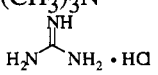
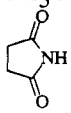
8 UV/Vis Spectroscopy

8.1 Correlation between Wavelength of Absorbed Radiation and Observed Color

Absorbed light		Observed (transmitted) color
Wavelength [nm]	Corresponding color	
400	violet	yellow-green
425	indigo blue	yellow
450	blue	orange
490	blue-green	red
510	green	purple
530	yellow-green	violet
550	yellow	indigo blue
590	orange	blue
640	red	blue-green
730	purple	green

8.2 UV/Vis Absorption of Simple Chromophores

Chromophore	Compound	Transition	λ_{max}	ε_{max}	Solvent
C–H	CH_4	$\sigma \rightarrow \sigma^*$	122	strong	gas
C–C	$CH_3–CH_3$	$\sigma \rightarrow \sigma^*$	135	strong	gas
C=C	$CH_2=CH_2$	$\pi \rightarrow \pi^*$	162	15000	heptane
	$(CH_3)_2C=C(CH_3)_2$	$\pi \rightarrow \pi^*$	196	11500	heptane
C=C=C	$CH_2=C=CH_2$		170	4000	
			227	630	
C≡C	CH≡CH		173	6000	gas
	n-C_5H_{11}–C≡C–CH_3		178	10000	hexane
			196	2000	
			222	160	
C–Cl	CH_3Cl	$n \rightarrow \sigma^*$	173	200	hexane
C–Br	n-C_3H_7Br	$n \rightarrow \sigma^*$	208	300	hexane
C–I	CH_3I	$n \rightarrow \sigma^*$	259	400	hexane

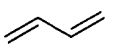
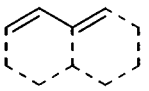
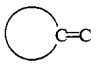
Chromophore	Compound	Transition	λ_{max}	ε_{max}	Solvent
C–O	CH_3OH	n→σ*	177	200	hexane
	CH_3OCH_3	n→σ*	184	2500	gas
C–N	$(C_2H_5)_2NH$	n→σ*	193	2500	hexane
	$(CH_3)_3N$	n→σ*	199	4000	hexane
C=N			265	15	water
	$(CH_3)_2C{=}NOH$		193	2000	ethanol
	$(CH_3)_2C{=}NONa$		265	200	ethanol
N=N	$CH_3{-}N{=}N{-}CH_3$		340	16	ethanol
N=O	$(CH_3)_3C{-}NO$		300	100	ether
			665	20	
	$(CH_3)_3C{-}NO_2$		276	27	ethanol
	$n\text{-}C_4H_9{-}O{-}NO$		218	1050	ethanol
			313–384	20–40	ethanol
	$C_2H_5{-}O{-}NO_2$		260	15	ethanol
C≡N	CH_3CN		<190		
X=Y=Z	$C_2H_5{-}N{=}C{=}S$		250	1200	hexane
	$C_2H_5{-}N{=}C{=}N{-}C_2H_5$		230	4000	
			270	25	
C–S	CH_3SH	n→σ*	195	1800	gas
		n→σ*	235	180	
	$C_2H_5{-}S{-}C_2H_5$	n→σ*	194	4500	gas
		n→σ*	225	1800	
	$C_2H_5{-}S{-}S{-}C_2H_5$	n→σ*	194	5500	hexane
		n→σ*	250	380	
C=S	$(CH_3)_2C{=}S$		460	weak	
			495	weak	ethanol
C=O	$(CH_3)_2C{=}O$	n→σ*	166	16000	gas
		π→π*	189	900	hexane
		n→π*	279	15	hexane
	CH_3COOH	n→π*	200	50	gas
	CH_3COONa	n→π*	210	150	water
	$CH_3COOC_2H_5$	n→π*	210	50	gas
	CH_3CONH_2	n→π*	220	63	water
			191	15200	CH_3CN
C=C=O	$(C_2H_5)_2C{=}C{=}O$		227	360	
			375	20	

8.3
UV/Vis Absorption of Conjugated Alkenes

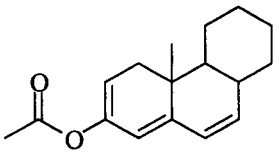
8.3.1
UV Absorption of Dienes and Polyenes

The π-π^* transition of conjugated double bonds is above ≈200 nm with typical intensities of the order of log $\varepsilon \approx 4$. Its position can be estimated with the Woodward-Fieser rule. For cross-conjugated systems, the value for the chromophore absorbing at the longest wavelength must be calculated.

Woodward-Fieser rule for estimating the position of the π-π^* transition *(λ_{max} in nm)*

Parent system		acyclic	217
		heteroannular	214
		homoannular	253
Increments	for each additional conjugated double bond		+30
	for each exocyclic double bond		+5
	for each substituent	C-substituent	+5
		Cl	+5
		Br	+5
		O-alkyl	+6
		$OCOCH_3$	0
		$N(alkyl)_2$	+60
		S-alkyl	+30
Solvent correction			≈0

Example: Estimation of the absorption maximum for

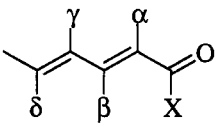


base value (homoannular)	253
1 additional conjugated double bond	30
1 exocyclic double bond	5
3 C-substituents	15
1 $OCOCH_3$	0
estimated	303
exp	306

8.3.2 UV Absorption of α,β-Unsaturated Carbonyl Compounds

The π-π* transition of α,β-unsaturated carbonyl compounds is above ≈200 nm with typical intensities of the order of log ε ≈ 4. Its position can be estimated with the extended Woodward rule. For cross-conjugated systems, the value for the chromophore absorbing at the longest wavelength should be calculated.

