# Colour and Constitution of Organic Molecules

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# Preface

Colour, more often than not, is responsible for one's first stirrings of interest in chemistry, and it is this visual aspect of the science that makes for much of its appeal to the embryo scientist. Colour has long been exploited by the industrialist and the research worker, and yet, in view of the vast range of applications of colour and colour change phenomena, it is surprising that no text has appeared for many years dealing specifically with theoretical aspects of the relationships between the colour and chemical constitution of organic molecules.*

The specialist colour chemist will be keenly aware of this gap in the chemical literature, whereas devotees of other branches of chemistry may feel that visible absorption spectroscopy is, after all, merely an extension of ultraviolet spectroscopy, for which several texts are already available. However, visible spectroscopy is a very complex and diffuse area, and cannot be handled simply by extrapolation of the basics of u.v. spectroscopy. The complexity of most coloured chromophoric systems contrasts markedly with the relatively simpler u.v. absorbing systems, and the diversity of chemical types exhibiting colour almost defies systematic classification. Understandably, therefore, no current u.v. spectroscopy book casts more than a cursory glance at this difficult topic.

It was with some trepidation, therefore, that I undertook the writing of this book. The volume of material published in this area is remarkable, and reaches back to the mid-nineteenth century, and thus it was obvious that some means of classifying coloured systems was essential, if the book was to be kept within reasonable dimensions. Fortunately, in the early stages of manuscript preparation a classification scheme did suggest itself, and whilst

* Mention should be made, however, of the excellent book by E. Sawicki ("Photometric Organic Analysis", Wiley-Interscience, New York, 1970), which deals with empirical spectral relationships for many visible and u.v. absorbing organic molecules of analytical interest.

imprecise from a theoretical point of view, it does have the advantages of conceptual simplicity and generality. Thus, without too much difficulty, any stable coloured organic molecule (excluding molecular complexes) can be assigned to one or more of four distinct chromogenic classes.

The book is intended as an introductory text dealing with the basics of colour and constitution relationships in organic chemistry, and is aimed primarily at the final year undergraduate and the postgraduate colour chemist. Whilst of direct relevance to colour chemists, it is hoped that the book will also be of general interest to organic chemists and analytical chemists, and indeed any research worker who meets or makes use of colour and colour change processes in his work. Some knowledge of organic resonance theory on the part of the reader is assumed throughout the text.

The first three chapters deal with physical and theoretical aspects of colour and visible absorption spectroscopy, whereas the fourth reviews qualitative colour-structure relationships. The remaining chapters deal with specific classes of coloured organic compounds, and the arrangement of material has been based on the aforementioned classification scheme, each chapter covering one particular chromogenic class. The choice of illustrative material for these later chapters posed great difficulties, as only a minute portion of published work could be included. The author apologises for the inevitable omissions, but believes that most of the main groups of coloured organic molecules, of both theoretical and commercial interest, have been represented.

To maintain a balance of interests, some biologically important systems have been included (*e.g.* natural pigments, the visual pigments), as have various systems of analytical interest (indicators, colour reactions *etc.*). The author hopes that for the non-specialist, this book will go some way towards providing a reference source for visible absorption spectroscopy.

Finally, I would like to record my gratitude to the late Dr. F. K. Sutcliffe, who first aroused my interest in this topic, and would like to thank my wife for her remarkable forbearance during the preparation of this book.

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# 1. Colour and Colour Measurement

## 1.1 Introduction

Colour plays a remarkably dominant role in our everyday lives, and yet for the most part it is a role that goes largely unappreciated. Most members of the human race have the ability to perceive colours, and since the dawn of civilisation man has attempted to reproduce the colours of nature, for both aesthetic and purely functional purposes. The exploitation of colour has never been as evident as it is today, and vast industries are now directly or indirectly dependent on the availability of artificial colorants. It is generally true that the colour making and colour using industries contribute greatly to the economy of any industrialised country. In view of the commercial importance of colouring matters, considerable interest has been shown in the theoretical and empirical evaluation of relationships between colour and molecular structure. This interest has been accentuated by the widening areas into which colour and colorants now intrude, and colour-structure relationships are now of value to scientists working in many seemingly unrelated disciplines. Liquid crystal display systems, high energy radiation sensors, and dye lasers are recent examples of the varied uses to which synthetic colouring matters can be put.

