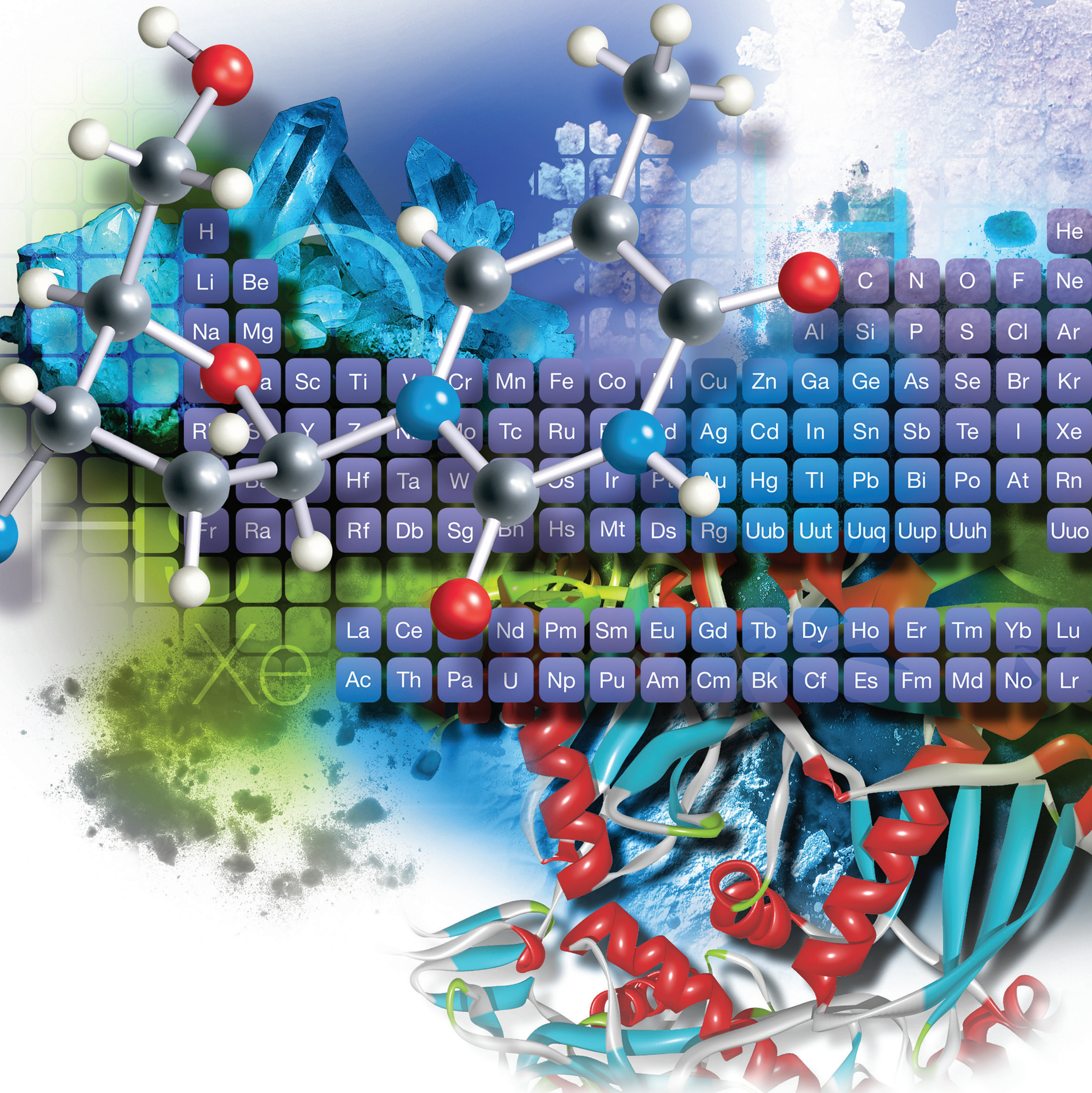
CHEMISTRY

4th Edition



Catherine E. Housecroft
Edwin C. Constable

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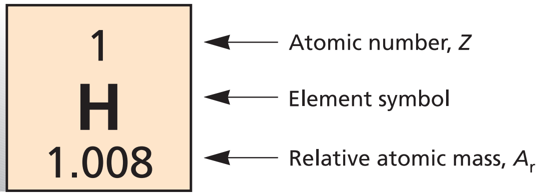
Periodic table