Extended Woodward rule for estimating the position of the π-π* transition *(λ_{max} in nm)*



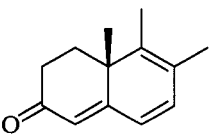
Parent system		X: alkyl	215
		X: H	207
		X: OH	193
		X: O-alkyl	193
			215
			202

Increments	for each additional conjugated double bond	+30
	for each exocyclic double bond 	+5
	for each homoannular diene system 	+39

For each substituent on double bond system	Increment α	β	γ	δ and beyond
C-substituent	+10	+12	+18	+18
Cl	+15	+12		
Br	+25	+30		
OH	+35	+30		+50
O–alkyl	+35	+30	+17	+31
O–$COCH_3$	+6	+6	+6	+6
S–alkyl		+85		
$N(alkyl)_2$		+95		

Solvent corrections	Solvent	Correction term
	water	-8
	hexane	+11
	cyclohexane	+11
	chloroform	+1
	methanol	0
	ethanol	0
	diethyl ether	+7
	dioxane	+5

Example: Estimation of the absorption maximum in ethanol for



base value	215
2 additional conjugated double bonds	60
exocyclic double bond	5
homoannular diene system	39
1 β-C-substituent	12
3 additional C-substituents	54
solvent correction	0
estimated	385
exp	388

8.4
UV/Vis Absorption of Aromatic Compounds

8.4.1
UV Absorption of Monosubstituted Benzenes

Typical Ranges for Monosubstituted Benzenes

Transition	λ_{max}	ε
π→π* (allowed)	180–230	2000–10000
π→π* (forbidden)	250–290	100–2000
π→π* (substituent delocalized by aryl; K Band)	220–250	10000–30000
n→π* (substituent with lone pair; R band)	275–350	10–100

Specific Examples of Monosubstituted Benzenes

	π→π* (allowed)		π→π* (forbidden)		π→π* (K band)		n→π* (R band)	
Substituent R (solvent)	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
–H (cyclohexane)	198	8000	255	230				
$-CH_3$ (hexane)	208	7900	262	230				
$-CH{=}CH_2$ (ethanol)			282	450	244	12000		
$-C{\equiv}CH$ (hexane)			278	650	236	12500		
–Cl (ethanol)	210	7500	257	170				
–OH (water)	211	6200	270	1450				
$-O^-$ (water)	235	9400	287	2600				
$-NH_2$ (water)	230	8600	280	1430				
$-NH_3^+$ (water)	203	7500	254	160				
$-NO_2$ (hexane)	208 213	9800 8100	270	800	251	9000	322	150
–CN (water)			271	1000	224	13000		
–CHO (hexane)			280	1400	242	14000	≈330	≈60
$-COCH_3$ (ethanol)			278	1100	243	13000	319	50
–COOH (water)	202	8000	270	800	230	10000		

8.4.2
UV Absorption of Substituted Benzenes

Estimation of the position of the allowed π-π^* transition in multiply substituted benzenes *(λ_{max} in nm, log ε: ≈4)*

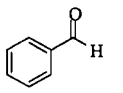
Base value: 203.5

Substituent	Increment [nm]
$-CH_3$	3.0
-Cl	6.0
-Br	6.5
-OH	7.0
$-O^-$	31.5
$-OCH_3$	13.5
$-NH_2$	26.5
$-NHCOCH_3$	38.5
$-NO_2$	65.0
-CN	20.5
-CHO	46.0
$-COCH_3$	42.0
-COOH	25.5

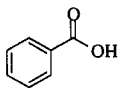
8.4.3
UV Absorption of Aromatic Carbonyl Compounds

Scott rules for estimating the position of the K band
(solvent: ethanol; λ_{max} in nm, ε: 10000–30000)

Parent system:



250



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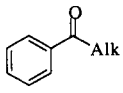

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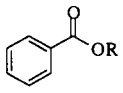
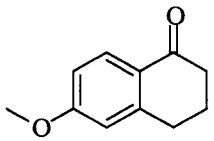


230

Increments

Substituent	*ortho*	*meta*	*para*
–alkyl	3	3	10
–cycloalkyl	3	3	10
–Cl	0	0	10
–Br	2	2	15
–OH	7	7	25
–O–alkyl	7	7	25
$-O^-$	11	20	78
$-NH_2$	13	13	58
$-N(CH_3)_2$	20	20	85
$-NHCOCH_3$	20	20	45

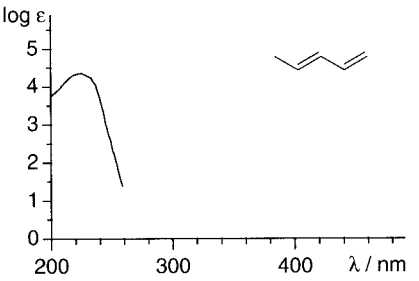
Example: Estimation of the absorption maximum (K band) for

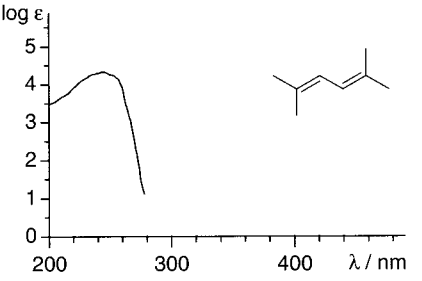


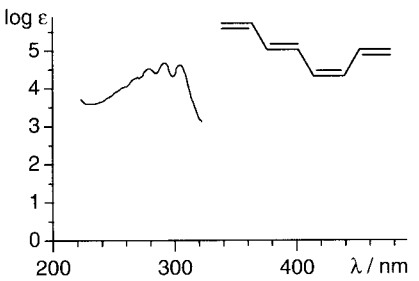
base value	246
ortho -cycloalkyl	3
para -O-alkyl	25
estimated	274
exp	276

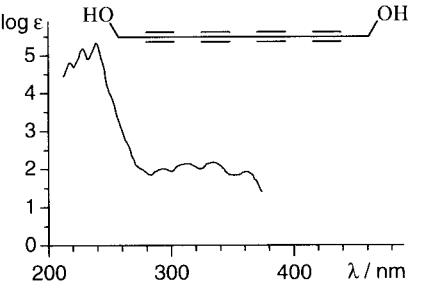
8.5
UV/Vis Reference Spectra

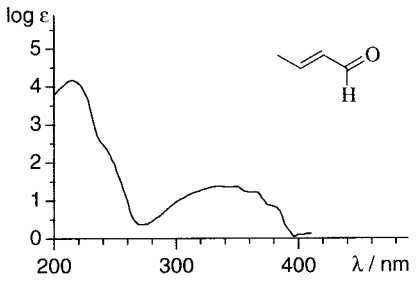
8.5.1
UV/Vis Spectra of Alkenes and Alkynes