A brief examination of his surroundings will soon convince the reader of how intimately colorants invade our environment. Clothing, carpets, painted walls, plastic veneers, food, all contain these substances. Even so-called white objects, such as this page, are normally rendered "whiter than white" by the incorporation of special dyes, known as fluorescent brightening agents. In the broad scientific field of analysis, colour is of paramount importance. Thus dyes and pigments become more than pretty chemical curiosities to the analytical chemist and forensic scientist, and also

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to the physician in diagnostic medicine, and to the biologist involved in histological studies. It is perhaps then not surprising that the organic chemist has been called upon to provide colorants for a bewildering range of applications, and this demand currently continues unchecked.

Prior to the mid-nineteenth century, dyes were always isolated from natural sources, which were mainly animal or vegetable in origin. Naturally the properties of many of these substances were far from ideal, and this, together with the commercial unreliability of the sources of supply, encouraged the early search for synthetic dyes of superior properties. It was curious, therefore, that the first synthetic dye to be produced and commercially exploited was discovered by chance. In 1856, William Henry Perkin was attempting to prepare the alkaloid quinine in his home laboratory, when he succeeded in isolating a water soluble dye, which dyed silk a beautiful shade of purple. Although he was only eighteen at the time, Perkin was quick to realise the significance of his discovery, and by the following year, with the assistance of his father, a factory was set up to produce the dye in large quantities. The dye was an immediate commercial success, and Mauveine, as it was subsequently to be called, can be regarded as the initiator of a great surge of interest in the synthesis of new dyes. Viable discoveries followed thick and fast, and the natural dyestuffs were almost completely displaced by synthetic colorants by the beginning of this century. Today, virtually all commercially available dyes and pigments are synthetic substances, with the exception of some important inorganic pigments, and every year hundreds of new coloured compounds are described in the patent literature for a multitude of applications.

Because of the technological importance of colorants, the measurement of colour has been studied closely for many years. Colour is a subjective phenomenon, as it is the response of the brain to the stimulation of the eye by light. Not surprisingly, many problems arise in attempting to define a colour precisely, since both physiological and physical factors have to be taken into account. The physical origins of colour were the first to receive any systematic attention, and it was early recognised that the absorption spectrum of a dye could give at least a rough indication of the colour of the dye in practical usage.

During the early years of the development of synthetic dyes, chemists were intrigued by the elusive relationships between absorption spectra and molecular structure, but up to the 1930's, progress was severely hampered by the lack of a suitable theory for the light absorption process itself. Today, thanks to the advent of quantum theory, we are in a more fortunate position, and mathematical treatments of varying levels of sophistication are available for the prediction of absorption spectra. Equally important are the qualitative treatments of light absorption, which have stemmed from valence bond

and molecular orbital theories, and which can be used to predict qualitatively the effects of structural changes on the absorption spectrum of a molecule. The latter approaches are of value not only to the colour chemist, but also to any scientist who uses coloured substances and colour change phenomena in his experimental work.

Although this book will be concerned primarily with the visible absorption spectra of organic molecules, and the quantitative and qualitative prediction of such spectra, it is useful first to consider briefly some of the physical and physiological aspects of colour.

## 1.2  What is Colour?

Colour is no more a *physical* property of an object than is, say, the odour of a rose a physical property of the flower. Both concepts are physiological sensations, and require the presence of an observer for their existence. However, the *causes* of both sensations do have a physical interpretation. In the absence of light of any kind, an observer cannot perceive colour, and thus it can be concluded that colour arises from an interaction of light with the eye. Colour is, in fact, the way in which the brain recognises the different qualities of light falling on the retina. A discussion of colour must therefore begin with an understanding of the properties of light.

Light has dual characteristics. More than a century ago, Maxwell suggested that light was electromagnetic in character, and consisted of mutually perpendicular electric and magnetic fields whose amplitudes varied in a wave-like manner, both with respect to time and to distance. The wave front travelled with a velocity of about $3 \times 10^{10}$ cm. sec$^{-1}$ in vacuo. An apparently irreconcilable model for electromagnetic radiation was the particle theory, established by Planck and Einstein in 1905. According to this theory, light was regarded as a stream of discrete particles of energy, or photons, travelling with the velocity accorded to the wave front in Maxwell's wave theory. We now know that both interpretations are equally valid, and the most appropriate model depends only on the nature of the phenomenon under investigation.

In wave theory, light can be characterised either by its wavelength ($\lambda$), *i.e.* the distance required for one complete oscillation of the wave, or by its frequency ($\nu$), the number of oscillations occurring in unit time. The velocity of the wave is thus given by the product of these two quantities,

$$c = \nu.\lambda \qquad (1.1)$$

In the particle theory, monochromatic radiation is characterised by the

energy of each photon. The well known Planck equation (1.2) relates this photon energy $(E)$ to the frequency of the wave.

$$E = h\nu \qquad (1.2)$$

The quantity $h$ is the Planck constant, and has a value of $6.625 \times 10^{-34}$ Js. It is apparent that when discussing the energetics of the light absorption process, the particle theory is more appropriate, whereas the treatment of colour arising from dispersion or diffraction effects is best handled by wave theory.

