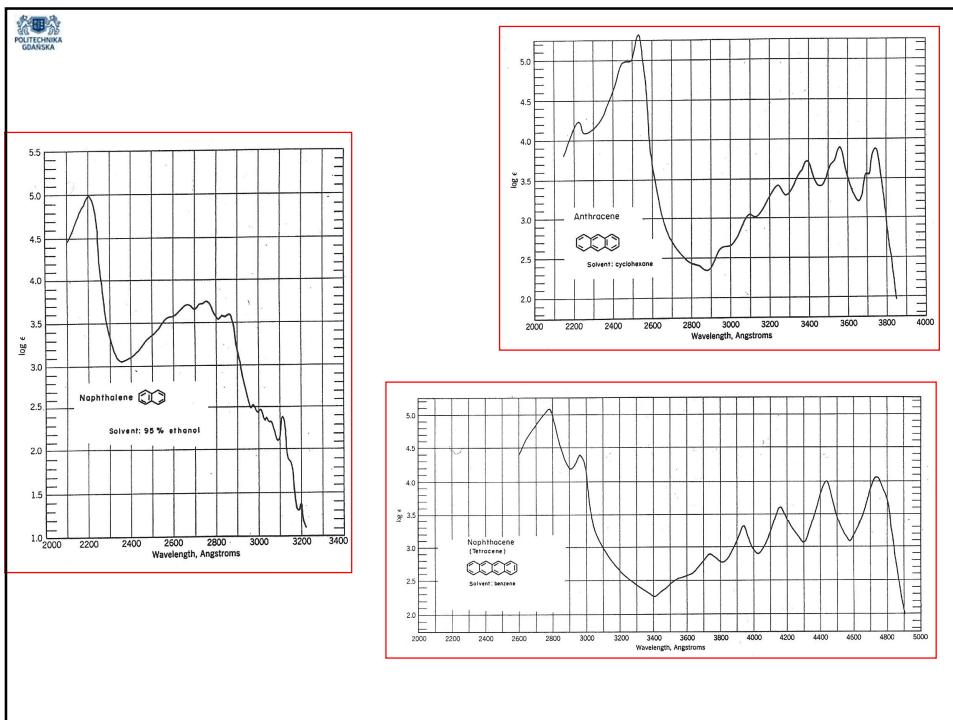
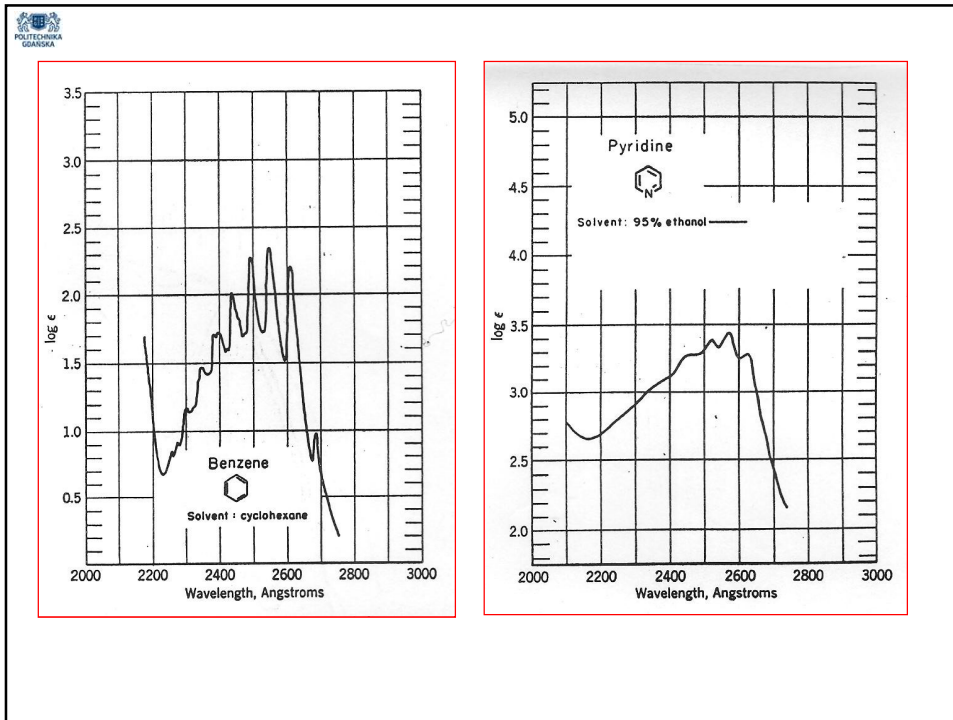
$n \rightarrow \pi^*$ 369 nm (ϵ 2)
 $\pi \rightarrow \pi^*$ 267 nm (ϵ 2)