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** 1.008																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.90	23 **V** 50.94	24 **Cr** 52.01	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.54	30 **Zn** 65.41	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.91	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** 98.91	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.40	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.30
55 **Cs** 132.91	56 **Ba** 137.34	**La–Lu**	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.37	82 **Pb** 207.19	83 **Bi** 208.98	84 **Po** 210	85 **At** 210	86 **Rn** 222
87 **Fr** 223	88 **Ra** 226.03	**Ac–Lr**	104 **Rf** [261]	105 **Db** [262]	106 **Sg** [266]	107 **Bh** [264]	108 **Hs** [277]	109 **Mt** [268]	110 **Ds** [271]	111 **Rg** [272]	112 **Uub** [285]	113 **Uut** [284]	114 **Uuq** [289]	115 **Uup** [288]	116 **Uuh** [291]		118 **Uuo** [294]

Lanthanoids	57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** 146.92	62 **Sm** 150.35	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.92	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
Actinoids	89 **Ac** 227.03	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** 237.05	94 **Pu** 239.05	95 **Am** 241.06	96 **Cm** 244.07	97 **Bk** 249.08	98 **Cf** 252.08	99 **Es** 252.09	100 **Fm** 257.10	101 **Md** 258.10	102 **No** 259	103 **Lr** 262