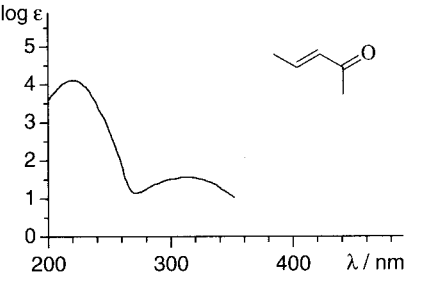


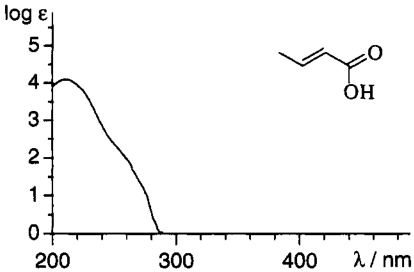


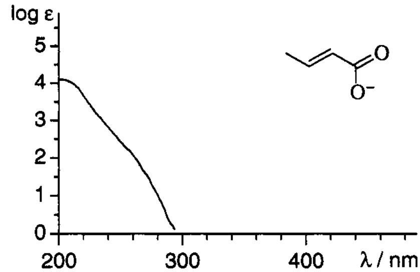




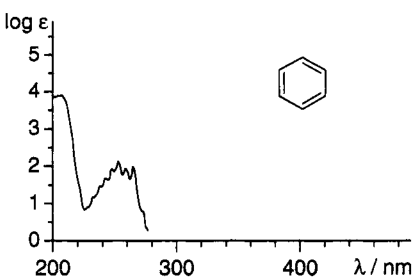


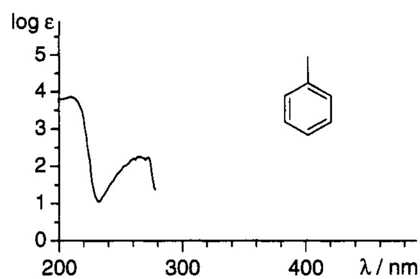


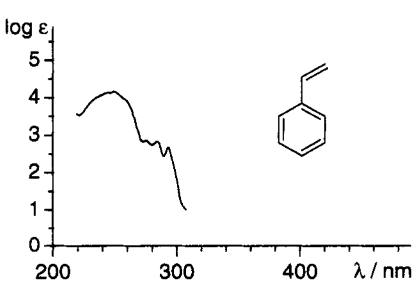


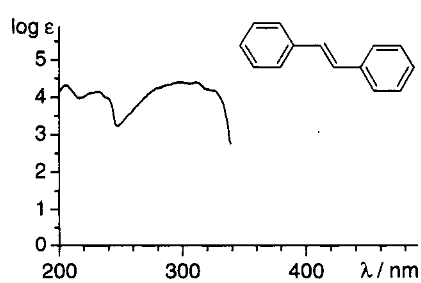


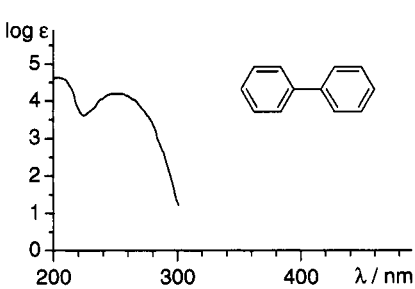
8.5.2 UV/Vis Spectra of Aromatic Compounds