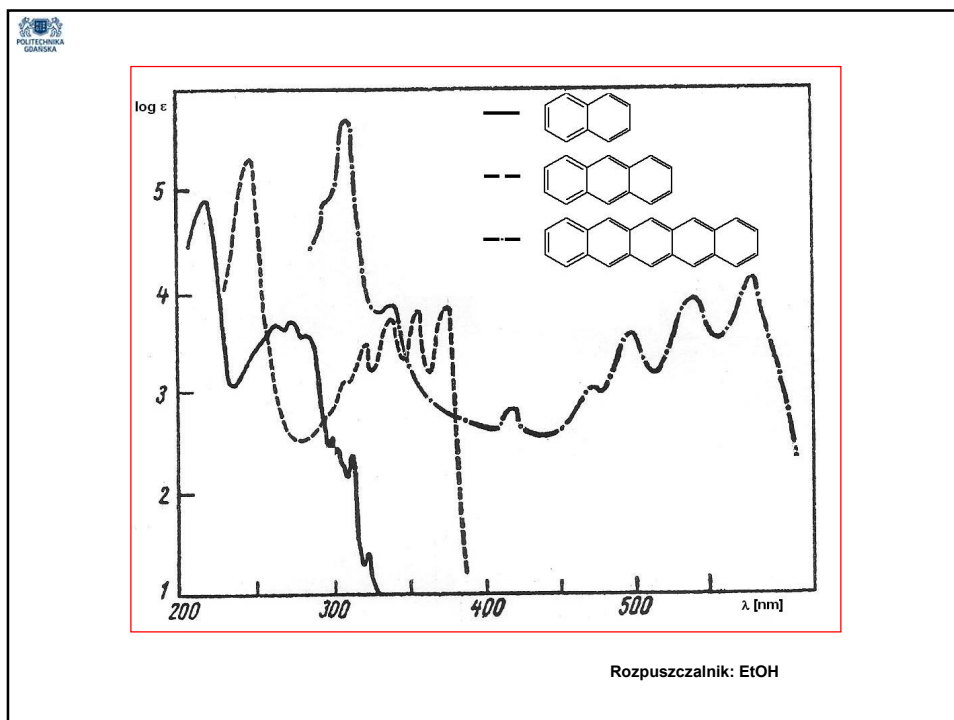
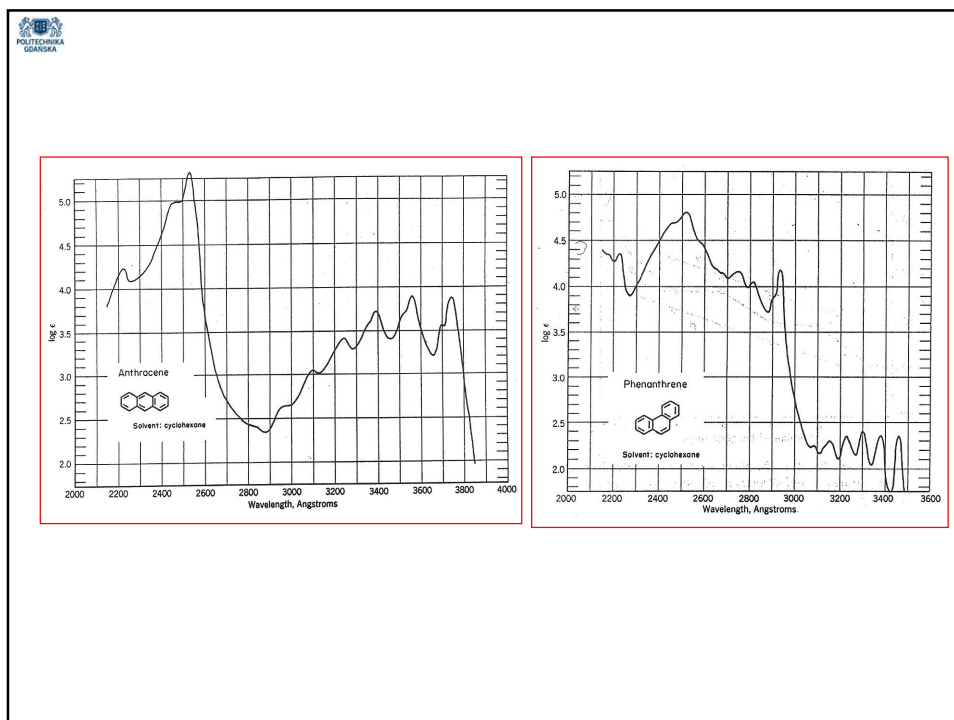
Me-N=N-Me

