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1. Ultraviolet and visible spectra

1.1 Introduction

The ultraviolet and visible spectra of organic compounds are associated with transitions between electronic energy levels in which an electron from a low-energy orbital in the ground state is promoted into a higher-energy orbital. Normally, the transition occurs from a filled to a formerly empty orbital (Fig. 1.1) to create a singlet excited state. The wavelength of the absorption is a measure of the separation E of the energy levels of the orbitals concerned.

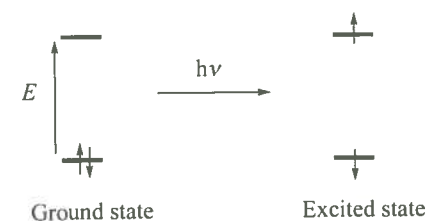


Fig. 1.1

Energy is related to wavelength by Eq. 1.1.

$$E(\text{kJmol}^{-1}) = \frac{1.19 \times 10^5}{\lambda(\text{nm})} \quad (1.1)$$

Thus, 297 nm, for example, is equivalent to 400 kJ (~96 kcal)—enough energy to initiate many interesting reactions; compounds should not, therefore, be left in the ultraviolet beam any longer than is necessary.

1.2 Chromophores

The word chromophore is used to describe the system containing the electrons responsible for the absorption in question. Chromophores leading to the shortest wavelength absorption, in other words the highest energy separation, are found when electrons in σ -bonds are excited, giving rise to absorption in the 120-150 nm ($1 \text{ nm} = 10^{-7} \text{ cm} = 10 \text{ \AA} = 1 \text{ \mu m}$) range, corresponding to the transition x in Fig. 1.2. Isolated double bonds like that in ethene give rise to a strong absorption maximum at 162 nm, corresponding to the transition y in Fig. 1.2. Since the air is full of σ and π bonds, it strongly absorbs UV light below 200 nm, and this range is known as the vacuum ultraviolet, since air must be excluded from the instrument in order to detect the

absorption. The absorption at these short wavelengths is difficult to measure and of little use in structure determination.

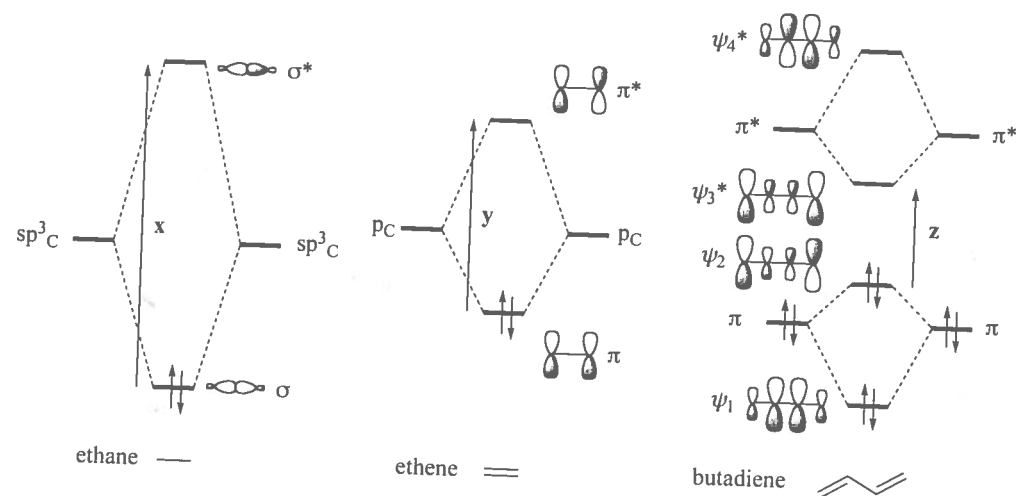


Fig. 1.2

Above 200 nm, however, excitation of electrons from conjugated π -orbitals, gives rise to readily measured and informative spectra. When two double bonds are conjugated, the energy level of the highest occupied molecular orbital ψ_2 (the HOMO) is raised in energy relative to the π orbital of the isolated double bonds, and that of the lowest unoccupied molecular orbital ψ_3^* (the LUMO) is lowered relative to π^* . The transition from ψ_2 to ψ_3^* is now associated with the even smaller value z in Fig. 1.2. This transition appears in the spectrum of butadiene as a strong, easily detected, and easily measured maximum at 217 nm. The same principle governs the energy levels when unlike chromophores, for example those of an α,β -unsaturated ketone, are conjugated together. Thus, methyl vinyl ketone has an absorption maximum at 225 nm, while neither a carbonyl group nor an isolated C=C double bond has a strong maximum above 200 nm. Since the longest wavelength absorption is usually that caused by promotion of an electron from the HOMO to the LUMO, it measures how far apart in energy those important orbitals are.

If yet another π -bond is brought into conjugation, the separation of the HOMO and LUMO is further reduced, and absorption occurs at a longer wavelength, with hexatriene absorbing at 267 nm. Each successive addition of a double bond reduces the energy gap, and moves the longest wavelength maximum further towards the visible. The long conjugated polyene lycopene, with 11 conjugated double bonds, has its longest wavelength absorption maximum at 504 nm (ϵ 158 000) with a tail reaching far into the visible region (absorbing the light in the blue to the orange range). Lycopene is responsible for the red colour of tomatoes. The most important point to be made is that, in general:

The longer the conjugated system, the longer the wavelength of the absorption maximum.

1.3 The absorption laws

Two empirical laws have been formulated about the absorption intensity. Lambert's law states that the fraction of the incident light absorbed is independent of the intensity of the source. Beer's law states that the absorption is proportional to the number of absorbing molecules. From these laws, the remaining variables give the Eq 1.2.

$$\log_{10} \frac{I_0}{I} = \epsilon.l.c \quad (1.2)$$

I_0 and I are the intensities of the incident and transmitted light respectively, l is the path length of the absorbing solution in centimetres, and c is the concentration in moles per litre. $\log_{10}(I_0/I)$ is called the absorbance or optical density; ϵ is known as the molar extinction coefficient and has units of $1000 \text{ cm}^2 \text{ mol}^{-1}$ but the units are, by convention, not normally expressed.

1.4 Measurement of the spectrum

The ultraviolet or visible spectrum is usually taken using a dilute solution. An appropriate quantity of the compound (often about 1 mg when the compound has a molecular weight of 100-400) is weighed accurately, dissolved in the solvent of choice (see below), and made up to, for instance, 100 ml. A portion of this solution is transferred to a silica cell 1 cm from front to back internally (the value l in Eq. 1.2), and the pure solvent is transferred into an accurately matched cell. Two equal beams of ultraviolet or visible light are passed, one through the solution of the sample, and one through the pure solvent. The intensities of the transmitted beams are then compared over the whole wavelength range of the instrument. The spectrum is plotted automatically on most instruments as a $\log_{10}(I_0/I)$ ordinate and λ abscissa and might look something like Fig. 1.3, which is the spectrum of styrene (molecular weight 104) as a solution of 0.535 mg in 100 ml of hexane and a path length of 1 cm. For publication and comparisons the optical density is

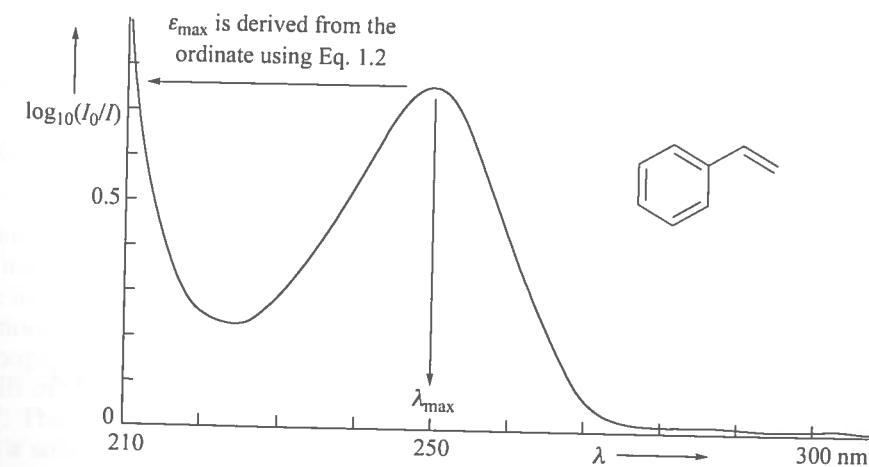


Fig. 1.3

converted to an ϵ versus λ or $\log \epsilon$ versus λ plot using Eq. 1.2. The unit of λ is almost always nm. The intensity of a transition is better measured by the area under an absorption peak (when plotted as ϵ against frequency), but for convenience, and because of the difficulty of dealing with overlapping bands, ϵ_{\max} , the maximum intensity of the absorption, is adopted in everyday use. Spectra are quoted, therefore, in terms of λ_{\max} , the wavelength at the maximum of the absorption peak read directly off the plot like that in Fig. 1.3, where it is 250 nm, and ϵ_{\max} is 14 700 calculated from the value of $\log_{10}(I_0/I)$, which is 0.756 on the plot in Fig. 1.3.

1.5 Vibrational fine structure

The excitation of electrons is accompanied by changes in the vibrational and rotational quantum numbers so that what would otherwise be an absorption line becomes a broad peak containing all the vibrational and rotational fine structure. Because of interactions of solute with solvent molecules this is usually not resolved, and a smooth curve is observed like that illustrated in Fig. 1.3. In the vapour phase, in non-polar solvents, and with certain peaks (e.g. benzene with the 260 nm band), vibrational fine structure is sometimes resolved.