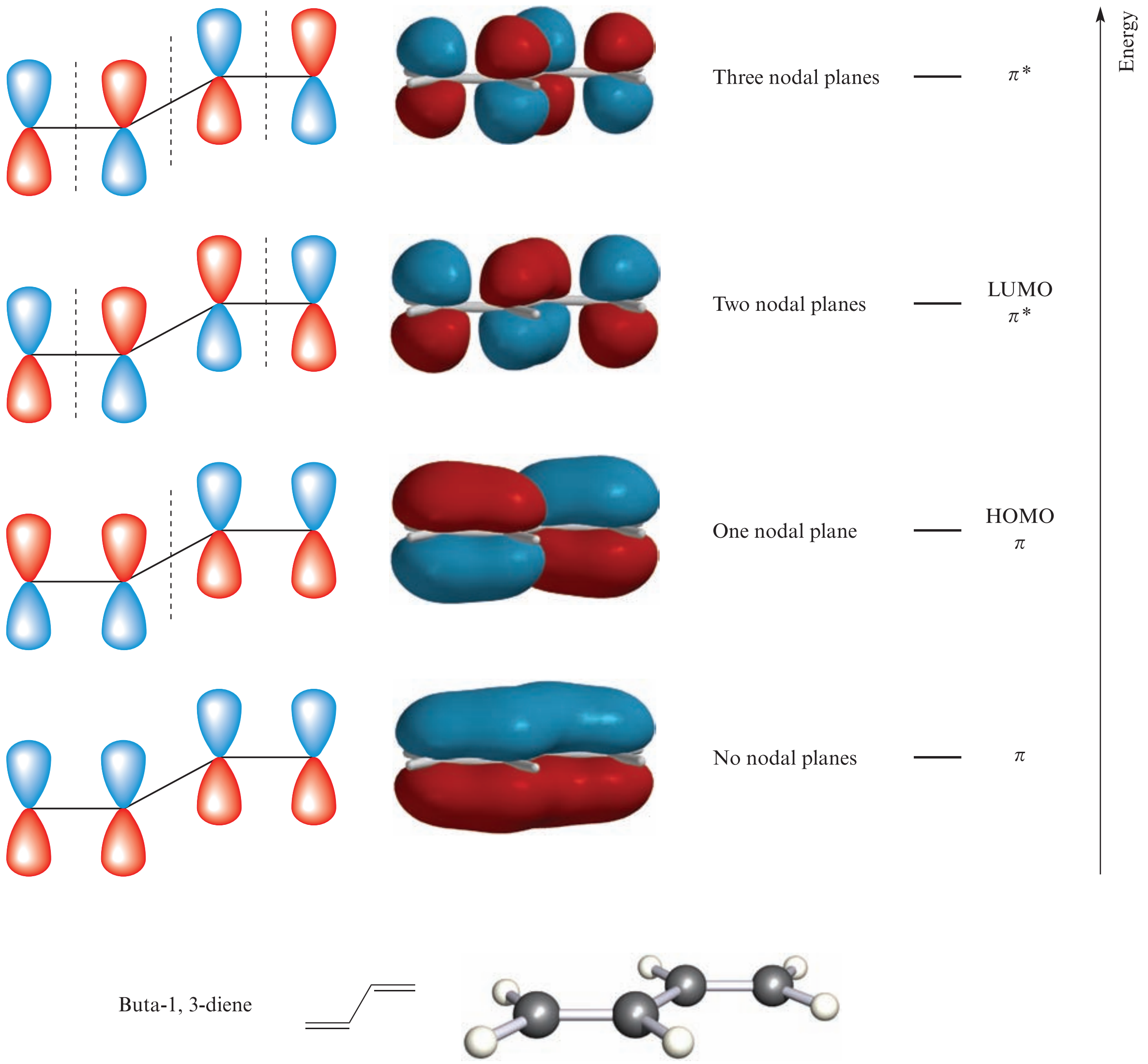


Fig. 13.7 The π MOs of buta-1,3-diene. Each dotted line represents a nodal plane. Each π-orbital also contains a nodal plane in the plane of the molecule. The figure shows schematic diagrams of the MOs and more realistic representations that have been generated computationally using Spartan '04, © Wavefunction Inc. 2003.

that the π-bonds are localized in particular positions, the π-character is actually spread out over the carbon chain. The molecule is *conjugated*.

The effect of conjugation on the $\pi^* \longleftarrow \pi$ transition

A consequence of *conjugation* is that the energy difference between the highest-lying π MO and the lowest-lying π^* MO is lowered, and the associated $\pi^* \longleftarrow \pi$ transition shifts to longer wavelength. In buta-1,3-diene, the $\pi^* \longleftarrow \pi$ transition corresponds to the HOMO–LUMO separation (Figure 13.7) and the transition is observed in the near-UV part of the spectrum ($\lambda_{max} = 217$ nm).

The –C=C–C=C– unit is called a *chromophore* – it is the group of atoms in buta-1,3-diene responsible for the absorption of light in the UV–VIS spectrum. The addition of another C=C bond increases the π-conjugation

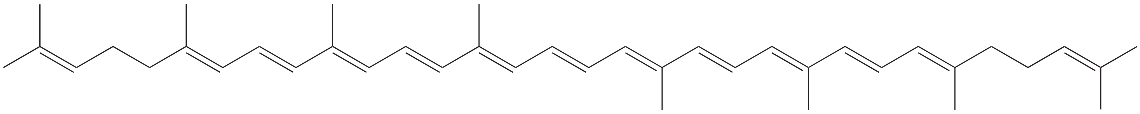
A ***chromophore*** is the group of atoms in a molecule responsible for the absorption of electromagnetic radiation.