The electromagnetic spectrum includes radiation ranging from very short wavelengths (high energy), such as X-rays and $\gamma$-rays, to radiation of very long wavelengths, such as radio waves. Only a very narrow portion of the total spectrum can produce a visual sensation when the radiation is incident on the eye, the limits of the visible region extending from about 400 nm to 800 nm in wavelength. In the restricted sense of the word, we refer to radiation in this region as *light*. The different "qualities" of light that are responsible for the sensation of colour are its wavelength, or equivalently, its photon energy.

If a reasonably homogenous mixture of all wavelengths of light between 400 and 800 nm is incident on the retina of the eye, then the sensation of white is manifested. White, like black or grey, is termed an *achromatic* colour. When such a mixture is passed through a suitable prism or diffraction grating, the beam is split up into a continuum of colours, the dominant hues occurring in the well known order: red, orange, yellow, green, blue and violet (Fig. 1.1). The wavelengths of the radiation giving rise to these colours
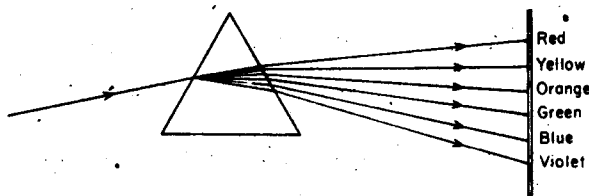


Fig. 1.1   The dispersion of white light into the visible spectrum.

decrease in the same order, from red to violet. Thus a low energy photon (say of 45 kcal. mol$^{-1}$) gives the sensation of red, whereas a high energy photon (say of 70 kcal. mol$^{-1}$) gives the sensation of violet. In practice, many more hues than those mentioned can be distinguished under suitable conditions, and many observers can identify about 150 different hues. However, for normal purposes, the visible spectrum can be divided into nine broad

regions, each readily distinguishable from the others, and these can be depicted in the form of a colour circle (Fig. 1.2).
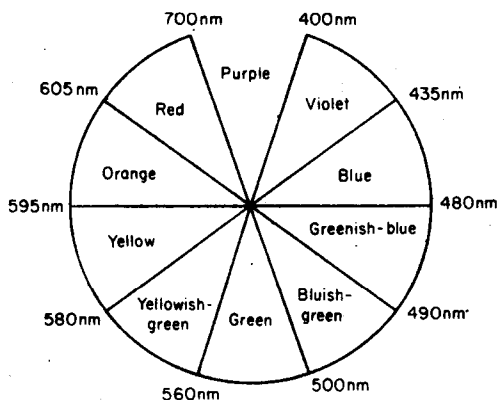


Fig. 1.2 The colour circle. Each sector corresponds to the wavelengths of monochromatic light giving a particular hue.

In Fig. 1.2 the wavelength scale around the circumference of the circle has no physical significance, but it will be noted that each sector has another sector diametrically opposed to it. It will also be noted that the colour purple is not duplicated by any single wavelength of light, and this this is called a *non-spectral* colour. Intuitively, purple is a colour falling midway between red and violet, and thus it can be assigned to the missing sector of the colour circle. Purple can in fact be synthesised by mixing red and violet monochromatic radiations.

The colour circle of Fig. 1.2 can now be used to discuss some interesting aspects of colour and colour mixing. All the colours of the circle, if mixed in the correct amounts, give white light. However, white light, at least as far as the human eye is concerned, is also produced by mixing two monochromatic radiations from any pair of opposite sectors. Such pairs of colour are said to be *complementary*. For example, the complementary colour of blue (sector 435–480 nm) will be yellow (580–595 nm), and white light can be produced by mixing blue and yellow lights. Particularly interesting is the green sector, which opposes the non-spectral colour purple. In fact these two colours are complementary, since if green light is mixed with purple light, the latter being a mixture of red and violet, white light is produced.

Mixing radiations in this way is called *additive* mixing, since the intensity of the resultant colour increases additively as more components are added to the mixture. Additive colour mixing is not a generally familiar process, and

can produce some surprising results. The colour of any zone on the colour circle can be duplicated by mixing radiations from the two flanking zones, or even near-flanking zones. This is intuitively obvious for some colours, *e.g.* orange from red and yellow, or green from yellow and bluish-green, but is less obvious for some other combinations. A particularly striking example is the synthesis of the colour yellow by mixing red and green radiations. For the reader who may not have seen this demonstration, he can verify this for himself by examining closely a patch of yellow on a colour television screen. The yellow area will be found to consist of hundreds of closely spaced red and green spots. The phosphors emit red and green radiation, and as the observer recedes from the screen, the eye blends these two colours additively to give the sensation of yellow.