1.6 Choice of solvent

The solvent most commonly used is 95% ethanol (commercial absolute ethanol contains residual benzene, which absorbs in the ultraviolet). It is cheap, a good solvent, and transparent down to about 210 nm. Fine structure, if desired, may be revealed by using cyclohexane or other hydrocarbon solvents which, being less polar, have less interaction with the absorbing molecules. Table 1.1 gives a list of common solvents and the minimum wavelength from which they may be used in 1 cm cells.

Table 1.1 Some solvents used in ultraviolet spectroscopy

<i>Solvent</i>	<i>Minimum wavelength for 1 cm cell, nm</i>
Acetonitrile	190
Water	191
Cyclohexane	195
Hexane	201
Methanol	203
Ethanol	204
Ether	215
Dichloromethane	220
Chloroform	237
Carbon tetrachloride	257

The effect of solvent polarity on the position of maxima is discussed in Sec. 1.8.

1.7 Selection rules and intensity

The irradiation of organic compounds does not always give rise to excitation of electrons from any filled orbital to any unfilled orbital, because there are rules based on symmetry

governing which transitions are allowed. The intensity of the absorption is therefore a function of the 'allowedness', or otherwise, of the electronic transition and of the target area able to capture the light. Equation 1.3 gives the relationship between these variables.

$$\epsilon = 0.87 \times 10^{20} P.a \quad (1.3)$$

where P is called the transition probability (with values from 0 to 1) and a is the target area of the chromophore in \AA^2 . With common chromophores having an area typically of the order of 10\AA^2 , a transition of unit probability will have an ϵ value of 10^5 , and longer chromophores will have values in excess of this. In practice, a chromophore with two double bonds conjugated together giving rise to absorption by a fully allowed transition will have ϵ values of about 10 000, while forbidden transitions (which in practice occur with low transition probabilities), will have ϵ values below 1000. The important point is that, in general:

The longer the conjugated system, the more intense the absorption.

There are many factors that affect the transition probability, but most important are the rules governing which transitions are allowed and which forbidden. These are a function of the symmetry and multiplicity both of the ground state and excited state orbitals concerned. A full theoretical picture is given in the books by Jaffe and Orchin and by Murrell, listed in the bibliography, but a simple knowledge of which of the commonly encountered transitions are allowed and which are forbidden is adequate for anyone using UV spectra simply to determine organic structures or to follow reaction kinetics. Thus, the important promotion of an electron from the HOMO of a linear conjugated system to the LUMO of the same system is allowed, and always leads to intense absorption. In contrast, two important forbidden transitions are the $n \rightarrow \pi^*$ band near 300 nm of ketones, with ϵ values of the order of 10 to 100, and the benzene 260 nm band and its equivalent in more complicated systems, with ϵ values from 100 upwards. 'Forbidden' transitions like these, with ϵ_{\max} typically less than 1000, are observed because the symmetry which makes absorption strictly forbidden is broken by molecular vibrations or by the presence of unsymmetrical substitution. Both types are discussed further under the sections on ketones and aromatic systems.

1.8 Solvent effects

$\pi \rightarrow \pi^*$. The Frank-Condon principle states that during an electronic transition atoms do not move. Electrons, however, including those of solvent molecules, may reorganise. Most transitions result in an excited state more polar than the ground state; the dipole-dipole interactions with solvent molecules will, therefore, lower the energy of the excited state more than that of the ground state. Thus, it is usually observed that ethanol solutions give longer wavelength maxima than do hexane solutions. In other words, there is a small red shift of the order of 10-20 nm in going from hexane as solvent to ethanol.

$n \rightarrow \pi^*$. The weak transition of the oxygen lone pair in ketones—the $n \rightarrow \pi^*$ transition—shows a solvent effect in the opposite direction. The solvent effect is now a result of the lesser extent to which solvents can hydrogen bond to the carbonyl group in the excited state than in the ground state. In hexane solution, for example, the absorption maximum

of acetone is at 278 nm ($\epsilon = 15$), whereas in aqueous solution the maximum is at 264.5 nm. The shift in this direction is known as a blue shift.

1.9 Searching for a chromophore

There is no easy rule or set procedure for identifying a chromophore—too many factors affect the spectrum and the range of structures that can be found is too great. The examination of a spectrum with particular regard for the following points is the first step to be taken.

The complexity and the extent to which the spectrum encroaches on the visible region.

A spectrum with many strong bands stretching into the visible shows the presence of a long conjugated or a polycyclic aromatic chromophore. A compound giving a spectrum with one band (or only a few bands) below about 300 nm probably contains only two or three conjugated units.

The intensity of the bands, particularly the principal maximum and the longest wavelength maximum. This observation can be very informative. Simple conjugated chromophores such as dienes and α,β -unsaturated ketones have ϵ values of 10 000–20 000. The longer simple conjugated systems have principal maxima (usually also the longest wavelength maxima) with correspondingly higher ϵ values. Low intensity absorption bands in the 270–350 nm region, on the other hand, with ϵ values of 10–100, are the result of the $n \rightarrow \pi^*$ transition of ketones. In between these extremes, the existence of absorption bands with ϵ values of 1000–10 000 almost always shows the presence of an aromatic system. Many unsubstituted aromatic systems show bands with intensities of this order of magnitude, the absorption being the result of a transition with a low transition probability, low because the symmetry of the ground and excited states make the transition forbidden. When the aromatic nucleus is substituted with groups that can extend the chromophore and break the symmetry, strong bands with ϵ values above 10 000 appear, but bands with ϵ values below 10 000 are often still present.

Confidence in the purity of the sample. It is always possible that weak bands are caused by small amounts of intensely absorbing impurities. Before any confidence can be put on an absorption with a low ϵ value, one must be sure of the purity of the sample.

Having made these observations, one should search for a model system which contains the chromophore and therefore gives a similar spectrum to that which is being examined. This may be difficult in rare cases; but so many spectra are now known, and the changes caused by substitution so well documented, that the task can be a simple one. The first tool which an organic chemist requires is a general knowledge of the simple chromophores and the changes which structural variations make in the absorption pattern. The remaining task, that of searching through the literature, is greatly facilitated by the existence of indexes and compilations. The major collection of data is *Organic Electronic Spectral Data*, Wiley, New York, Vols. 1–31 (1960–96). This most valuable collection has been prepared by a complete search of the major journals from 1945 until 1989, but has been discontinued since then. The compounds are indexed by their empirical formulae, and λ_{\max} and $\log_{10}\epsilon$ values are quoted together with literature references.

The search for a chromophore is likely to be assisted by the other and more powerful physical methods described in this book. The UV spectrum will mainly help to decide on the likely degree to which the functional groups are conjugated, and is often the last of the physical methods to be turned to. The range of structures in which a search must be made can be narrowed, for example, to aromatic compounds on the strength of infrared or ^1H NMR aromatic C—H absorptions. Similarly the presence of an α,β -unsaturated

ketone may be inferred from the C=O stretching vibration observed in the infrared spectrum, the presence of a low-field carbon resonance in the ^{13}C NMR spectrum and then confirmed by an appropriate ultraviolet spectrum. One area where the UV spectrum can be especially important at an early stage is in the assignment of a structure to a natural product. These compounds, isolated from a natural source, have no history to help in the structure determination, in contrast to the products of a reaction between two known chemicals. The positive identification of a likely chromophore in a natural product can help to identify to which class the natural product belongs.

1.10 Definitions

The following words and symbols are commonly used:

Red shift or *bathochromic effect*. A shift of an absorption maximum towards longer wavelength. It may be produced by a change of medium or by the presence of an auxochrome.

Auxochrome. A substituent on a chromophore which leads to a red shift. For example, the conjugation of the lone pair on the nitrogen atom of an enamine shifts the absorption maximum from the isolated double bond value of 190 nm to about 230 nm. The nitrogen substituent is the auxochrome. An auxochrome, then, extends a chromophore to give a new chromophore.

Blue shift or *hypsochromic effect*. A shift towards shorter wavelength. This may be caused by a change of medium and also by such phenomena as the removal of conjugation. For example, the conjugation of the lone pair of electrons on the nitrogen atom of aniline with the π -bond system of the benzene ring is removed on protonation. Aniline absorbs at 230 nm (ϵ 8600), but in acid solution the main peak is almost identical with that of benzene, being now at 203 nm (ϵ 7500). A blue shift has occurred on protonation.

Hypochromic effect. An effect leading to decreased absorption intensity.

Hyperchromic effect. An effect leading to increased absorption intensity.

λ_{\max} . The wavelength of an absorption maximum.

ϵ . The extinction coefficient defined by Eq. 1.2.

$E_{1\text{cm}}^{1\%}$. Absorption [$\log_{10}(I_0/I)$] of a 1% solution in a cell with a 1 cm path length. This is used in place of ϵ when the molecular weight of a compound is not known, or when a mixture is being examined, so that Eq. 1.2 cannot be used to define the intensity of the absorption.

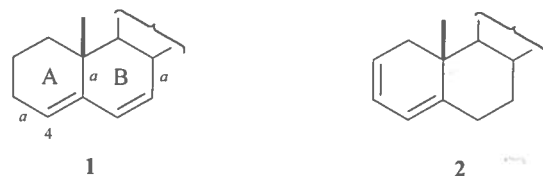
Isosbestic point. A point common to all curves produced in the spectra of a compound taken at several pH values—the one point where the absorption intensity does not change as the pH changes.