BIOLOGY AND MEDICINE

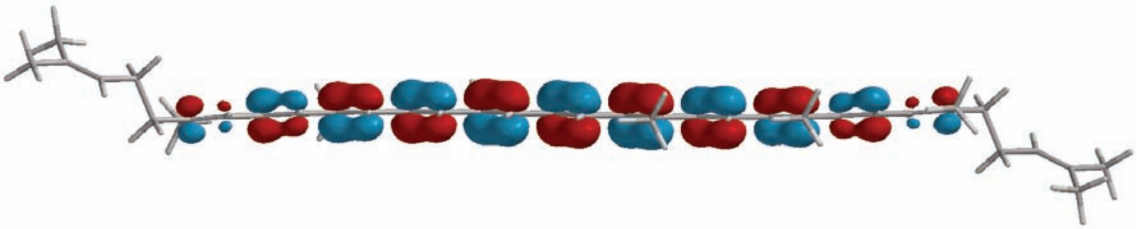
Box 13.1 Carotenoids: naturally occurring polyenes

Nature provides examples of extended π-systems for which the electronic absorption maxima lie in the visible region of the electromagnetic spectrum. Carotenoids are a group of polyenes that are natural colouring agents, providing yellow, orange and red pigments in a variety of plant and animal tissues. Most carotenoids possess 40 carbon atoms. Lycopene is the red pigment in ripe tomatoes, and is a useful starting point for looking at the structures of carotenoids. Its structure (shown below) consists of a 32-atom chain containing 13 carbon-carbon double bonds, 11 of which are conjugated. The extent of the π-system can be seen in the representation of the highest occupied molecular orbital shown below.

The red colour in tomatoes comes from lycopene.



Lycopene

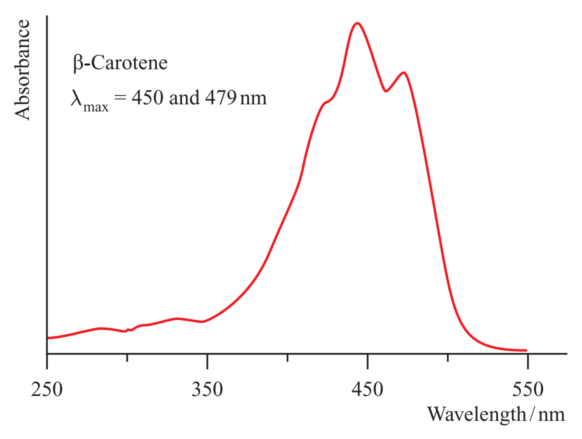


The structure of lycopene and the HOMO generated using Spartan '04 ©Wavefunction Inc. 2003.

Compare this MO with the HOMO of buta-1,3-diene in Figure 13.7. Lycopene absorbs light of wavelengths 444, 470 and 502 nm and appears red (see Table 11.2).

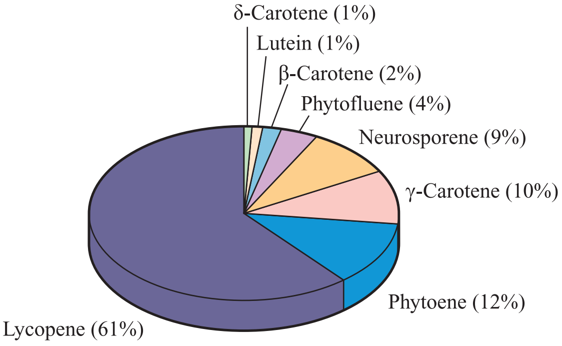
Carotenoids fall into two groups: the carotenes and the xanthophylls. Carotenes are hydrocarbons (i.e. they contain only C and H) and are *hydrophobic*. They dissolve in non-polar organic solvents but are essentially insoluble in water. Xanthophylls are derivatives of carotenes with hydroxy (OH) or other oxygen-containing substituents; the presence of these polar groups increases the *hydrophilic* character of the molecule (see Section 30.3).