A pure spectral hue is afforded by a monochromatic light wave. Alternatively, as we have seen, the same hue can be accurately duplicated by mixing two different monochromatic radiations. In fact, the hue may be synthesised from any number of combinations of monochromatic radiations, and it is apparent that the eye can register the same colour sensation for a wide variation in the quality of the radiation entering the eye. This serves to emphasise the physiological basis of colour, and the fact that the eye is not capable of assessing the characteristics of light in the same way that a spectrophotometer can.

If three monochromatic radiations are selected so that they are well separated on the colour circle, then it is found that every possible hue can be reproduced by additive mixing of these colours. The trio can then be called *additive primary colours*, and their choice is entirely arbitrary. In colour television, for example, the remarkably good colour reproduction that can be obtained depends solely on three phosphors, giving the primary colours red, green and blue. However, pure spectral (*i.e.* monochromatic) colours or additively mixed colours are rare in nature. Examples include bioluminescence (*e.g.* fireflies) or the diffraction colours of certain minerals, or mother-of-pearl. In the animal kingdom, diffraction colours are observed on the bodies and wings of certain birds and insects. These colours are characterised by their brightness and irridescent qualities, and the tendency of the colour to vary with angle of view. By various fascinating devices, nature has evolved ways of minimising the angular dependence, restricting the diffraction colour to a narrow band of wavelengths. The brilliant irridescent violet wings of the South American *Morpho* butterfly provide a prime example of this.

The vast majority of colours that pervade our environment are not of this type, however, and in fact arise from what is known as a *subtractive* colour mixing process. We have seen that mixing a pair of complementary colours gives an apparent sensation of white light. If one of the components of such a

mixture is removed, *e.g.* by passing the beam through a filter, then the remaining component will obviously be detected by the eye. A similar situation arises with white light that actually consists of a mixture of all wavelengths, such as daylight. If one wavelength, or a narrow band of wavelengths is removed from the mixture, the colour registered by the eye *is the complementary colour of the radiation removed.* This is in spite of the fact that the light falling on the eye is still an extremely complex mixture of wavelengths. To take one example, if sunlight is passed through a filter that removes a band of wavelengths in the region of 495 nm (*i.e.* bluish-green light), the eye will perceive the complementary colour of blue-green, namely red. Conversely, if the filter had removed red light, the emergent beam would appear blue-green. It is interesting that the non-spectral colour purple can be produced by removing green light from the beam of white light. Colours formed by removal of radiations from white light are said to be produced by *subtractive* colour mixing. Dyes, pigments and other coloured substances appear coloured because of this type of phenomenon, the molecules selectively filtering certain wavelengths from normal daylight.

The production of green by a subtractive process is worthy of comment. The complementary colour of green is the non-spectral colour purple, so the problem arises as to how one can remove purple light, which does not exist as monochromatic radiation, from white light. The answer is to remove not one, but two wavelengths of light from the incident beam. Purple may be regarded as a mixture of red and violet light, and thus filtration of these two components (wavelengths *ca.* 650 and 420 nm respectively) from white light gives green. Thus, whereas all other hues can be produced subtractively by dyes with one absorption band, green is unique in that it requires that the dye absorbs simultaneously in two regions of the visible spectrum. Chlorophyll, the most abundant green pigment, provides a good example, and absorbs near 660 and 430 nm. This requirement that a green dye must have two absorption bands poses many synthetic problems, and accounts largely for the dearth of commercially available green dyes and pigments. Green shades are preferably produced by mixing blue and yellow dyes, despite the problems that this can introduce.