1.11 Conjugated dienes

The energy levels of butadiene have been illustrated in Fig. 1.2. The transition z gives rise to strong absorption at 217 nm (ϵ 21 000). Alkyl substitution extends the chromophore, in the sense that there is a small interaction (called hyperconjugation) between the σ -bonded electrons of the alkyl groups and the π -bond system. The result is a small red shift with alkyl substitution, just as there is a red shift (though a relatively large one) in going from an isolated double bond to a conjugated diene or to an enamine.

The effect of alkyl substitution, in dienes at least, is approximately additive, and a few rules suffice to predict the position of absorption in open chain dienes and dienes in six-

membered rings. Open chain dienes exist normally in the energetically preferred *s-trans* conformation, while homoannular dienes must be in the *s-cis* conformation. These conformations are illustrated in the part structures 1 (heteroannular diene) and 2 (homoannular diene). It is not clear why, but the *s-cis* arrangement, as in the diene 1, leads to longer wavelength absorption than does the *s-trans* arrangement in the diene 2. Also, because of the shorter distance between the ends of the chromophore, *s-cis* dienes give maxima of lower intensity ($\epsilon \sim 10\,000$) than the maxima of *s-trans* dienes ($\sigma \sim 20\,000$).



The rules for predicting the absorption of open chain and six-membered ring dienes were first made by Woodward in 1941, and were a breakthrough in showing that physical methods could be used in the details of structure determination. Since that time they have been modified by Fieser and by Scott as a result of experience with a larger number of dienes and trienes. The modified rules are given in Table 1.2.

		Table 1.2 Rules for diene and triene absorption	
	Value assigned to parent <i>s-trans</i> diene (like 1)	214 nm	
	Value assigned to parent <i>s-cis</i> diene (like 2)	253 nm	
Increment for:			
	(a) each alkyl substituent or ring residue	5 nm	
	(b) the exocyclic nature of any double bond	5 nm	
	(c) a double-bond extension	30 nm	
	(d) auxochrome:		
	—OAcyl	0 nm	
	—OAlkyl	6 nm	
	—SAlkyl	30 nm	
	—Cl, —Br	5 nm	
	—NAlkyl ₂	60 nm	
λ_{calc}	Total		

(Reprinted with permission from A. I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*, Pergamon Press, Oxford, 1964.)

For example, the diene 1 would be calculated to have a maximum at 234 nm by the following addition:

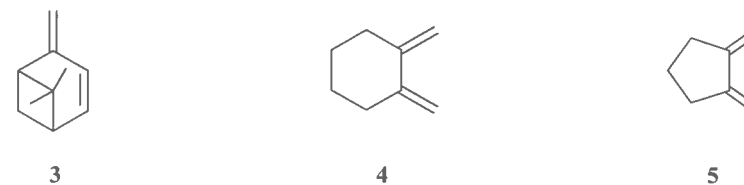
Parent value	214 nm
Three-ring residues (marked <i>a</i>) $3 \times 5 =$	15 nm
One exocyclic double bond (the Δ^4 bond is exocyclic to ring B)	5 nm
Total	234 nm

A typical value observed for a steroid with this part structure is 235 nm (ϵ 19 000).



By similar calculation, the diene 2 would be expected to have a maximum at 273 nm, and steroids like this typically have one at 275 nm. Though ethanol is the usual solvent, change of solvent has little effect.

There are a large number of exceptions to the rules, where special factors can operate. Distortion of the chromophore may lead to red or blue shifts, depending on the nature of the distortion.



Thus, the strained molecule verbenene 3 has a maximum at 245.5 nm, whereas the usual calculation gives a value of 229 nm. The diene 4 might be expected to have a maximum at 273 nm, but distortion of the chromophore, presumably out of planarity with consequent loss of conjugation, causes the maximum to be as low as 220 nm with a similar loss in intensity (ϵ 5500). The diene 5, in which coplanarity of the diene is more likely, gives a maximum at 248 nm (ϵ 15 800), but it still does not agree with the expected value. Change of ring size in the case of simple homoannular dienes also leads to departures from the predicted value of 263 nm as follows: cyclopentadiene, 238.5 nm (ϵ 3400); cycloheptadiene, 248 nm (ϵ 7500); while cyclohexadiene is close at 256 nm (ϵ 8000). The lesson, an important one, is that when the ultraviolet spectrum of an unknown compound is to be compared with that of a model compound, then the choice of model must be a careful one. Allowance must be made for the likely shape of the molecule and for any unusual strain. Some general comments on the effect of steric hindrance to coplanarity are given in Sec. 1.24.

1.12 Polyenes

As the number of double bonds in conjugation increases, the wavelength of maximum absorption encroaches on the visible region. A number of subsidiary bands also appear and the intensity increases. Table 1.3 gives examples of the longest wavelength maxima of some simple conjugated polyenes showing these trends.

Table 1.3 Longest wavelength maxima of some simple polyenes

<i>n</i>	<i>trans</i> -Me(CH=CH) _{<i>n</i>} Me		<i>trans</i> -Ph(CH=CH) _{<i>n</i>} Ph	
	λ_{max} , nm	ϵ	λ_{max} , nm	ϵ
3	274.5	30 000	358	75 000
4	310	76 500	384	86 000
5	342	122 000	403	94 000
6	380	146 500	420	113 000
7	401	-	435	135 000
8	411	-	-	-

The appearance of the spectra of some of these simple polyenes is illustrated in Fig. 1.4, which shows vividly the two main lessons enshrined in the boxes on pp. 2 and 5. In

addition, in each spectrum, shorter wavelength absorption maxima are visible. They are the result of other transitions than just the HOMO-LUMO transition that is responsible for the longest wavelength maximum. The longer the conjugated system the more transitions become possible, and the pattern of the maxima is characteristic of the polyene concerned. It can be used as a kind of fingerprint, but in using UV spectra for structure determination we largely concentrate on the longest wavelength maximum, and the hint it gives us about the length of the conjugated system.

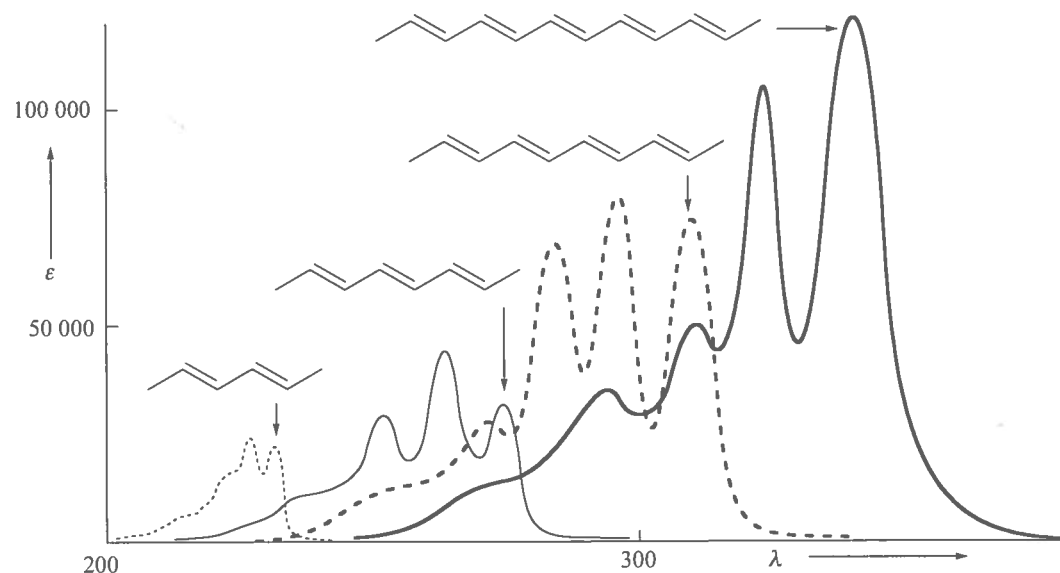
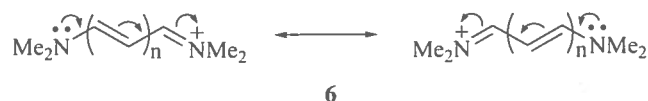


Fig. 1.4

(Replotted from P. Nayler and M. C. Whiting, *J. Chem. Soc.*, 1955, 3042.)

Several attempts, both empirical and theoretical, have been made to correlate quantitatively the principal or longest wavelength maximum with chain length. Some of the theoretical treatments have been based on the simple 'electron in the box' wave equation, in which the walls of the box are usually considered to be one average bond length beyond each end of the chromophore. Increasing values of λ_{max} are found for increasing length in a conjugated polyene, but quantitatively the correlation is less satisfactory. For example, the simple theory might indicate that, as the chain length increases, the value of λ_{max} for long chains would increase proportionately, whereas in practice there is a convergence, which can be seen already in Table 1.4. More sophisticated treatments, allowing for the variation in bond lengths between the double and single bonds, have been made and are described in Murrel's book. An interesting simplification is provided by the cyanine dye analogues **6** in which overlap leads to



6

uniform bond lengths and bond orders along the polyene chain. Calculations based on the 'electron in the box' lead in this case to values close to those observed: $\lambda_{\text{max}} = 309$ ($n = 1$), 409 ($n = 2$) and 511 ($n = 3$) nm.