Cyclization of one end of a molecule of lycopene leads to γ-carotene, while cyclization of both ends gives α- or β-carotene. α-Carotene and β-carotene are isomers which differ only in the position of one of the double bonds (right-hand ring in the diagrams on the next page). The electronic absorption spectrum of each of the carotenes exhibits two or three maxima, as illustrated opposite for a hexane solution of β-carotene. The change in the position of one C=C bond on going from β- to α-carotene influences the π-conjugation, and as a result, the absorption maxima in α-carotene (445 and 473 nm) are at slightly lower wavenumbers than in β-carotene. The observed colour changes from orange-yellow (β-carotene) to pale yellow (α-carotene). γ-Carotene is



red-orange and the electronic absorption spectrum exhibits bands between those of lycopene and β-carotene, consistent with the structural relationships between the three compounds. Molar extinction coefficients for the absorption bands in the spectra of lycopene and the carotenes are in the range 132 000 and 185 000 $dm^3\ mol^{-1}\ cm^{-1}$.

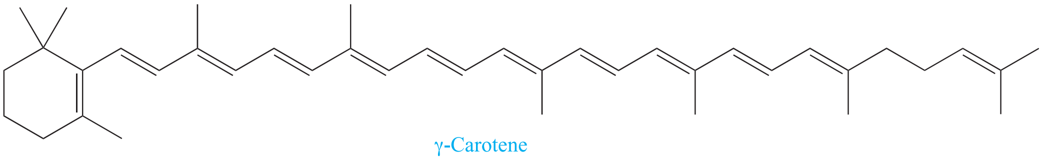
β-Carotene is a precursor to vitamin A (a *provitamin A carotenoid*) and is essential to human health. About 60 carotenoids possess provitamin A activity. Although lycopene does not show this activity, it is important because it is a powerful antioxidant, possessing a very high singlet-oxygen quenching capacity. Singlet-oxygen is the first excited state of O_2, and, if not scavenged, can cause damage to DNA and enzymes. The presence of lycopene in the body is associated with reduced risks of cardiovascular disease and some cancers. Despite their importance, carotenoids cannot be synthesized by the human body and we rely upon their uptake in our diets. Important sources of β-carotene are carrots, oranges, pink grapefruit and cantaloupe melons. Tomatoes and tomato-containing food products are the major sources of lycopene, and the chart opposite shows the approximate carotenoid profile of tomato products. Cooking tomatoes greatly increases the bioavailability of lycopene to the human body. The carotenoids phytoene and phytofluene possess three and five conjugated C=C bonds, respectively. Both are colourless, their electronic spectra being blue shifted with respect to that of β-carotene. In neurosporene, the π-conjugation spreads over nine C=C bonds, and the compound absorbs around 450 nm and is orange in colour.



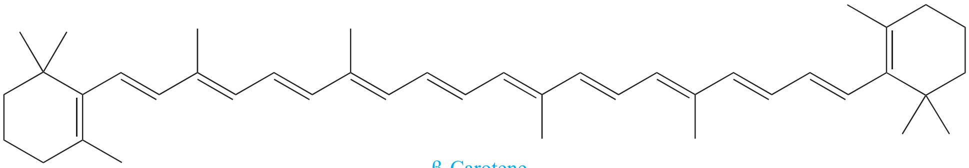
[Data: J. M. Roldán-Gutiérrez *et al.* (2007) *Trends Anal. Chem.*, vol. 26, p. 163.]

Lutein (see on the next page) is an example of a hydroxy-substituted carotenoid. Lutein and zeaxanthin are structurally related in the same way that β- and α-carotene are, and the electronic absorption spectra of lutein and zeaxanthin (both yellow in colour and important components of egg yolks) are similar to those of β- and α-carotene, respectively. Lutein extracted from marigold flowers is used extensively as a colouring agent in foods, and can be recognized on food packaging by the E-number E161b (European Union regulations). Being soluble in oils rather than water makes lutein suitable for colouring margarines and other fat-based products.