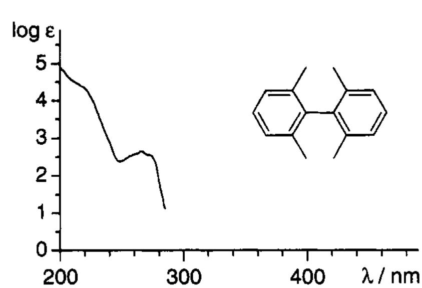


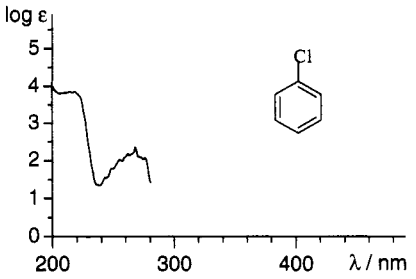


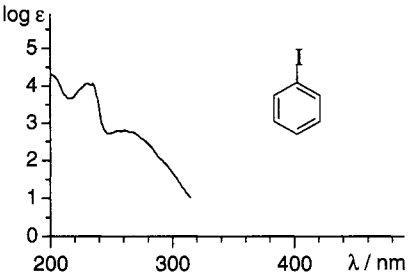


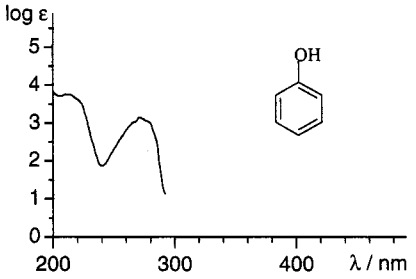


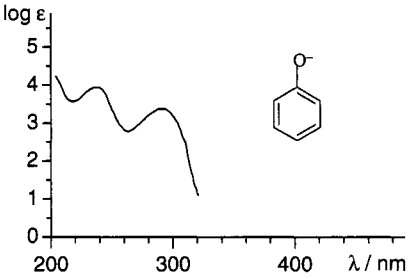


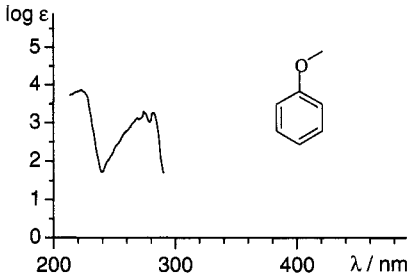


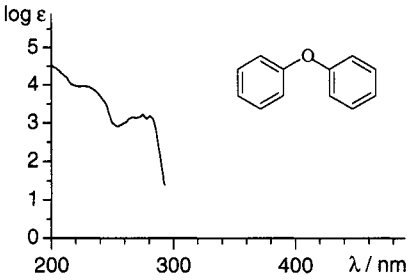

log ε
5
4
3
2
1
0
200
300
400
λ / nm
Cl

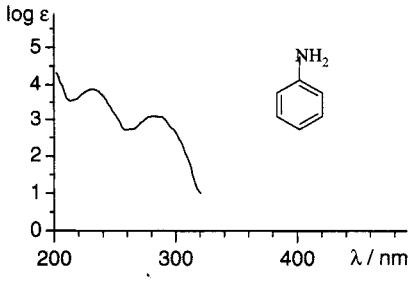

log ε
5
4
3
2
1
0
200
300
400
λ / nm
I

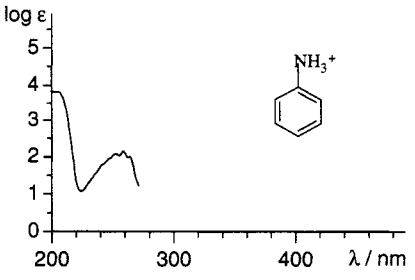

log ε
5
4
3
2
1
0
200
300
400
λ / nm
OH

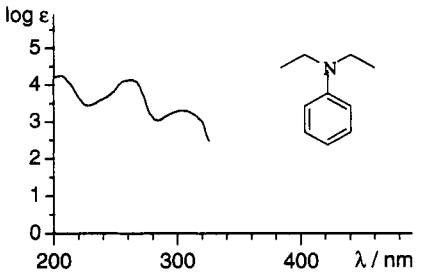

log ε
5
4
3
2
1
0
200
300
400
λ / nm
O⁻

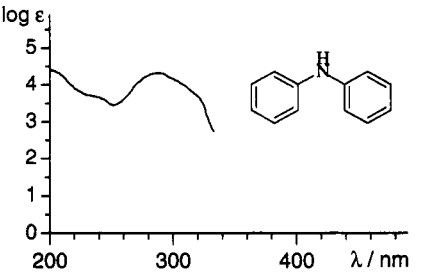

log ε
5
4
3
2
1
0
200
300
400
λ / nm
O

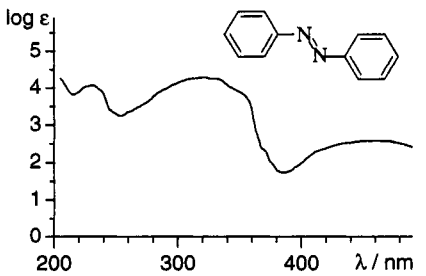

log ε
5
4
3
2
1
0
200
300
400
λ / nm
O

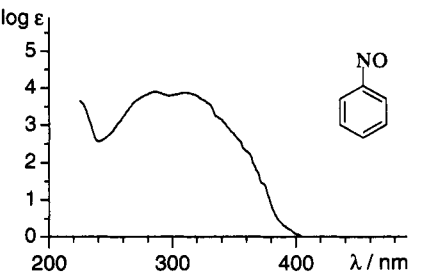

log ε
5
4
3
2
1
0
200
300
400
λ / nm
NH2

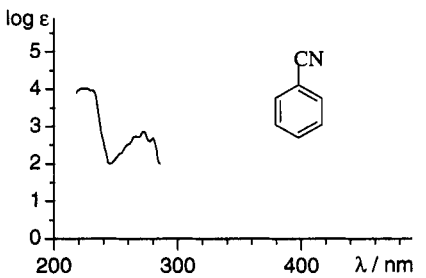

log ε
5
4
3
2
1
0
200
300
400
λ / nm
NH3+

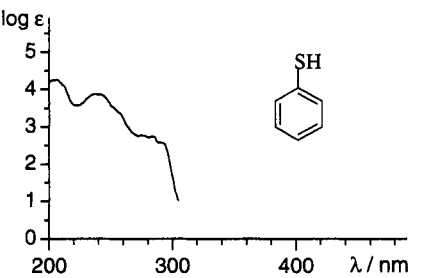

log ε
5
4
3
2
1
0
200
300
400
λ / nm
N

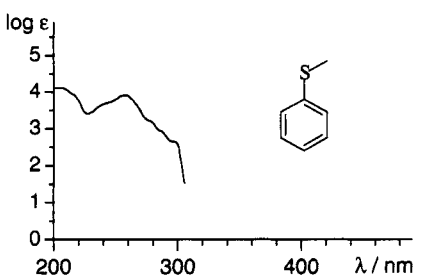

log ε
5
4
3
2
1
0
200