In a long-chain polyene, change from a *trans* to a *cis* configuration at one or more double bonds lowers both the wavelength and the intensity of the absorption maximum as a result of steric problems in attaining coplanarity.

1.13 Polyeneynes and poly-yenes

The ultraviolet spectra of many natural polyeneynes and poly-yenes are known, and have been used in the elucidation of structure. They illustrate how a family of natural products can be detected and identified. A distinctive feature in the UV spectrum, when more than two triple bonds are conjugated, is a series of low-intensity 'forbidden' bands ($\epsilon \sim 100$ -200) at regular intervals of 2300 cm^{-1} (note the frequency units, frequency being directly proportional to energy whereas wavelength is not) together with high-intensity bands ($\epsilon \sim 10^5$) at intervals of 2600 cm^{-1} . This characteristic spiky appearance of the spectra was helpful in screening crude plant extracts for acetylenic compounds. The principal maxima from each of these groups of lines are listed in Table 1.4, in which the trends closely resemble those for polyenes in Table 1.3.

In a representative application in structure determination, Fig. 1.5 shows the UV spectrum of dehydromatricaria ester **8**. In this compound, the longer wavelength bands are considerably more intense than in simple poly-yenes, but they are, like a fingerprint, characteristic of an enetriyne chromophore. The structure of a natural product **7** was assigned with the help of its UV spectrum, which showed a similar pattern, with each of

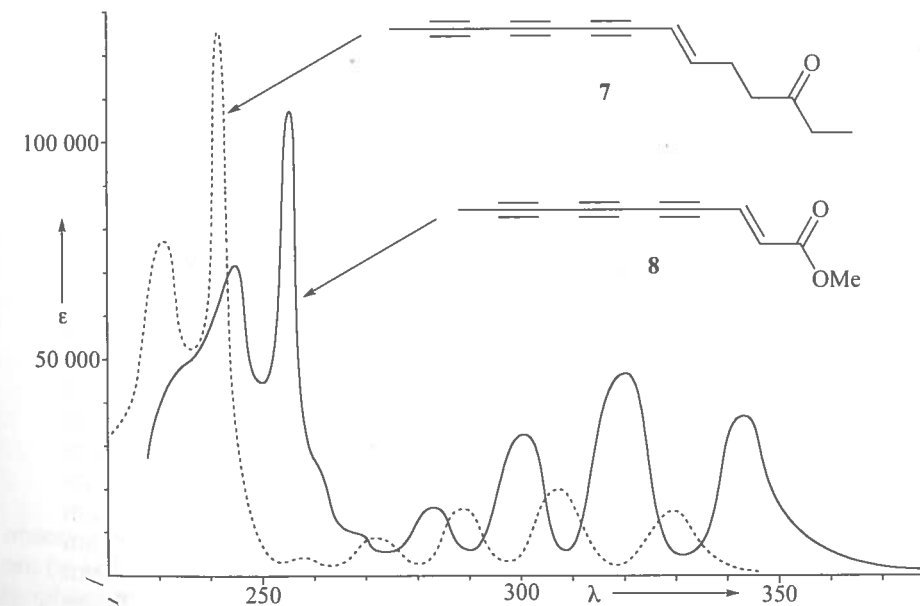


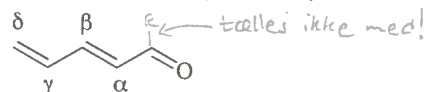
Fig. 1.5

(Replotted from J. S. Sørensen, T. Bruun, D. Holme and N. A. Sørensen, *Acta Chem. Scand.*, 1954, **8**, 28 and F. Bohlmann, H.-J. Mannhardt, and H. G. Viehe, *Chem. Ber.*, 1955, **88**, 361.)

Table 1.4 Principal maxima for conjugated poly-yne $\text{Me}(\text{C}=\text{C})_n\text{Me}$

n	λ_{max} , nm	ϵ	λ_{max} , nm	ϵ
2	-	-	250	160
3	207	135 000	306	120
4	234	281 000	354	105
5	260.5	352 000	394	120
6	284	445 000	-	-

the peaks shifted to shorter wavelength. Thus, the UV spectrum indicated that the structure might be an enetriyne without the extra conjugation of the ester carbonyl group. When the particular enetriyne **7** was synthesised, it proved to be identical to the natural product. This is an example of the way in which an organic chemist deals with the comparison of UV spectra: the enetriyne chromophore of the ester **8** is present in the ketone **7**, and the latter therefore continues to show similar features to those of the former, with a blue shift because of the relatively shorter conjugated system.

Table 1.5 Rules for α,β -unsaturated ketone and aldehyde absorption in ethanol

aldehyder og ketoner:

ϵ values are usually above 10 000 and increase with the length of the conjugated system.

Value assigned to parent α,β -unsaturated six-ring or acyclic ketone	215 nm
Value assigned to parent α,β -unsaturated five-ring ketone	202 nm
Value assigned to parent α,β -unsaturated aldehyde	207 nm
Increments for	
(a) a double bond extending the conjugation	30 nm
(b) each alkyl group or ring residue	
α	10 nm
β	12 nm
γ and higher	18 nm
(c) lone-pair auxochromes	
(i) —OH	α 35 nm
	β 30 nm
	γ 50 nm
(ii) —OAc	α, β, γ 6 nm
(iii) —OMe	α 35 nm
	β 30 nm
	γ 17 nm
	δ 31 nm
(iv) —SAlk	β 85 nm
(v) —Cl	α 15 nm
	β 12 nm
(vi) —Br	α 25 nm
	β 30 nm
(vii) —NR ₂	β 95 nm
(d) the exocyclic nature of any double bond	5 nm
(e) homodiene component	39 nm

$\lambda_{\text{calc}}(\text{EtOH})$

Total

(Reprinted with permission from A. I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*, Pergamon Press, Oxford, 1964.)

1.14 Ketones and aldehydes; $\pi \rightarrow \pi^*$ transitions

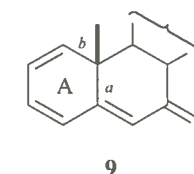
As with dienes, Woodward formulated a set of rules for predicting the UV absorption of α,β -unsaturated ketones and aldehydes in ethanol. These rules, subsequently modified by Fieser and by Scott, are given in Table 1.5. For λ_{calc} in other solvents, a solvent correction from Table 1.6 must be subtracted from the above value, because the spectra are affected significantly by the solvent as a result of the change in polarity on excitation.

Table 1.6 Solvent corrections for α,β -unsaturated ketones

Solvent	Correction, nm
Water	-8
Ethanol	0
Methanol	0
Chloroform	+1
Dioxan	+5
Ether	+7
Hexane	+11
Cyclohexane	+11

(Reprinted with permission from A. I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*, Pergamon Press, Oxford, 1964.)

For example, mesityl oxide ($\text{Me}_2\text{C}=\text{CHCOMe}$) may be calculated to have λ_{max} at $215 + (2 \times 12) = 239$ nm. The observed value is 237 nm (ϵ 12 600). A more complicated example, the trienone chromophore of **9**, would be calculated to have a maximum at 349 nm by the following addition.

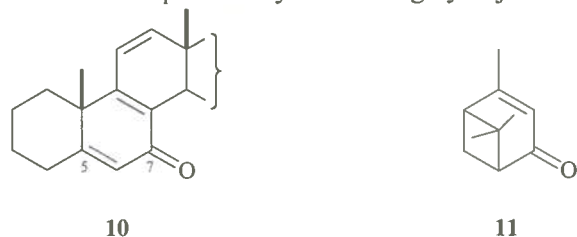


Parent value	215 nm
β -Alkyl substituent (marked a)	12 nm
ω -Alkyl substituent (marked b)	18 nm
2 \times Extended conjugation	60 nm
Homoannular diene component	39 nm
Exocyclic double bond (the α,β -double bond is exocyclic to ring A)	5 nm
Total	349 nm

The observed values of λ_{max} for a trienone with this substructure are 230 nm (ϵ 18 000), 278 nm (ϵ 3720) and 348 nm (ϵ 11 000). As was the case with simple polyenes, the long chromophore present in this example gives rise to several peaks, with the longest wavelength peak in good agreement with the prediction.

An important general principle is illustrated by the calculation for the cross-conjugated trienone **10**. In this case the main chromophore is the linear dienone portion,

since the Δ^5 -double bond is not in the longest conjugated system. The calculation, along the lines above, gives a value of 324 nm. The observed values are 256 nm and 327 nm. The former might be from the Δ^5 -7-one system ($\lambda_{\text{calc}} = 244$ nm), but a positive identification of this sort in a complicated system is largely unjustified.



Certain special changes in structure, as noted in the case of dienes in Sec. 1.11, also lead to departures from the rules given above. The effect of the five-membered ring in cyclopentenones is accommodated in the rules; but when the carbonyl group is in a five-membered ring and the double bond is exocyclic to the five-membered ring, a parent value of about 215 nm holds. Another special case, verbenone **11**, would be calculated to have a maximum at 239 nm but actually has a maximum at 253 nm, an increment for strain of 14 nm, close to the increment for the corresponding diene **3**.

1.15 Ketones and aldehydes; $n \rightarrow \pi^*$ transitions

Saturated ketones and aldehydes show a weak symmetry-forbidden band, in the 275-295 nm range ($\epsilon \sim 20$), from excitation of an oxygen lone-pair electron ($n = p_O$) into the antibonding π^* orbital of the carbonyl group, as shown on the left of Fig. 1.6.