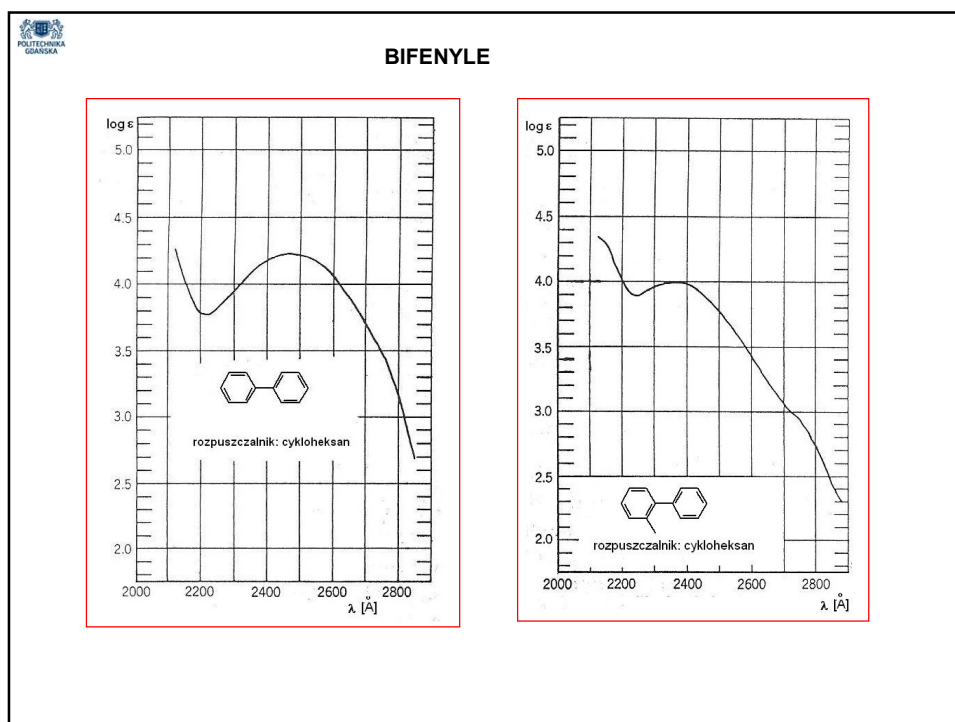
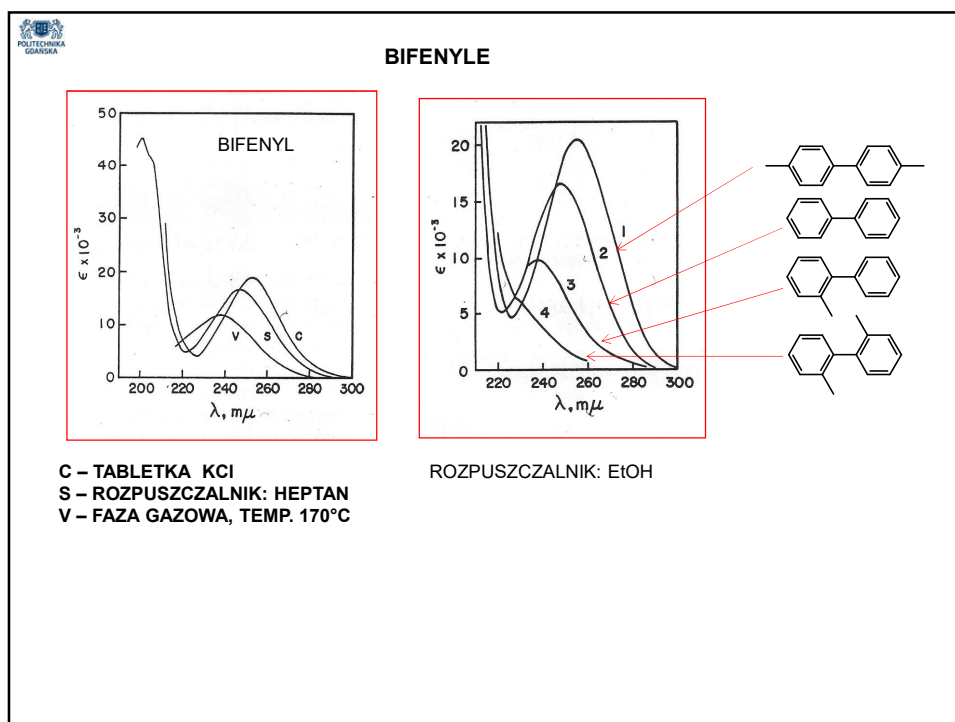
$n \rightarrow \pi^*$ 347 nm (ϵ 5)