300
400
λ / nm
H
N

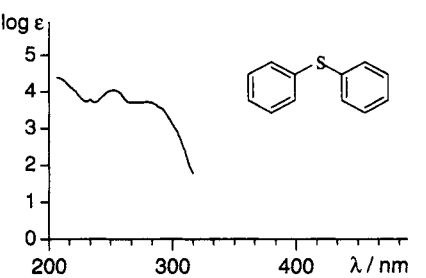

log ε
5
4
3
2
1
0
200
300
400
λ / nm
N
N

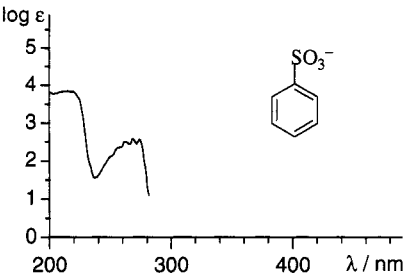

log ε
5
4
3
2
1
0
200
300
400
λ / nm
NO

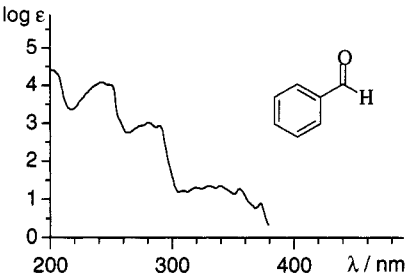

log ε
5
4
3
2
1
0
200
300
400
λ / nm
CN

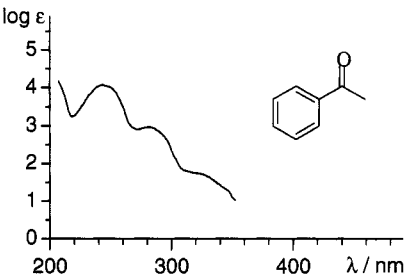

log ε
5
4
3
2
1
0
200
300
400
λ / nm
SH

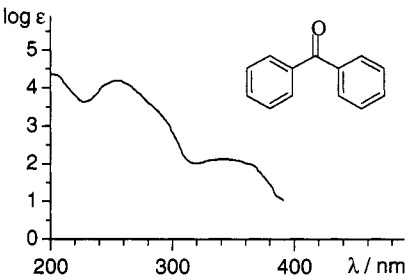

log ε
5
4
3
2
1
0
200
300
400
λ / nm
S

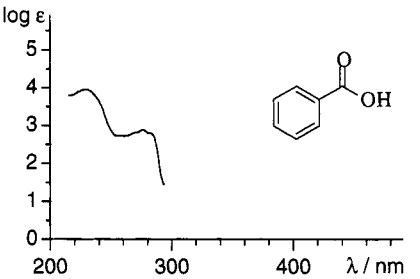

log ε
5
4
3
2
1
0
200
300
400
λ / nm
S

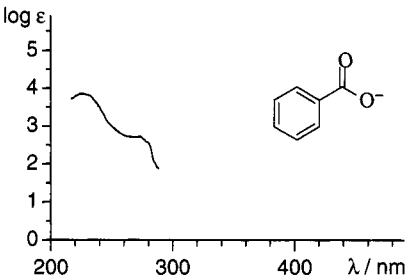

log ε
5
4
3
2
1
0
200
300
400
λ / nm
SO3−

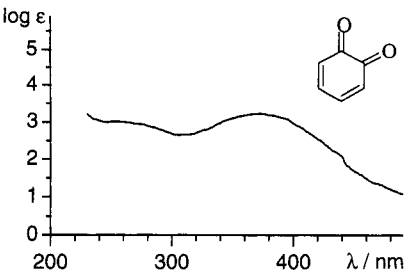

log ε
5
4
3
2
1
0
200
300
400
λ / nm
O
H

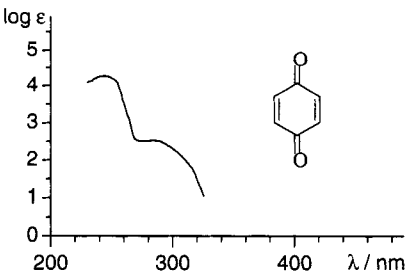

log ε
5
4
3
2
1
0
200
300
400
λ / nm
O

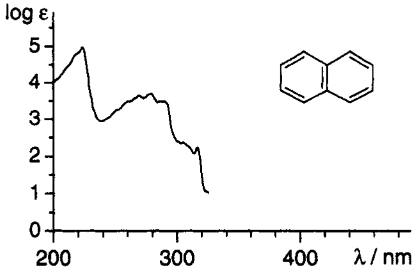

log ε
5
4
3
2
1
0
200
300
400
λ / nm
O

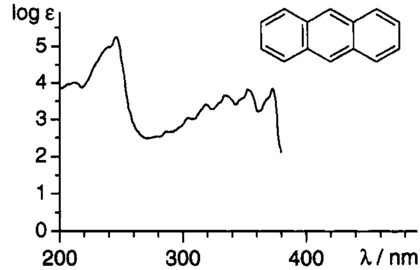

log ε
5
4
3
2
1
0
200
300
400
λ / nm
O
OH

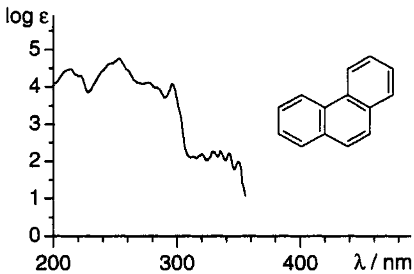

log ε
5
4
3
2
1
0
200
300
400
λ / nm
O
O−

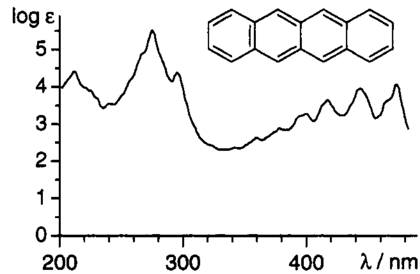

log ε