Aldehydes and the more heavily substituted ketones absorb at the long wavelength end of this range. Electronegative substituents on the α -carbon atoms increase (when oriented like an axial substituent on C-2 in a cyclohexanone) or decrease (when equatorial) the wavelength. When the carbonyl group is directly attached to an electronegative element X—as in an ester, an acid, or an amide—the π^* orbital is slightly raised in energy because the substituent, having a lone pair, is a π -donor. The n (p_O) level of the lone pair, on the other hand, is lowered because it is conjugated to the C—X bond, which is a σ -withdrawing group. The result is that the $n \rightarrow \pi^*$ transition of these compounds is shifted to shorter wavelength into the relatively inaccessible 200-215 nm range. The presence, therefore, of a weak band in the 275-295 nm region is positive identification of a ketone or aldehyde carbonyl group (nitro groups show a similar band and, of course, impurities must be absent). In contrast, if the carbonyl group is directly attached to an electropositive substituent—as in an acylsilane where the silyl group is σ -donating and π -withdrawing—the π^* orbital is lowered in energy, the n orbital is raised in energy and the $n \rightarrow \pi^*$ transition is shifted to longer wavelength, close to 370 nm for saturated acylsilanes and 420 nm for aryl or α, β -unsaturated acylsilanes. These compounds are yellow and green, respectively, as a consequence of the tail of these absorptions reaching into the visible.

α, β -Unsaturated ketones show slightly stronger $n \rightarrow \pi^*$ absorption ($\epsilon \sim 100$) in the 300-350 nm range, since the ψ_3^* orbital is lowered in energy by conjugation relative to the π^* level of a simple carbonyl group, but the n level of the lone pair is largely unaltered, as shown on the right in Fig. 1.6. The precise position of these bands is not predictable from the extent of alkylation, but is a regular function of the conformation of γ -substituents,

substituents oriented so that they overlap with the π -system shifting the absorption to longer wavelength, since they extend the conjugation. The position and intensity of $n \rightarrow \pi^*$ bands are also influenced by transannular interactions (see Sec. 1.23) and by solvent (see Sec. 1.8).

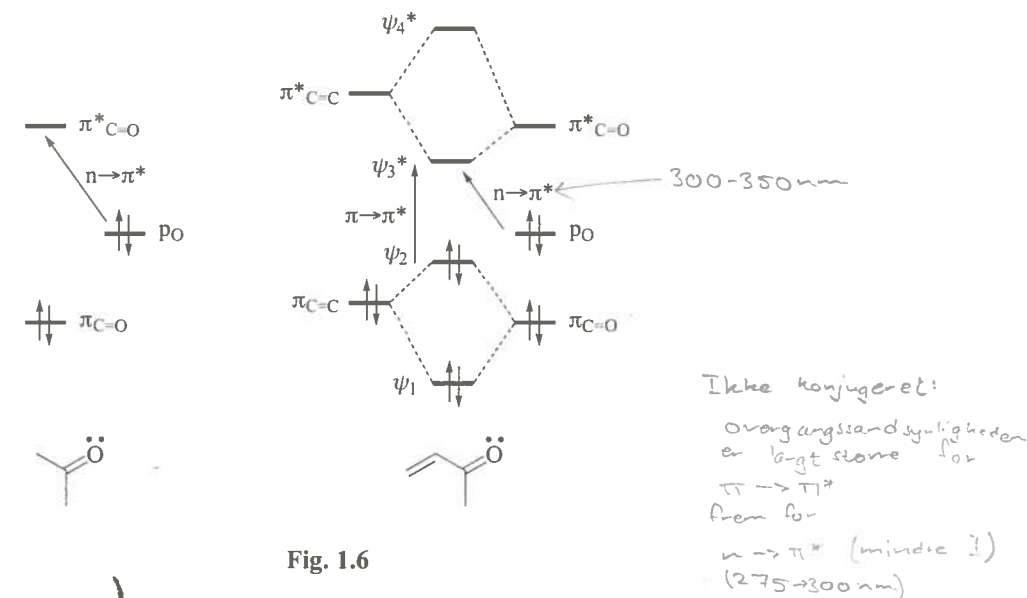


Fig. 1.6

The $n \rightarrow \pi^*$ transitions of α -diketones in the diketo form give rise to two bands, one in the usual region near 290 nm ($\epsilon \sim 30$) and a second ($\epsilon \sim 10$ -30) that stretches into the visible in the 340-440 nm region, and gives rise to the yellow colour of some of these compounds. (See also quinones in Sec. 1.21, quinones being α -, or vinylogous α -, diketones.)

1.16 α, β -Unsaturated acids, esters, nitriles and amides

α, β -Unsaturated acids and esters follow a trend similar to that of ketones but at slightly shorter wavelength. The rules for alkyl substitution, summarised by Nielsen, are given in Table 1.7. The change in going from acid to ester is usually not more than 2 nm.

α, β -umattede,

- syrer
- estere
- amider
(- nitriler)

Table 1.7 Rules for α, β -unsaturated acids' and esters' absorption (ϵ values are usually above 10 000)

β -Monosubstituted	208 nm
$\alpha\beta$ - or $\beta\beta$ -disubstituted	217 nm
$\alpha\beta\beta$ -Trisubstituted	225 nm
Increment for:	
(a) a double bond extending the conjugation	30 nm
(b) the exocyclic nature of any double bond	5 nm
(c) when the double bond is endocyclic in a five- or seven-membered ring	5 nm
λ_{calc}	Total



α,β -Unsaturated nitriles absorb at wavelengths slightly lower than the corresponding acids, and α,β -unsaturated amides lower still, usually near 200 nm ($\epsilon \sim 8000$). α,β -Unsaturated lactams have an additional band at 240-250 nm ($\epsilon \sim 1000$).

1.17 The benzene ring

Benzene absorbs at 184 (ϵ 60 000), 203.5 (ϵ 7400) and 254 (ϵ 204) nm in hexane solution; it is illustrated by the dashed line in Fig. 1.7. The latter band, sometimes called the *B*-band, shows vibrational fine structure. Although a 'forbidden' band, it owes its appearance to the loss of symmetry caused by molecular vibrations; indeed, the 0 \rightarrow 0 transition (the transition between the ground state vibrational energy level of the electronic ground state to the ground state vibrational energy level of the electronic excited state) is not observed.

When the aromatic ring is substituted by alkyl groups, for example, or is an aza analogue such as pyridine, the symmetry is lowered and the 0 \rightarrow 0 transition is then observed, although the spectrum is little changed otherwise. The presence of fine structure resembling that shown in Fig. 1.7 is characteristic of the simpler aromatic molecules.

Table 1.8 Absorption maxima of substituted benzene rings Ph—R

R	λ_{\max} nm (ϵ)	(solvent H ₂ O or MeOH)	
—H	203.5 (7400)	254	(204)
—NH ₃ ⁺	203 (7500)	254	(160)
—Me/alkyl	206.5 (7000)	261	(225)
—I	207 (7000)	257	(700)
—Cl	209.5 (7400)	263.5	(190)
—Br	210 (7900)	261	(192)
—OH	210.5 (6200)	270	(1450)
—OMe	217 (6400)	269	(1480)
—SO ₂ NH ₂	217.5 (9700)	264.5	(740)
—CN	224 (13 000)	271	(1000)
—CO ₂ ⁻	224 (8700)	268	(560)
—CO ₂ H	230 (11 600)	273	(970)
—NH ₂	230 (8600)	280	(1430)
—O ⁻	235 (9400)	287	(2600)
—NHAc	238 (10 500)		
—COMe	245.5 (9800)		
—CH=CH ₂	248 (14 000)	282 (750)	291 (500)
—CHO	249.5 (11 400)		
—Ph	251.5 (18 300)		
—OPh	255 (11 000)	272 (2000)	278 (1800)
—NO ₂	268.5 (7800)		
—CH=CHCO ₂ H	273 (21 000)		
—CH=CHPh	295.5 (29 000)		

(Most values taken with permission from H. H. Jaffe and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, Wiley, New York, 1962.)

K-bånd

B-bånd

When the benzene ring has a lone-pair or π -bonded substituent, in other words an auxochrome, the chromophore is extended. Quantitative prediction of the effects of such substituents is not as simple as it was with dienes and unsaturated ketones, but Sec. 1.18 gives an account of some of the trends observed with substituted benzene rings.

1.18 Substituted benzene rings

Table 1.8 gives the wavelength of absorption maxima in the spectra of a range of monosubstituted benzenes, showing how, as usual, the wavelength and intensity of the absorption peaks increase with an increase in the extent of the chromophore.

As more conjugation is added to the benzene ring, the band originally at 203.5 nm (sometimes called the *K*-band) effectively 'moves' to longer wavelength, and moves 'faster' than the *B*-band, which was originally at 254 nm, eventually overtaking it. This can be seen in the two other spectra recorded on Fig. 1.7: benzoic acid (the solid line) shows the *K*-band at 230 nm with the *B*-band still clearly visible at 273 nm; but with the longer chromophore of cinnamic acid (bold solid line) the *K*-band has moved to 273 nm and the *B*-band is completely submerged. In the latter case, we can see how the even stronger band, originally at 184 nm, has also moved, but has still not reached the accessible region. It is responsible for what is called end absorption, that is the long-wavelength side of an absorption peak, the maximum of which is below the range of the instrument.