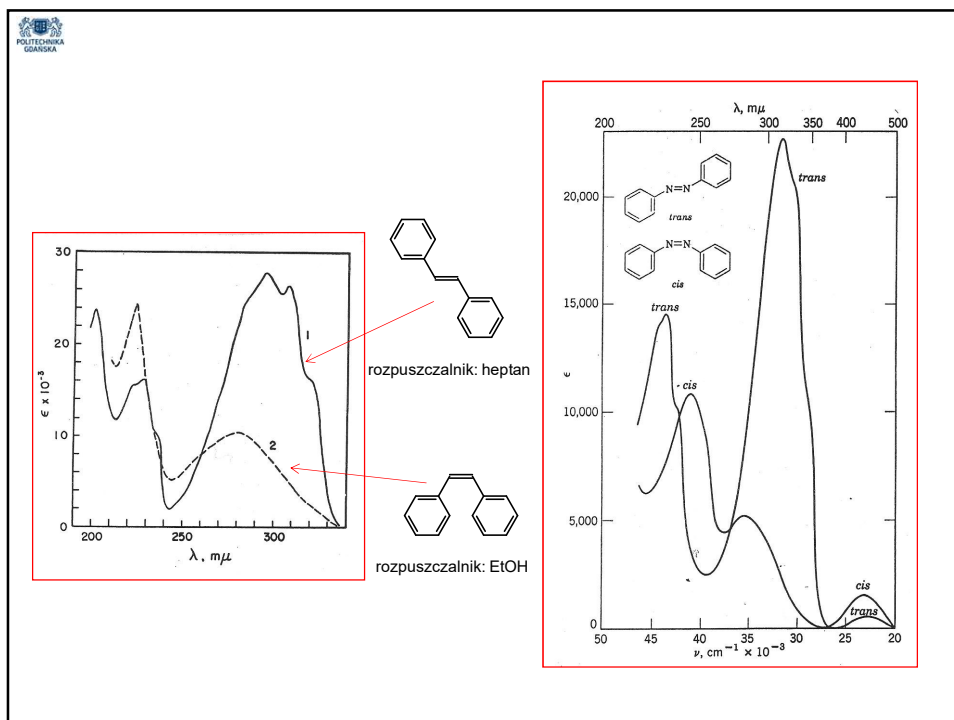












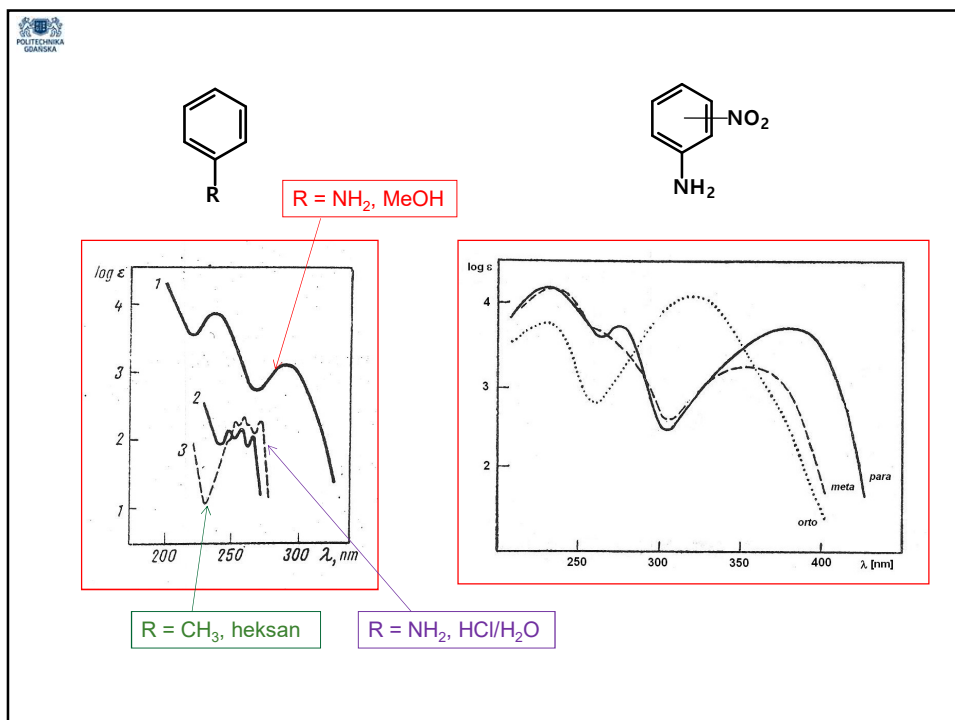
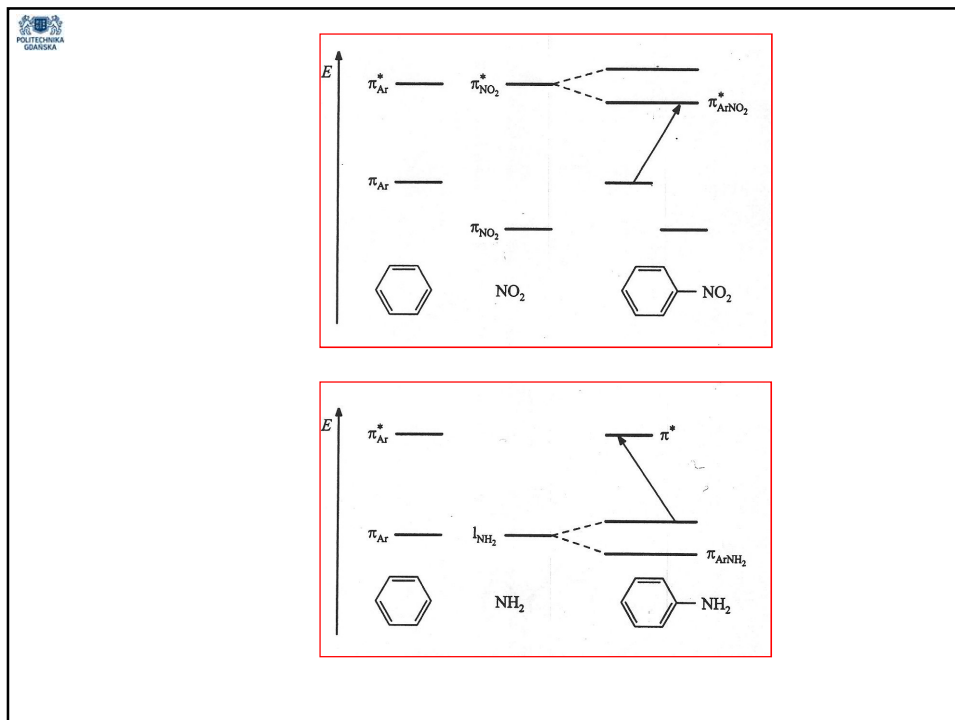
POLITECHNIKA GDAŃSKA