5
4
3
2
1
0
200
300
400
λ / nm
O
O

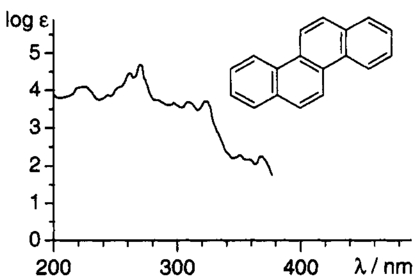

log ε
5
4
3
2
1
0
200
300
400
λ / nm
O
O

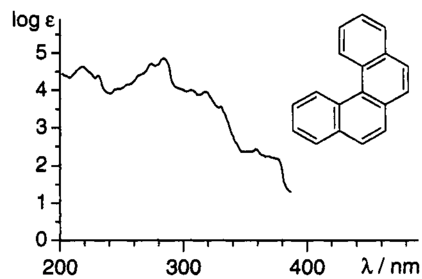

log ε
5
4
3
2
1
0
200
300
400
λ / nm

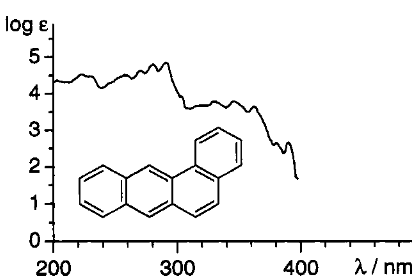

log ε
5
4
3
2
1
0
200
300
400
λ / nm

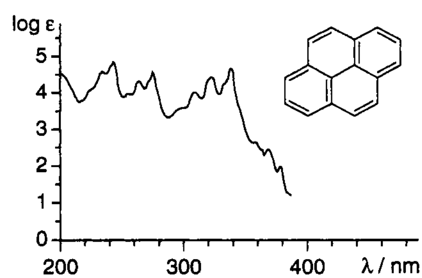

log ε
5
4
3
2
1
0
200
300
400
λ / nm

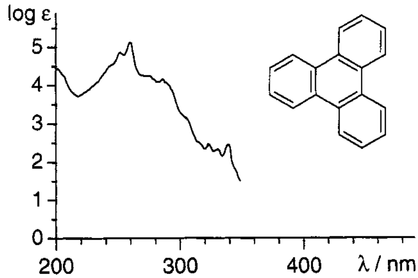

log ε
5
4
3
2
1
0
200
300
400
λ / nm

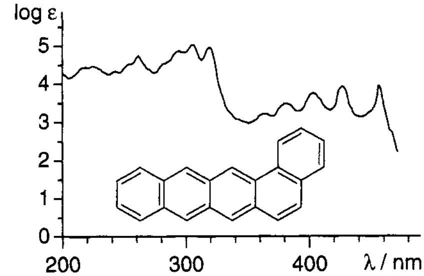

log ε
5
4
3
2
1
0
200
300
400
λ / nm

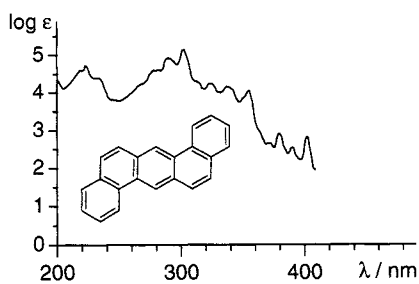

log ε
5
4
3
2
1
0
200
300
400
λ / nm

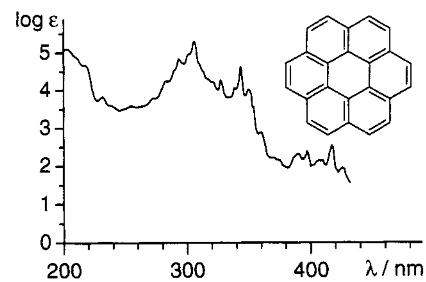

log ε
5
4
3
2
1
0
200
300
400
λ / nm

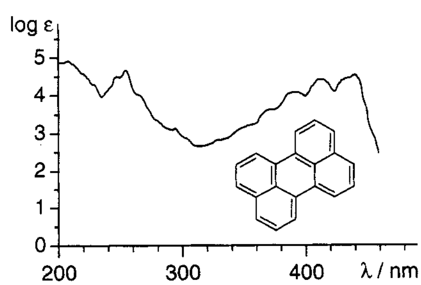

log ε
5
4
3
2
1
0
200
300
400
λ / nm

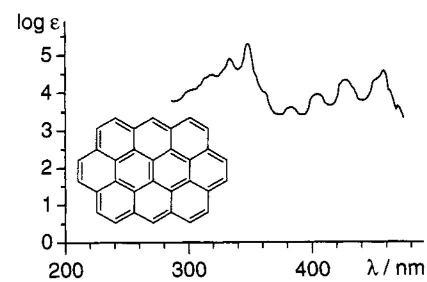




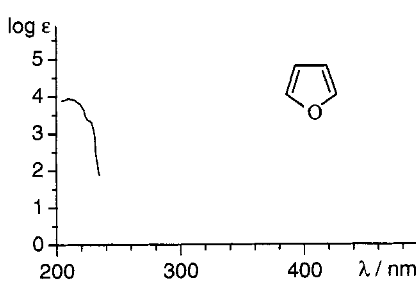


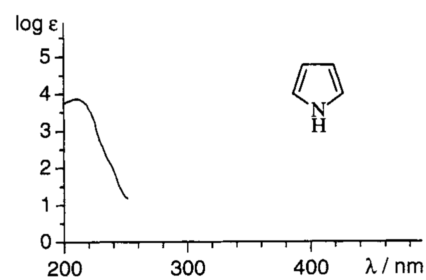


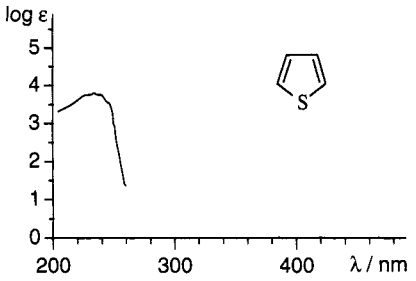


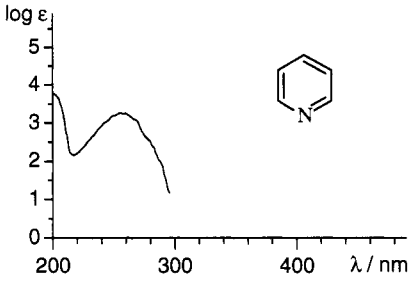


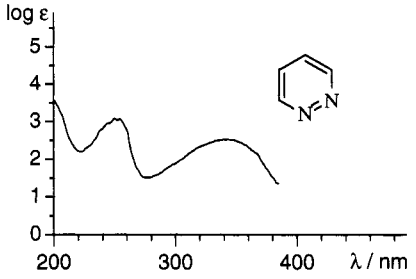
8.5.3 UV/Vis Spectra of Heteroaromatic Compounds