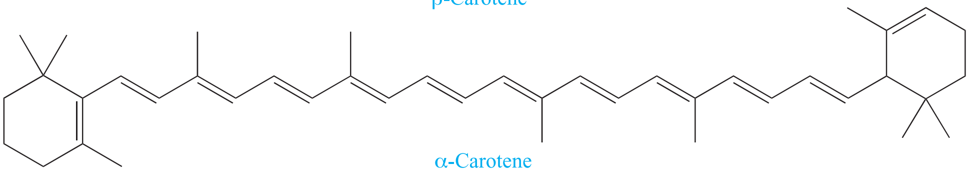
Carotenoids occur more widely in plants than in animals. However, xanthophylls such as lutein occur in the skin and flesh of some fish, while astaxanthin is responsible for the pink colour of salmon. In lobsters and prawns, astaxanthin is non-covalently bound to proteins, but is freed when crustacea are cooked. This leads to a colour change from blue to pink, corresponding to a dramatic hypsochromic shift in the absorption maximum from ≈630 to ≈480 nm.



γ-Carotene

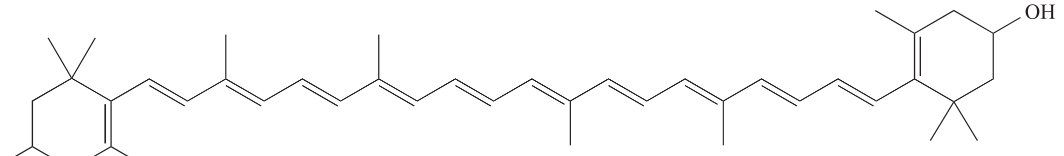


β-Carotene

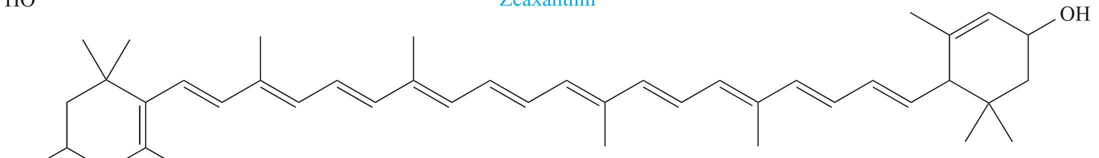


α-Carotene

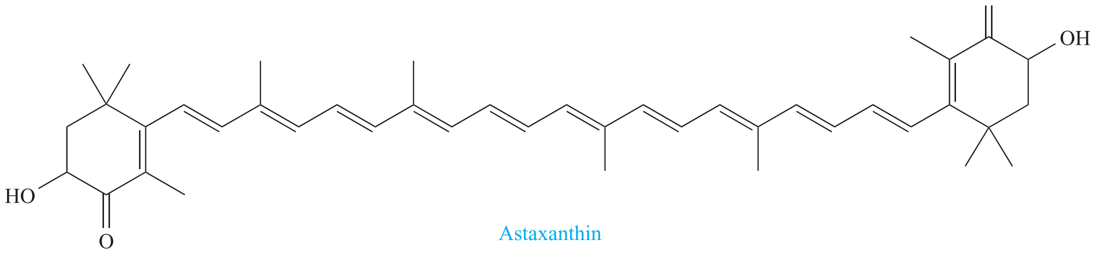
continued



Zeaxanthin



Lutein



Astaxanthin

and causes a further shift in the $\pi^* \longleftarrow \pi$ transition to a longer wavelength (see Figure 13.5). This is called a *red shift* (because the shift in absorption is towards the red end of the spectrum; see Table 11.2) or *bathochromic effect*. The shift to longer wavelength for each additional C=C bond added to the alternating –C=C–C=C– chain is ≈30 nm. The absorption also becomes more intense (larger ε_{max}). The opposite effect, a shift to shorter wavelength, is known as a hypsochromic or blue shift.