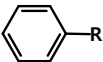
ALKILOWANE BIFENYLE

BIFENYL	ROZPUSZCZALNIK	λ_{\max} , m μ	ϵ_{\max}
NIEPODSTAWIONY	E	247.7	16600
4-Methyl-	H	247.4	16700
3-Methyl-	E	253	19000
2-Methyl-	P	249	16300
2-Ethyl-	E	235	10500
2-n-Propyl-	E	233	10500
2-Isopropyl-	E	233	10000
2-n-Butyl-	E	233	11000
4,4'-Dimethyl-	E	255.6	20500
4,4'-Diethyl-	E	256.5	22500
4,4'-Diisopropyl-	E	256.5	23500
3,3'-Dimethyl-	P	250.5	16100
2,2'-Dimethyl-	E	227*	6800
2,2'-Diethyl-	E	227*	6000
2,2'-Diisopropyl-	E	227*	5500
2,6-Dimethyl-	P	231*	5600
2,6,2'-Trimethyl-	P	230**	4000

a) * - on wavelength values denotes inflections; ** - denotes a very faint inflection

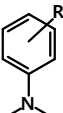
ROZPUSZCZALNIK: E - EtOH
H - HEPTAN
P - ETER NAFTOWY, tw. 100-120





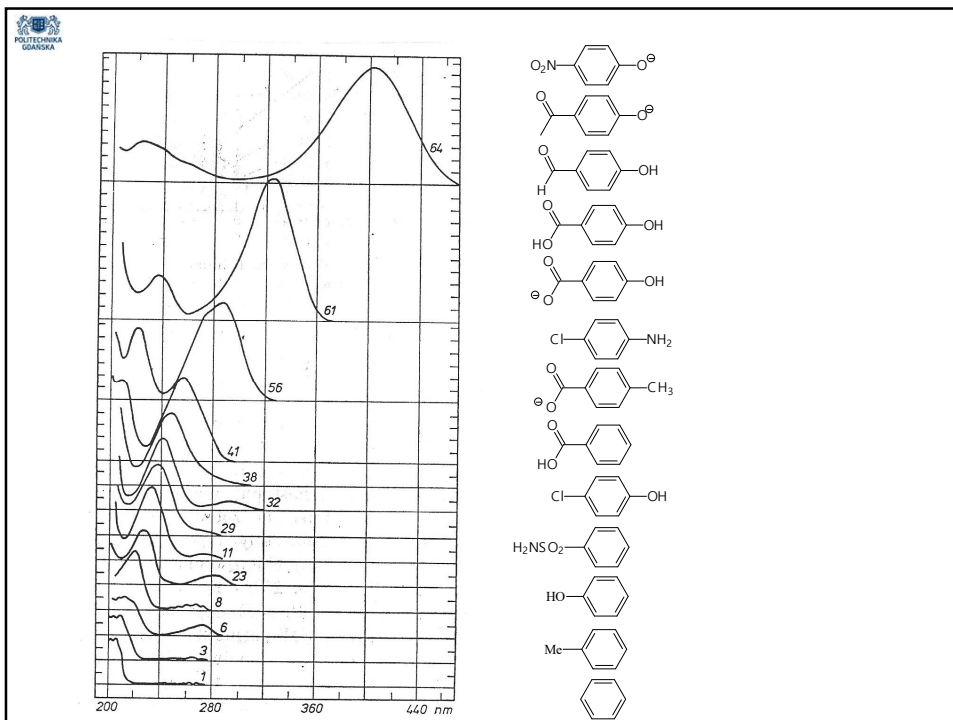
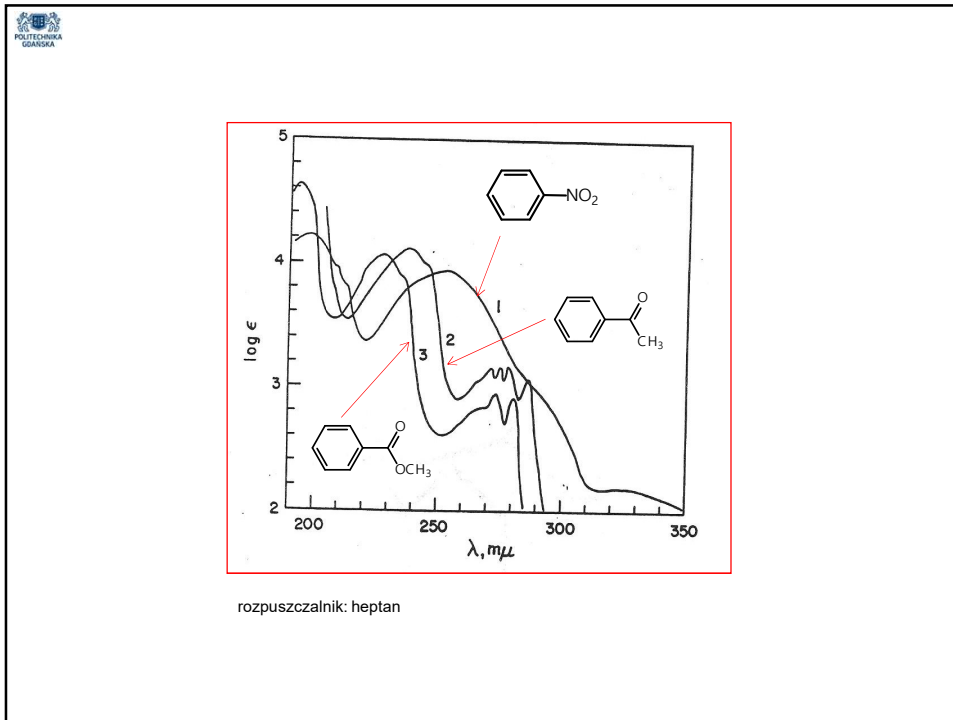
R	PASMO PIERWSZE (1L_a)		PASMO DRUGIE (1L_b)		$\lambda_{\text{sec}}/\lambda_{\text{pri}}$
	$\lambda_{\text{max}}, \text{m}\mu$	ϵ_{max}	$\lambda_{\text{max}}, \text{m}\mu$	ϵ_{max}	
H	203.5	7,400	254	204	1.25
NH ₃ ⁺	203	7,500	254	160	1.25
CH ₃	206.5	7,000	261	225	1.25
I	207 ^b	7,000	257	700	1.24
Cl	209.5	7,400	263.5	190	1.25
Br	210	7,900	261	192	1.24
OH	210.5	6,200	270	1450	1.28
OCH ₃	217	6,400	269	1480	1.24
SO ₂ NH ₂	217.5	9,700	264.5	740	1.22
CN	224	13,000	271	1000	1.21
CO ₂ ⁻	224	8,700	268	560	1.20
CO ₂ H	230	11,600	273	970	1.19
NH ₂	230	8,600	280	1430	1.22
O ⁻	235	9,400	287	2600	1.22
NHCOCH ₃ ^e	238	10,500
COCH ₃	245.5	9,800
CHO	249.5	11,400
NO ₂	268.5	7,800