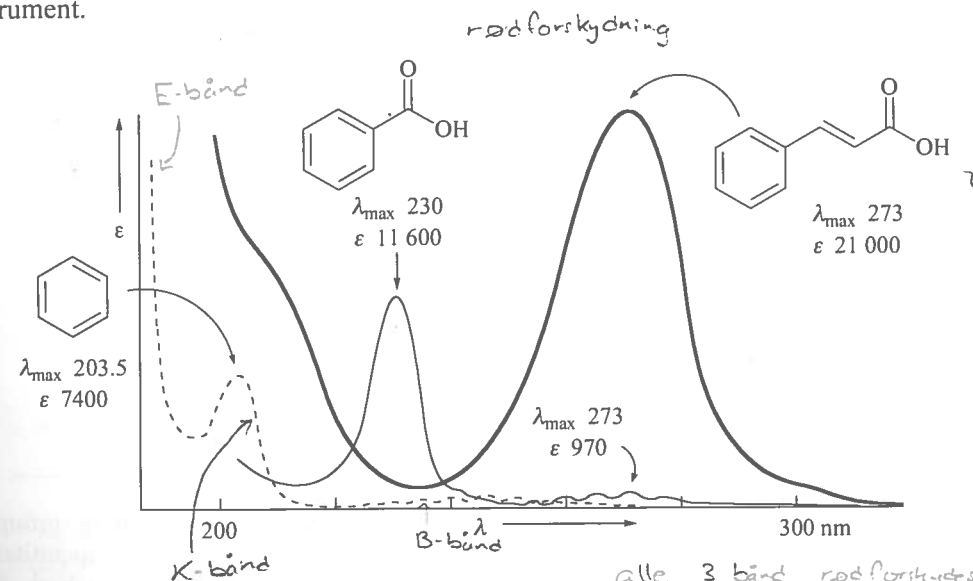
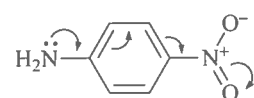


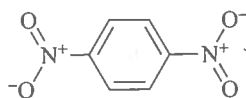
Fig. 1.7

In disubstituted benzenes, two situations are important. When electronically complementary groups, such as amino and nitro, are situated *para* to each other as in *p*-nitroaniline 12, there is a pronounced red shift in the main absorption band, compared to the effect of either substituent separately, caused by the extension of the chromophore from the electron-donating group to the electron withdrawing group through the benzene ring, as symbolised by the curly arrows. Alternatively, when two groups are situated *ortho* or *meta* to each other, or when the *para* disposed groups are not complementary, as in *p*-dinitrobenzene 13, then the observed spectrum is usually close to that of the separate,

non-interacting, chromophores. These principles are illustrated by the examples in Table 1.9. The values in this table should be compared with each other and with the values for the single substituents separately given in Table 1.8.



12

 λ_{\max} 375 nm (ϵ 16 000)


13

 λ_{\max} 260 nm (ϵ 13 000)

In particular it should be noted that those compounds with non-complementary substituents, or with an *ortho* or *meta* substitution pattern, actually have a band (though a much weaker one) at longer wavelength than the compounds with interacting *para*-disubstituted substituents. This fact is not in accord with the simple resonance picture; neither is the similarity of the *ortho* to the *meta* disubstituted cases. This is another case in which molecular orbital theory (too complicated to be introduced here, but dealt with in Murrell's book) gives a better picture.

Table 1.9 Absorption maxima of disubstituted benzene rings

R ¹		R ²		R ¹ -C ₆ H ₄ -R ²			
				λ_{\max} (EtOH) nm (ϵ)			
-OH	-OH	<i>o</i>	214 (6000)	278 (2630)			
-OMe	-CHO	<i>o</i>	253 (11 000)	319 (4000)			
-NH ₂	-NO ₂	<i>o</i>	229 (16 000)	275 (5000)	405 (6000)		
-OH	-OH	<i>m</i>	277 (2200)				
-OMe	-CHO	<i>m</i>	252 (8300)	314 (2800)			
-NH ₂	-NO ₂	<i>m</i>	235 (16 000)	373 (1500)			
-Ph	-Ph	<i>m</i>	251 (44 000)				
-OH	-OH	<i>p</i>	225 (5100)	293 (2700)			
-OMe	-CHO	<i>p</i>	277 (14 800)				
-NH ₂	-NO ₂	<i>p</i>	229 (5000)	375 (16 000)	(kratig rozdelenie)		
-Ph	-Ph	<i>p</i>	280 (25 000)				

In the case of disubstituted benzene rings in which the electron-donating group is complemented by an electron-withdrawing carbonyl group, some quantitative assessments may be made. These apply to the compounds RC₆H₄COX in which X is alkyl, H, OH, or OAlkyl, and refer to the strongest band in the accessible region, which is often the only measured band in the highly conjugated *para*-disubstituted systems. The calculation is based on a parent value with increments for each substituent. Polysubstituted benzene rings should be treated with caution, particularly when the substitution might lead to steric hindrance preventing coplanarity of the carbonyl group and the ring. Table 1.10 gives the rules for this calculation. In the absence of steric hindrance to coplanarity, the calculated values are usually within 5 nm of the observed values.

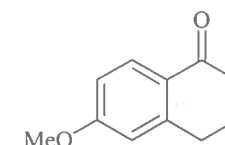
Rule for K-band by λ_{\max}

Table 1.10 Rules for the principal band of substituted benzene derivatives RC₆H₄COX

Parent chromophore:			λ_{\max} (EtOH) nm		
X					
alkyl or ring residue					246
H					250
OH or Oalkyl					230
Increment (nm) for each substituent:			Increment (nm) for each substituent:		
R	<i>o, m</i> or <i>p</i>	Increment	R	<i>o, m</i> or <i>p</i>	Increment
Alkyl or ring residue	<i>o, m</i>	3	Br	<i>o, m</i>	2
	<i>p</i>	10		<i>p</i>	15
OH, OMe, Oalkyl	<i>o, m</i>	7	NH ₂	<i>o, m</i>	13
	<i>p</i>	25		<i>p</i>	58
O	<i>o</i>	11	NHAc	<i>o, m</i>	20
	<i>m</i>	20		<i>p</i>	45
	<i>p</i>	78	NHMe	<i>p</i>	73
Cl	<i>o, m</i>	0	NMe ₂	<i>o, m</i>	20
	<i>p</i>	10		<i>p</i>	85

(Reprinted with permission from A. I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*, Pergamon Press, Oxford, 1964.)

6-Methoxytetralone 14 provides an example:



14

Parent value	246 nm
<i>ortho</i> alkyl	3 nm
<i>para</i> MeO	25 nm
λ_{calc}	274 nm

The maximum actually occurs at 276 nm (ϵ 16 500).

Other electron withdrawing groups, like cyano and nitro, show similar trends but with different and less well documented substituent effects.

1.19 Polycyclic aromatic hydrocarbons

The range of polycyclic aromatic hydrocarbons is too great for detailed consideration in this book. Because there are many energy levels between which electronic transitions can take place, their spectra are usually complicated, and for that reason are useful as fingerprints. When they only have relatively non-polar substituents, such as alkyl and acetoxy groups, the spectra are similar in the shape and position of the absorption peaks

to the unsubstituted hydrocarbons. The degradation products of natural products often contain polycyclic nuclei which can be identified in this way as, for example, a phenanthrene or a perylene. The spectra of a typical series, naphthalene, anthracene, and naphthacene, are illustrated in Fig. 1.8; note that this figure uses a logarithmic ordinate in order to encompass the range of intensities.