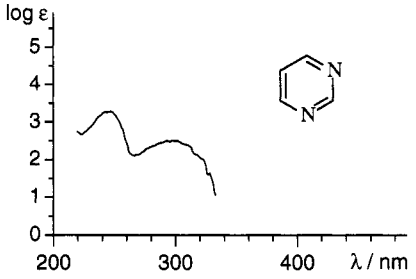


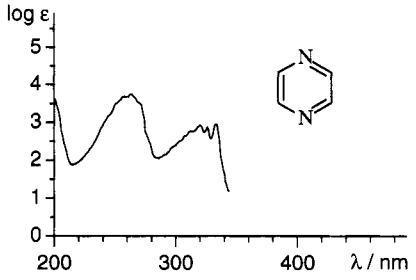


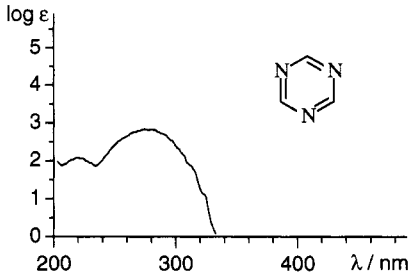

log ε
5
4
3
2
1
0
200
300
400
λ / nm
S

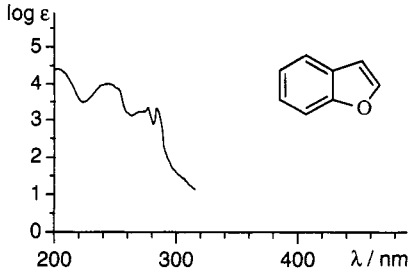

log ε
5
4
3
2
1
0
200
300
400
λ / nm
N

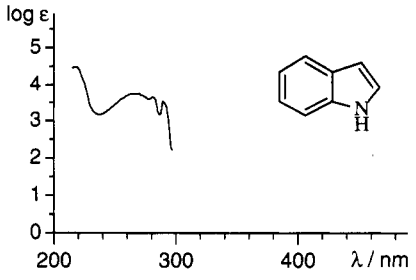

log ε
5
4
3
2
1
0
200
300
400
λ / nm
N
N

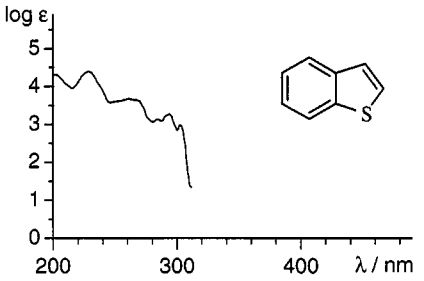

log ε
5
4
3
2
1
0
200
300
400
λ / nm
N
N

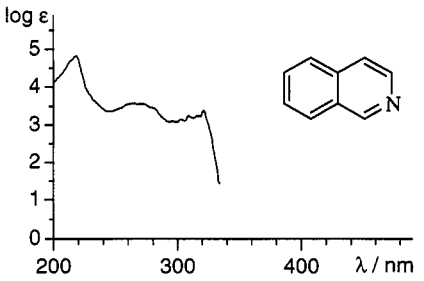

log ε
5
4
3
2
1
0
200
300
400
λ / nm
N
N

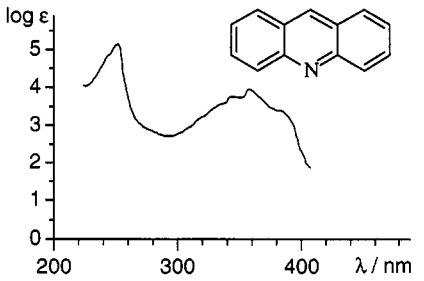

log ε
5
4
3
2
1
0
200
300
400
λ / nm
N
N
N


log ε
5
4
3
2
1
0
200
300
400
λ / nm
O

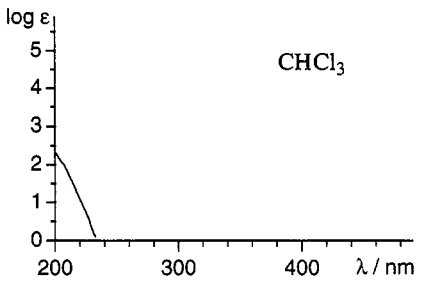

log ε
5
4
3
2
1
0
200
300
400
λ / nm
N
H

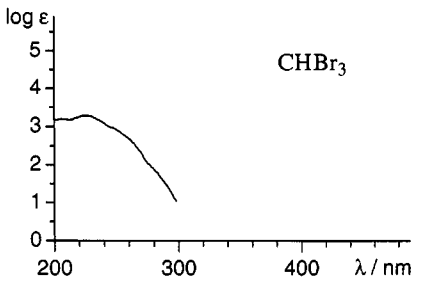


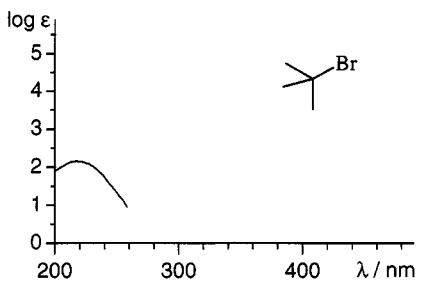


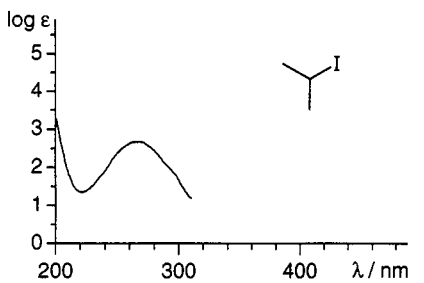


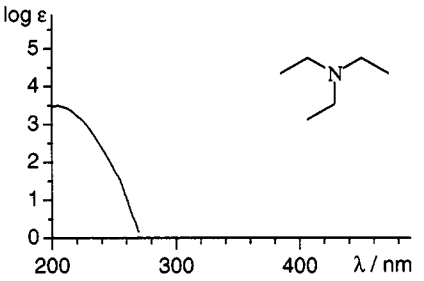
8.5.4
UV/Vis Spectra of Miscellaneous Compounds