An understanding of the principles of subtractive coloration is essential if one wishes to be able to relate the absorption spectrum of a substance to its observed colour or *vice versa*. As the absorption maximum of a substance moves from short to long wavelengths (*i.e.* from left to right on most recording spectrometers), the colour of the light absorbed progresses through the sequence violet, blue, greenish blue, bluish green, green, yellowish green, yellow, orange and red (Fig. 1.2). The *observed* sequence of colours can be deduced from Fig. 1.2, by noting the complementary colour of that absorbed. For most purposes only seven complementary colours
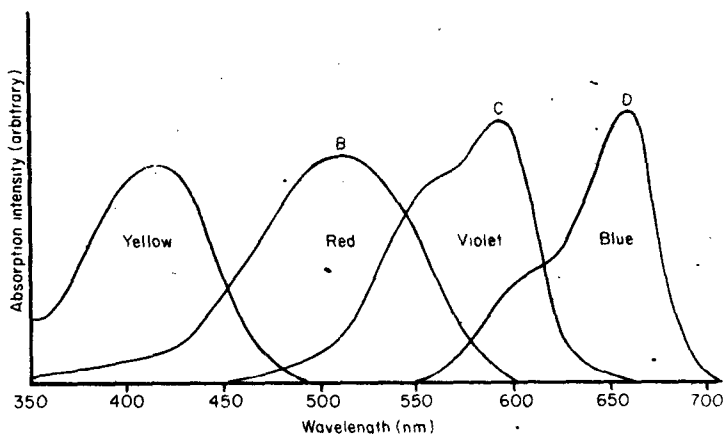
Fig. 1.3 Visible absorption spectra of (A) 2-aminoanthraquinone, (B) 1-methyl-aminoanthraquinone, (C) Crystal Violet, and (D) Methylene Blue, measured in ethanol. The observed colours of the solutions are indicated.

need be memorised, and these are, ranging from left to right for the absorption band of a substance on our recorded spectrum: yellow, orange, red, purple, violet, blue and bluish green. This can be made more clear by examination of Fig. 1.3, which shows the absorption spectra and observed colours of representative dyes.

Figure 1.4 shows the absorption spectrum of a typical green dye, Malachite Green, with two absorption bands in the red and violet regions of
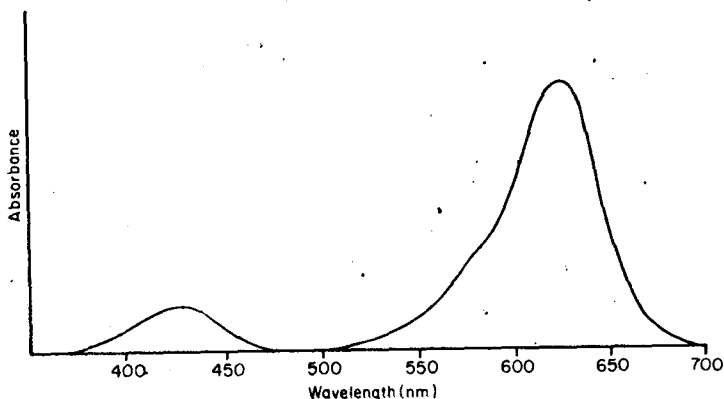


Fig. 1.4    Absorption spectrum of Malachite Green (in ethanol).

the spectrum. The different intensities of the two peaks affects the shade of green observed, and in this example the red-absorbing peak (giving a blue visual sensation) is more intense than the violet-absorbing peak (yellowish green sensation), and thus the observed shade is a rather dull green with a blue cast.

When dyes or pigments are mixed together, a wide variety of colours can be produced, as they can by the additive mixing of coloured lights. In the former case however, it is found that as more and more components are added to the mixture, the resultant colour becomes darker and darker, until eventually black is produced, whereas in the latter case, white is produced. The production of black is easy to understand for subtractive mixing, since the addition of more absorbing molecules to the mixture results in an increase in the amount of incident light absorbed, until eventually almost complete absorption occurs. As in additive mixing, three primary colours can be recognised, which can be used to duplicate all other hues. These are the three essential ingredients of any paintbox, namely red, yellow and blue.

Some colours produced by subtractive mixing are not easily described by hue alone, and these are the dark or dull shades, such as browns, maroons, olive greens *etc.* These shades are actually provided by substances that absorb over a relatively high proportion of the visible spectrum, but which still absorb most intensely at those wavelengths that provide the dominant hue. Single compounds with broad absorption bands, or mixtures of dyes with overlapping bands are used commercially to provide colours of this type. On the other hand, the most brilliant, pure colours are provided by dyes with very narrow absorption bands, or by dyes which fluoresce and absorb light simultaneously.

## 1.3 Other Factors Influencing Colour

Although the colour of a substance is controlled very largely by its absorption or reflectance spectrum, other external factors can affect the observed colour. For example, the spectral composition of the illuminant used to observe a coloured surface can affect the apparent colour quite dramatically. An extreme example would be where the incident white light was actually composed of two monochromatic wavelengths only, say 450 nm and 590 nm (blue and yellow respectively). If this light impinged on a normally bright green pigment, absorbing at 450 and 590 nm, the colour would look almost black. This apparent change in colour with the external illuminating source is a type of *dichroism*, and is familiar to all of us who have bought clothing when viewed under fluorescent lighting, and have found the colours to be quite different in normal daylight.