^b woda jako rozpuszczalnik; dodatek MeOH dla polepszenia rozpuszczalności



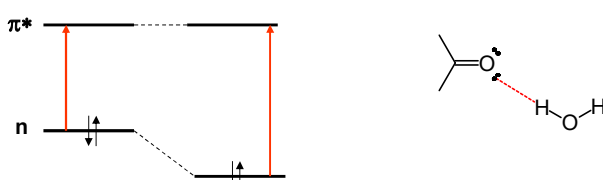
Substituent(s)	$\lambda_{\text{max}}, \text{m}\mu$	ϵ_{max}	ϵ/ϵ^0	θ, deg
H	251	15,500	(1)	(0)
2-Me	248	6,360	0.41	50
2-Et	249	4,950	0.32	56
2- <i>i</i> -Pr	248	4,300	0.28	58
2- <i>t</i> -Bu	250*	630*	0.04	78
2,6-Me ₂	262	2,240	0.14	68
2,4,6-Me ₃	257	2,500	0.16	66
2,3,5,6-Me ₄	(256)	2,090	0.13	68
2,4,6-(<i>i</i> -Pr) ₃	250*	1,540*	0.099	72
2,4-Me ₂ -6- <i>t</i> -Bu	250*	800*	0.052	77
2-Me-4,6-(<i>t</i> -Bu) ₂	250*	840*	0.054	77

^a Starred values of λ_{max} and ϵ_{max} refer to spectra without a maximum.



ROZPUSZCZALNIKI

$n - \pi^*$ PRZESUNIĘCIE HYPPOCHROMOWE (*ang.* BLUE SHIFT) W ROZPUSZCZALNIKACH POLARNYCH



$\pi - \pi^*$ PRZESUNIĘCIE BATOCHROMOWE (*ang.* RED SHIFT) W ROZPUSZCZALNIKACH POLARNYCH