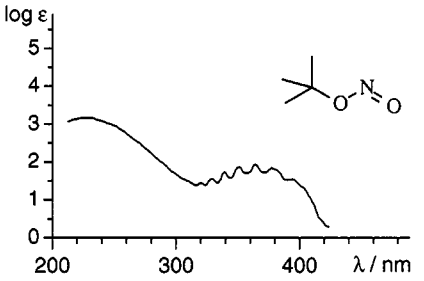


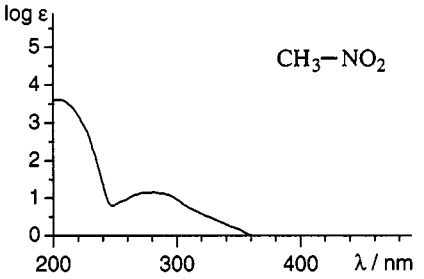


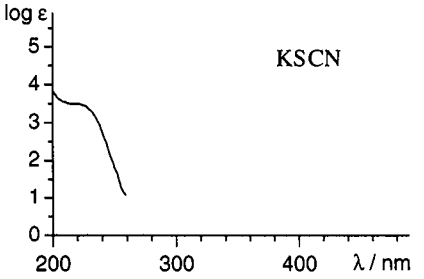


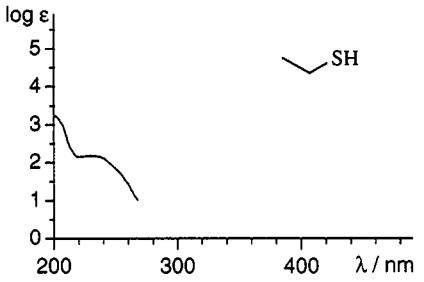


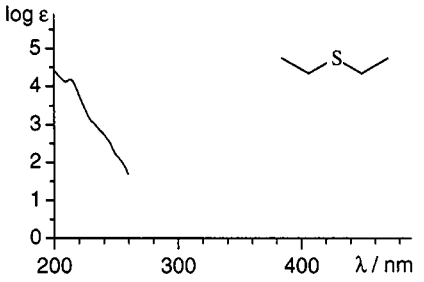

log ε
5
4
3
2
1
0
200
300
400
λ / nm
N

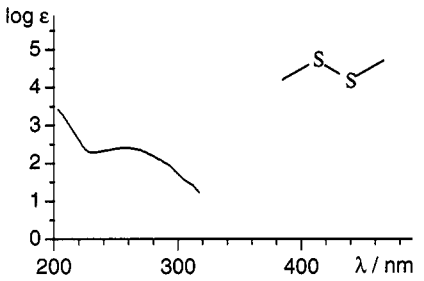

log ε
5
4
3
2
1
0
200
300
400
λ / nm
O
N
O

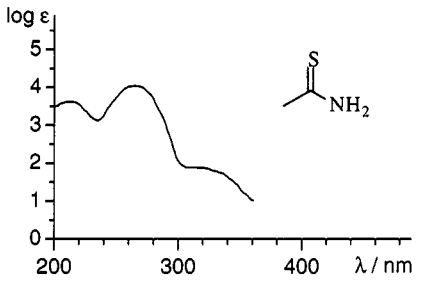

log ε
5
4
3
2
1
0
200
300
400
λ / nm
CH3–NO2

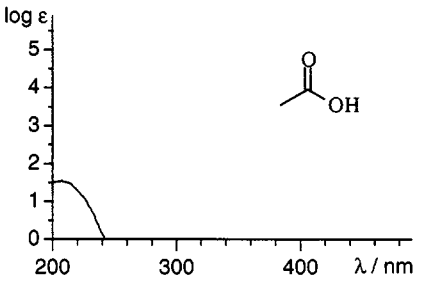

log ε
5
4
3
2
1
0
200
300
400
λ / nm
KSCN

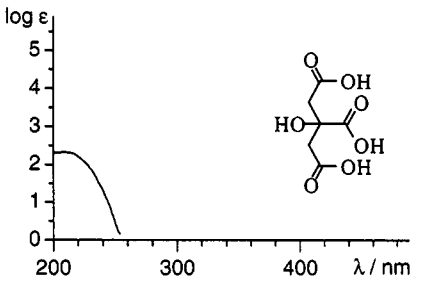

log ε
5
4
3
2
1
0
200
300
400
λ / nm
SH

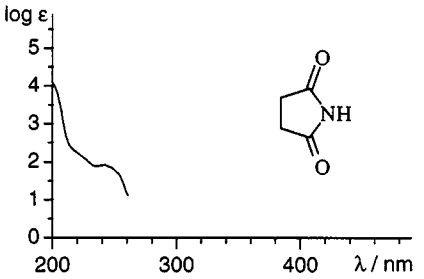

log ε
5
4
3
2
1
0
200
300
400
λ / nm
S

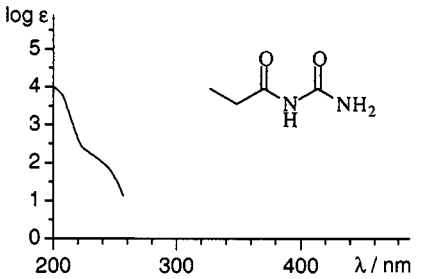

log ε
5
4
3
2
1
0
200
300
400
λ / nm
S
S


log ε
5
4
3
2
1
0
200
300
400
λ / nm
S
NH2

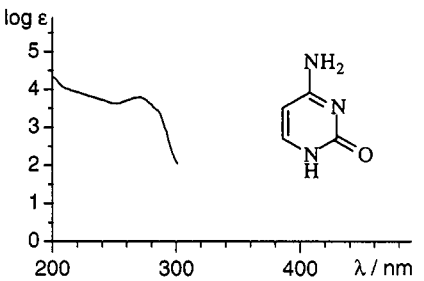


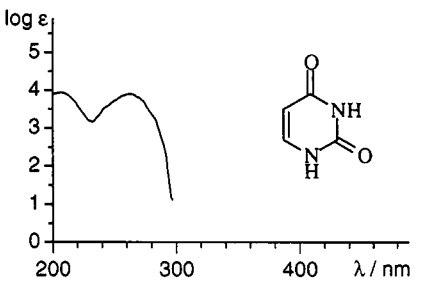


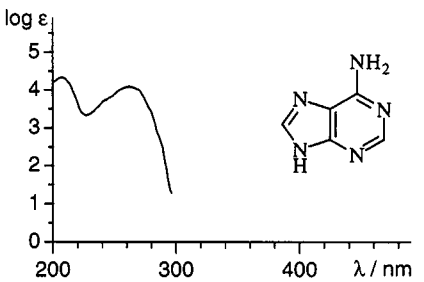


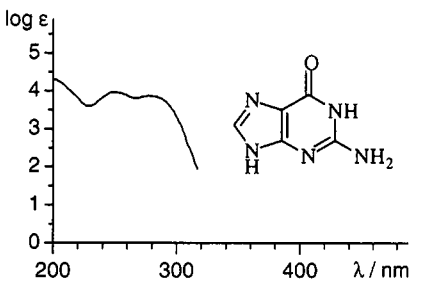


8.5.5
UV/Vis Spectra of Nucleotides









8.6
UV/Vis Absorption of Common Solvents

The end absorption, λ_{end}, of several common solvents is given here as the wavelength at which the solvents absorb 80% of the irradiated light (λ_{end} in nm; cell length, 1 cm; reference, water).

Solvent	λ_{end}
acetone	335
acetonitrile	190
benzene	285
carbon disulfide	380
carbon tetrachloride	265
chloroform	245
cyclohexane	210
dichloromethane	230
diethyl ether	210
1,4-dioxane	215
ethanol	205

Solvent	λ_{end}
ethyl acetate	205
heptane	195
hexane	195
methanol	205
pentane	200
2-propanol	205
pyridine	305
tetrahydrofuran	230
toluene	285
2,2,4-trimethylpentane	210
xylene	290