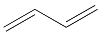
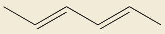
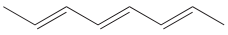
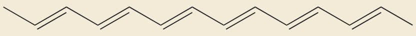
The addition of an alkyl substituent to a carbon atom in the chromophore also leads to an increase in conjugation, but as this is due to an interaction between the σ-electrons in the alkyl group and the π-electrons in the alkene chain, the effect is only small. The result is a red shift of ≈5 nm per alkyl substituent. The data in Table 13.1 illustrate the effects of conjugation in some polyenes, and if the extent of conjugation is great enough, the absorption maximum moves into the visible region. This is illustrated in nature by the chromophores in carotenoids as described in Box 13.1.

A ***bathochromic shift or effect*** is a shift in an absorption towards the red end of the spectrum (longer wavelengths); it is also called a ***red shift***. A ***hypsochromic shift or effect*** is a shift in an absorption towards the blue end of the spectrum (shorter wavelengths); it is also known as a ***blue shift***.

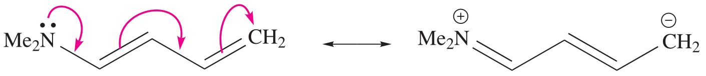
In a ***polyene***, the π-conjugation and, therefore, the ***chromophore*** can be extended by adding another C=C bond or adding an alkyl substituent.

Abbreviated structural formulae are explained in Section 24.2

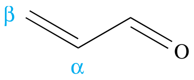
Table 13.1 Observed values of λ_{max} for some conjugated polyenes. Compare these values with those predicted (see text) using buta-1,3-diene as your starting point.

Compound	**λ_{max} / nm**	**ε_{max} / dm^3 mol^{-1} cm^{-1}**
	217	21 000
	227	23 000
	263	30 000
	352	147 000

The addition of substituents other than alkyl groups may also affect the position of the absorption maximum in the electronic spectrum. For example, an OR substituent (R = alkyl) causes a red shift of ≈6 nm, an SR group, a red shift of ≈30 nm, and an NR_2 group, a red shift of ≈60 nm. Each of these groups can donate electron density from a lone pair into the carbon π-system, thereby increasing the conjugation in the molecule and extending the chromophore. This is illustrated in resonance structures **13.6**.



(13.6)

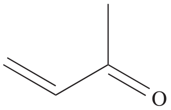


(13.7)

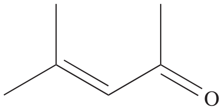
Conjugation also occurs in alkynes with alternating C–C and C≡C bonds. As the length of the chromophore increases, the absorption in the electronic spectrum undergoes a red shift and becomes more intense.

α,β-Unsaturated ketones and aldehydes: see Section 33.15

Conjugation involving π-electrons is not restricted to carbon–carbon multiple bonds. Other compounds that exhibit absorption spectra in the near-UV region include α,β-unsaturated ketones and aldehydes. Structure **13.7** shows the group of atoms that must be present; the carbon atoms of the C=C group are labelled α and β as shown in the diagram.



(13.8)



(13.9)

The π-electrons in an α,β-unsaturated ketone or aldehyde are delocalized in the same way as in an alternating C=C/C–C chain. This leads to a $\pi^* \leftarrow \pi$ transition characterized by an intense absorption around 220 nm. The presence of substituents on the α and β carbon atoms may cause significant shifts in the absorption maximum: the $\pi^* \leftarrow \pi$ transition in **13.8** has λ_{max} 219 nm ($\varepsilon_{max} = 3600\ dm^3\ mol^{-1}\ cm^{-1}$), but in **13.9**, it is 235 nm ($\varepsilon_{max} = 14\,000\ dm^3\ mol^{-1}\ cm^{-1}$).