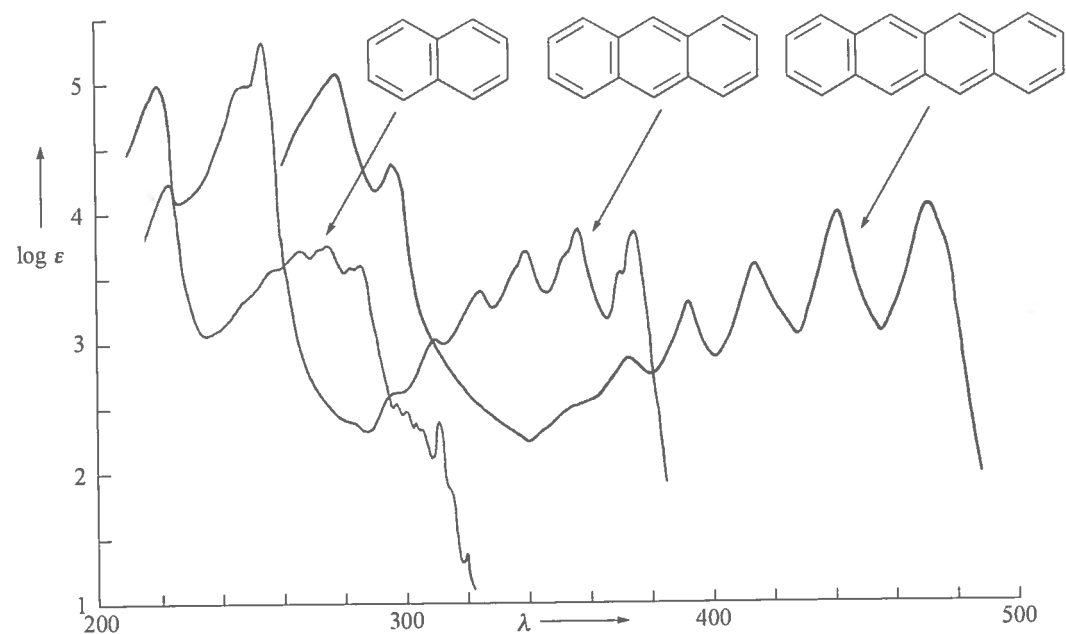
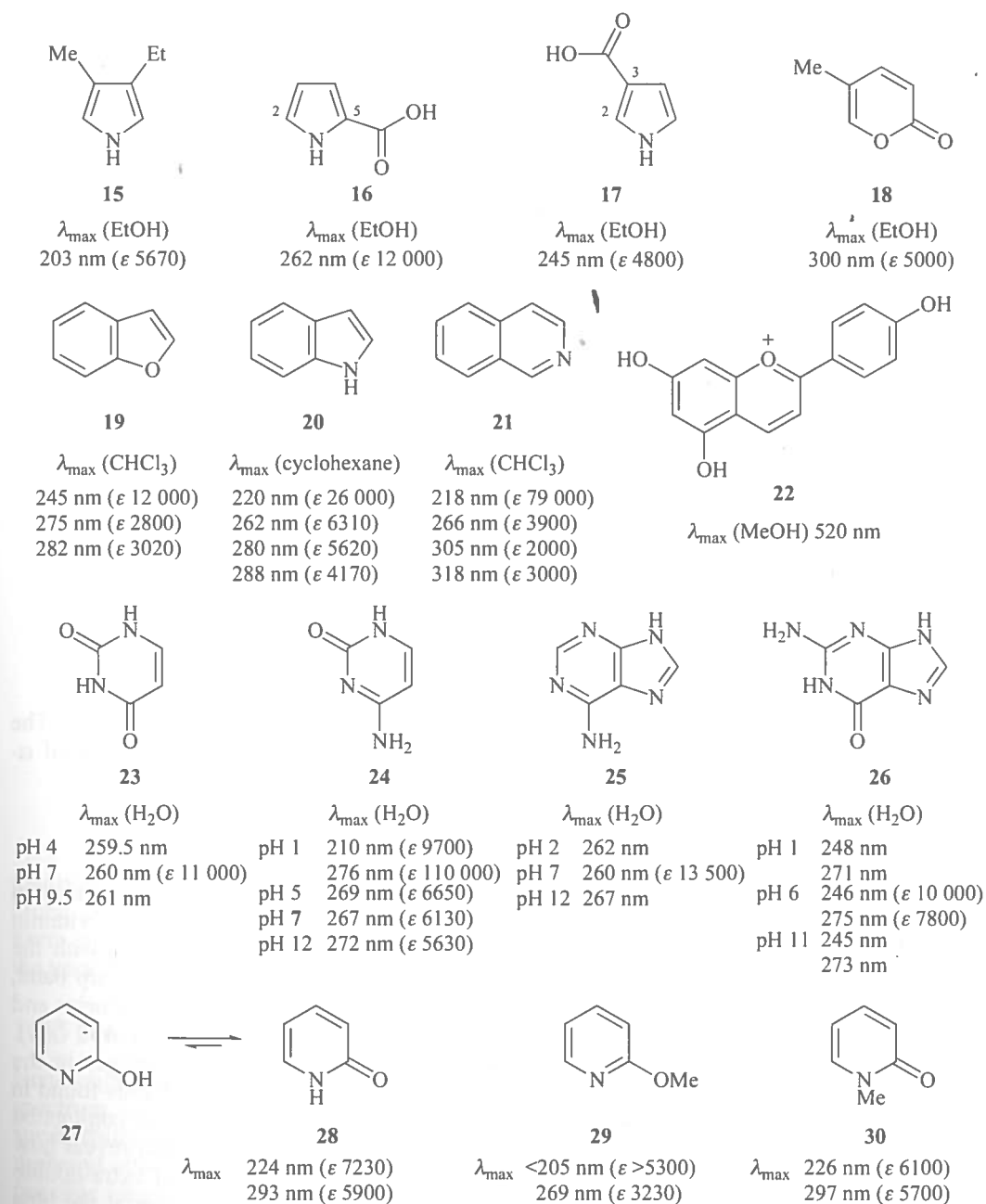


Fig. 1.8

(Spectra taken with permission from R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, Wiley, New York, 1951.)

1.20 Heteroaromatic compounds

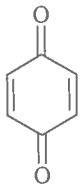
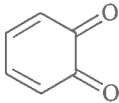
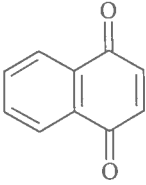
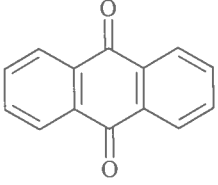
In general heteroaromatic compounds resemble the spectra of their corresponding hydrocarbons, but only in the crudest way. The heteroatom, whether like that in a pyrrole or that in a pyridine, leads to pronounced substituent effects which depend on the electron-donating or withdrawing effect of the substituent and the heteroatom and on their orientation. The effects of these factors are predictable in a qualitative way using the same sorts of criteria as were used in Sec. 1.18 when considering the effects of more than one substituent on a benzene ring. For example, a simple pyrrole **15** and a pyrrole with an electron-withdrawing substituent **16** have strikingly different absorption maxima. The conjugation present from the nitrogen lone pair through the pyrrole ring to the carbonyl group increases the length of the chromophore and leads to longer wavelength absorption. The conjugation to the 5-position in the pyrrole **16** provides a longer conjugated system than the conjugation to the 3-position in the pyrrole **17**, giving rise to a longer wavelength and more intense absorption. The following illustrations of some common heterocyclic systems, including the four nucleoside bases **23-26**, give some indication of the spectra observed.



In the case of tautomeric molecules it is sometimes possible, using ultraviolet spectroscopy, to identify which is the stable tautomer. For example, the equilibrium between 2-hydroxypyridine **27** and pyridin-2-one **28** has been shown to lie far to the right; the ultraviolet spectrum of the solution resembles that of a solution of *N*-methylpyridin-2-one **30** and is different from that of 2-methoxypyridine **29**. The change in the absorption maxima with the change of pH in tautomeric molecules is due sometimes to a change in

the chromophore as a result of the tautomerism and sometimes to simple protonation or deprotonation. This point is mentioned here in order to stress the importance of careful control of the medium in which spectra are taken. The changes in absorption maxima with change of pH are useful diagnostically, since they serve in some systems to identify the pattern of substitution.

1.21 Quinones

			
31	32	33	34
λ_{\max}	λ_{\max}	λ_{\max}	λ_{\max}
(hexane)	(EtOH)	(hexane)	(EtOH)
242 nm (ϵ 24 000)	276 nm (ϵ 2000)	241 nm (ϵ 20 000)	243.5 nm (ϵ 33 000)
281 nm (ϵ 400)	387 nm (ϵ 800)	246 nm (ϵ 23 500)	252.5 nm (ϵ 51 500)
434 nm (ϵ 20)		251 nm (ϵ 19 000)	263 nm (ϵ 20 000)
		256 nm (ϵ 13 000)	272 nm (ϵ 20 000)
		330 nm (ϵ 2750)	325 nm (ϵ 5600)
			405 nm (ϵ 90)

The quinones **31-34** are a representative series of these usually coloured compounds. The colour of the simpler members is from the weak $n \rightarrow \pi^*$ transition, similar to that of α -diketones.

1.22 Corroles, chlorins and porphyrins

Fig. 1.9 shows the visible spectra of representative members of each of the three main classes of pyrrole pigments: hydrogenobyrinic acid **35**, with the chromophore of vitamin B₁₂, chlorophyll **36**, and protoporphyrin IX **37**. The long conjugated systems, with the chromophores emphasised in black, give rise to an exceptionally strong and sharp band, the shoulder of which can be seen on the left in each spectrum in Fig. 1.9. In chlorins and porphyrins this band is called the Soret band, and it occurs near 400 nm (ϵ 100 000). Changes in the chromophore in each class can often be recognised by changes in the position and relative intensity of the four or more weaker, but still strong, bands found in the visible region. These spectra illustrate the general principle that the longer conjugated systems lead to more intense absorption at longer wavelength, and they also reveal how the detailed pattern changes diagnostically with the presence or absence of extra double bonds. The chlorophyll spectrum, in particular, shows the strong absorption at the blue and the red end of the spectrum, leaving the green colour with which we are so familiar. Another conjugated macrocyclic aromatic system, [18]-annulene, shows a similar intense band at 369 nm (ϵ 303 000).