In addition to the band assigned to the $\pi^* \leftarrow \pi$ transition, the electronic spectrum of an α,β-unsaturated ketone or aldehyde contains a less intense absorption that is due to an electronic transition involving an oxygen lone pair of electrons: a $\pi^* \leftarrow n$ transition. Aldehydes, ketones, acid chlorides, carboxylic acids, esters and azo compounds are among those for which $\pi^* \leftarrow n$ transitions can also be observed, and some typical spectroscopic data are listed in Table 13.2.

Table 13.2 Selected electronic spectroscopic data for compounds exhibiting $\pi^* \leftarrow n$ transitions.

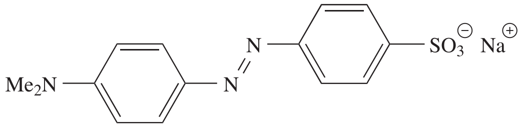
Compound type (R = alkyl)	**λ_{max} / nm**	**ε_{max} / $dm^3\ mol^{-1}\ cm^{-1}$**
$R_2C{=}O$ (ketone)	270–290	10–20
RHC=O (aldehyde)	290	15
RCOCl (acid chloride)	280	10–15
RC(O)OR' (ester) or RCO_2H (carboxylic acid)	≤200–210	40–100
RN=NR (azo compound)	350–370	10–15

13.6 The visible region of the spectrum

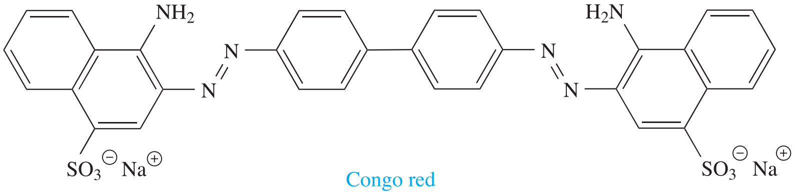
The –N=N– chromophore

Although we have seen that extending a conjugated π-system can ultimately shift an electronic absorption maximum into the visible region of the spectrum, many organic compounds have absorptions *only* in the near-UV region, and the compounds are colourless. However, Table 13.2 indicates that azo compounds absorb light of wavelength approaching the ultraviolet–visible boundary. Just as the absorption maximum for polyenes can be shifted by introducing substituents to the carbon chain or lengthening the polyene chain, so λ_{max} for the –N=N– chromophore can be shifted into the visible region. This has important consequences. Most azo compounds are coloured and many are used commercially as dyes. Two examples are shown in Figure 13.8, and the UV–VIS spectrum of methyl orange is shown in Figure 13.9. The azo dye Sudan IV is shown in Box 13.2. This is one of a series of oil-soluble Sudan dyes used to colour commercial products such as waxes and polishes. Their addition as colouring agents to foodstuffs is legislated against in the European Union, the US and Japan, and imported foods such as chilli and curry powders are monitored for the presence of

Fig. 13.8 Examples of azo dyes, all of which contain the –N=N– chromophore. Congo red is used as a biological stain, and methyl orange is an acid–base indicator. Congo red is also used to estimate free mineral acids.



Methyl orange
λ_{max} = 464 nm



Congo red
λ_{max} = 488 nm

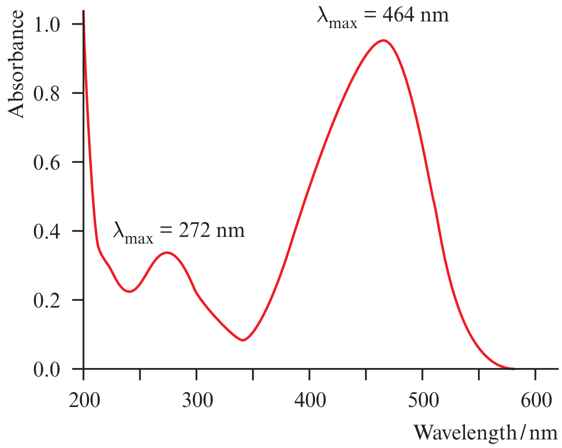


Fig. 13.9 The UV–VIS spectrum of aqueous methyl orange.