The pyrrole pigments are mentioned here to stress the importance and usefulness of ultraviolet and visible spectroscopy in the study of groups of compounds possessing a long, complicated chromophore. The large number of model systems available makes it

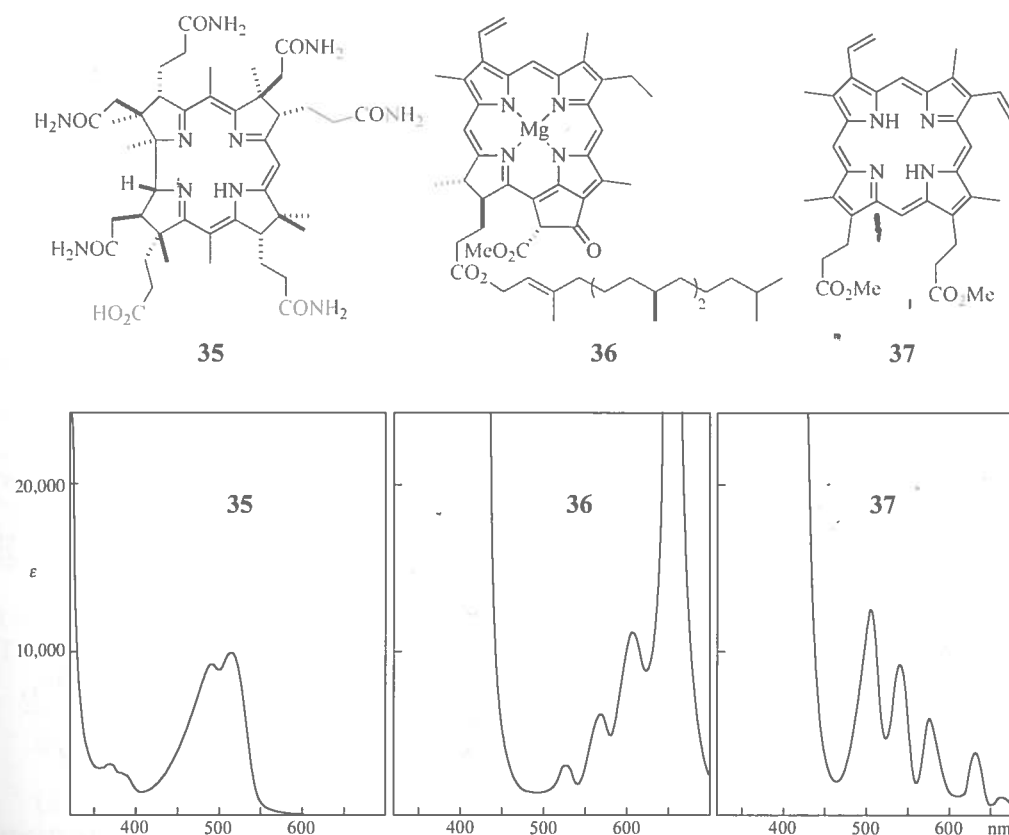
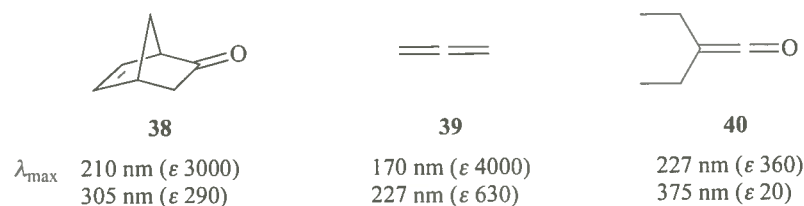


Fig. 1.9

relatively easy to recognise a chromophore, which the other spectroscopic methods do not probe. For example, the oxidations involved in the biodegradation of chlorophyll and haem interrupt the conjugated system in the middle, and are immediately picked up by the very dramatic changes in the visible absorption spectra.

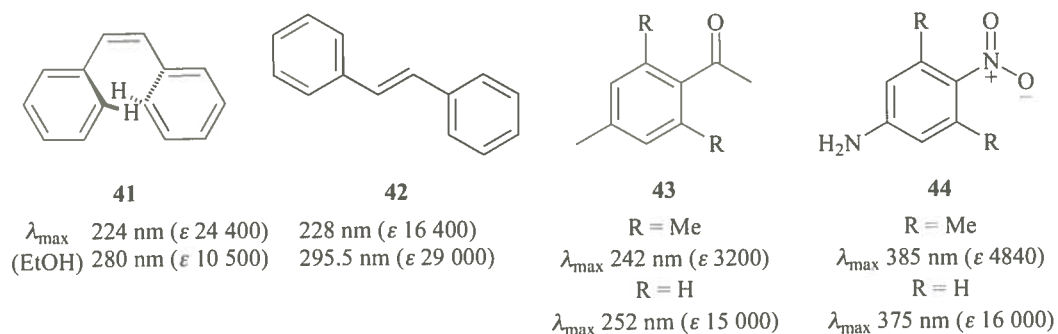
1.23 Non-conjugated interacting chromophores

Non-conjugated systems usually have little effect on each other; diphenyl methane has a spectrum similar to that of toluene; the cross-conjugation of the trienone **10** was successfully ignored when calculating the expected absorption maximum; and even diphenyl ether is not very different from anisole. However, conjugation through space is possible when an auxochrome is held close enough to a conjugated system without being directly conjugated to it. Thus, the $\beta\gamma$ -unsaturated ketone norbornenone **38** shows $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions shifted towards the blue relative to the absorptions of the isolated components. There is evidently some conjugation across space raising the HOMO and lowering the LUMO, but not as effectively as in $\alpha\beta$ -unsaturated ketones. Also, the cumulated double bonds in allenes **39** and ketenes **40**, although not formally conjugated, cause some ultraviolet light to be absorbed weakly in the accessible region.

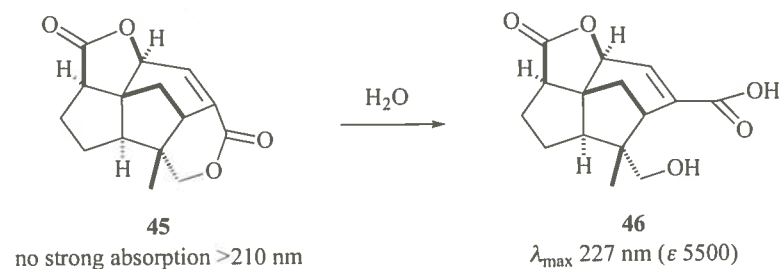


1.24 The effect of steric hindrance to coplanarity

Steric hindrance preventing full coplanarity in a conjugated system, as in *cis*-stilbene **41**, interferes with the effect conjugation has on the energy of the HOMO and the LUMO. In a poorly conjugated system, the HOMO is not raised in energy to the same extent, and the LUMO is not lowered in energy to the same extent. As a result the gap (λ in Fig. 1.2) is larger. The result for the longest wavelength absorption band in *cis*-stilbene **41** is a shorter wavelength and less intense maximum than for *trans*-stilbene **42**. Similarly, the *ortho* substituents in 2,4,6-trimethylacetophenone **43** (R = Me) prevent the carbonyl group from lying coplanar with the benzene ring; this ketone has weaker absorption at shorter wavelength than *p*-methylacetophenone **43** (R = H).



On the other hand, the absorption maximum of 3,5-dimethyl-*p*-nitroaniline **44** (R = Me) shows the usual reduction in intensity but this time a red shift relative to that of the parent compound *p*-nitroaniline **44** (R = H). It is possible that the former absorption is from a different transition to that monitored in the latter case.



The dilactone **45** produced from shellolic acid misleadingly showed no maximum in the accessible ultraviolet region, but hydrolysis gave a product which showed the expected

absorption for an $\alpha\beta$ -unsaturated acid **46**. The steric constraints in the polycyclic structure had prevented effective conjugation between the double bond and the carbonyl group, but the release of this constraint allowed the two π -bonds to overlap.

This observation provides an opportunity to stress that changes between the ultraviolet spectrum of a starting material and a product make it one of the easiest tools to use for following the kinetics of a chemical reaction, and that ultraviolet spectroscopy is possibly used more for this purpose than in structure determination. Nevertheless, the immediate and highly sensitive detection of conjugated systems is still a powerful application for this the oldest of the spectroscopic methods.

1.25 Internet

The Internet is a continuously evolving system, with links and protocols changing frequently. The following information is inevitably incomplete and may no longer apply, but it gives you a guide to what you can expect. Some websites require particular operating systems and may only work with a limited range of browsers, some require payment, and some require you to register and to download programs before you can use them.

For guides to spectroscopic data on the Internet, see the websites at MIT, the University of Waterloo and the University of Texas, representative of several others. They are tailored for internal use, but are informative nevertheless:

http://libraries.mit.edu/guides/subjects/chemistry/spectra_resources.htm
http://lib.uwaterloo.ca/discipline/chem/spectral_data.html
<http://www.lib.utexas.edu/chem/info/spectra.html>

Ultraviolet spectroscopy is not as well served on the Internet as the other spectroscopic methods. The set of books, *Organic Electronic Spectral Data*, is still the best source for UV and visible spectroscopic data.

There is a database of 1600 compounds with UV data on the NIST website belonging to the United States Secretary of Commerce:

<http://webbook.nist.gov/chemistry/name-ser.html>

Type in the name of the compound you want, check the box for UV/Vis spectrum, and click on Search, and if the ultraviolet spectrum is available it will show it to you.

ACD (Advanced Chemistry Development) Spectroscopy sell proprietary software called ACD/SpecManager that handles all four spectroscopic methods, as well as other analytical tools:

http://www.acdlabs.com/products/spec_lab/exp_spectra/

It is able to process and store the output of the instruments that take spectra, and can be used to catalogue, share and present your own data. It also gives access to a few free databases for UV spectra.

Wiley-VCH keep an up-to-date website on their spectroscopic books and provide links. The URL giving access to information about spectroscopy, including UV, is:
<http://www.spectroscopynow.com/Spy/basehtml/SpyH/1,1181,7-4-773-0-773-directories--0,00.html>