Chapter 5
Industrial Photochromism

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Abstract This chapter outlines how industrial photochromic dyes are designed, manufactured and used. It explains the properties that are crucial to their commercial utility and, in doing so, gives a definition of ‘industrial photochromism’. Such colorants possess several key molecular features. This Chapter reveals how these structural elements influence photochromism. Additionally, it describes the typical chemistries employed in dye construction and takes a critical look at the limitations of current commercial colorants. Along the way, the directions that the exploitation of existing types might take in order to improve performance receive attention as do the potential future industrial applications to which photochromic dyes may be put.

5.1 Introduction

Global business worth many millions of dollars relies on photochromic colorants. The industrial utility of these dyes depends upon their defining characteristic, which is a reversible colour change that occurs in response to differing ambient light levels [1]. Their most important commercial application is the production of ophthalmic lenses that darken reversibly when exposed to strong sunshine. While industry actively tries to improve upon current light-responsive systems, researchers continue to attempt to develop disruptive new technologies that might capture, grow or kick-start new markets for industrial photochromism. This Chapter aims to give the reader an overview of the phenomenon and the colorants behind it, concentrating on those in commercial use today.

Numerous types of photochromic materials are known to science [2–4]. Collectively they exhibit wide variations in behaviour. Currently, however, commerce exploits only a limited number of these colorant classes for niche industrial applications. The properties demanded of them are narrow but exacting. This Chapter prescribes these traits, providing a definition for industrial photochromism. It outlines the history of its successful exploitation over the past 25 years, describing how industry took advantage of photochromic colorant chemistry.

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Developing commercial products from photochromic colorants presents a different set of challenges to that posed by conventional dyes and pigments. Not only are these light responsive organic compounds less robust and orders of magnitude more expensive, but their dynamic nature also adds extra dimensions of complexity to their application. These additional requirements must be tackled by appropriate molecular design. The structures of industrial photochromic dyes may appear at first glance to be arbitrary and complicated, but each feature serves at least one purpose: this Chapter delineates their influence on properties and performance. It also puts into context important external factors that significantly impact colorant behaviour. The medium into which the dye is incorporated, as well as the additives that accompany it, exert a profound effect. In addition, the means by which photochromic colorants are applied can make the difference between success and failure because they are relatively delicate and sensitive to their environment. Since the manufacture of ophthalmic lenses consumes the bulk of photochromic dyes produced industrially, this Chapter will focus primarily on properties which matter most to this particular technology. However, consideration will also be given to other outlets, providing the reader with a deeper appreciation for the limitations of photochromic dyes as well as which techniques are appropriate for their application.

What follows is therefore not intended to be a comprehensive account of the synthesis or photochemistry of photochromic colorants – there are plenty of resources which go into such detail elsewhere as will be pointed out later. Instead, this Chapter provides the reader with an introduction to the design, manufacture and application of industrial photochromic dyes. It aims to furnish insights into the molecular features encountered in the structures of such colorants and impart rules of thumb that describe their influence on behaviour.

Finally, against the backdrop of numerous successful years of industrial photochromic dye use, much effort continues to be dedicated to bringing new technologies to market based on photochromism. While this endeavour has not yet borne fruit, it could lead, if successful, to the commercialisation of colorant classes at unprecedented industrial scales. Consequently, these applications will receive brief mention along with the dyes that form the focus for what could be the next ‘killer app’ for photochromism.

Before then, we shall take a look at what is meant by photochromism as exhibited by industrial photochromic dyes.

5.2 Industrial Photochromism

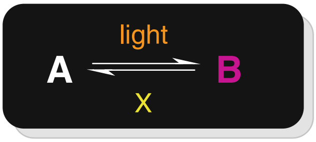
The conventional definition of photochromic behaviour is much broader than the type of light-responsive effect which forms the basis for most industrial activity. Photochromism is usually defined as a reversible colour change that is driven in one or both directions by the action of light [5]. The word “reversible” is of key importance. If light causes an irreversible colour change, then the effect should not be described as photochromism. In certain fields, a permanent one-way switch in colour though exposure to light is said to be “irreversibly photochromic”. However, this phrase is incorrect by definition. Just as one would not describe the permanent fading in colour of a dyed fabric as an example of photochromism, an irreversible change in coloration must not be referred to as a photochromic effect. The reversible appearance of colour, disappearance of colour, or alteration in hue are all phenomena validly described as photochromism. This section attempts to narrow down the above behaviour into a definition of industrial photochromic behaviour.

5.2.1 A Definition of Industrial Photochromism

Photochromic phenomena can be split into one of two types as shown in Fig. 5.1. Those materials in which colour changes are driven entirely photochemically in both directions exhibit what is known as “P-type” photochromism. In contrast, illumination switches “T-type” compounds in only one direction – they return to their original state in its absence. The reversion occurs thermally. An easy way to remember this distinction between the two kinds of behaviour is that the label T-type denotes that a Thermal transformation is involved, whereas P-type signals that purely Photochemical changes are concerned.

P-type compounds typically change colour upon irradiation with ultraviolet (UV) or visible light and remain in that state, even when no longer exposed to the illumination. They only return to their original state after light of another range of wavelengths strikes them. True P-type colorants therefore generally behave like switches. They flip between states of different absorption profiles, but only by subjecting them to appropriate wavelengths of light. As shall be mentioned later in this Chapter, the potential for the states of P-type materials to be manipulated in a controlled way has captured the attention of many researchers and technologists for use in a wide variety of different fields [6].

Despite this interest, the most commercially important photochromic compounds have a T-type character. The vast majority of such colorants in industrial use exhibit a specific subset of T-type photochromism: UV radiation, and in some cases short wavelength visible light, triggers the conversion of colourless (or almost colourless) species to coloured forms. Although the exact wavelengths of light that effect the change are dependent on dye structure, they typically lie within the UV-A region (320–400 nm) for commercial photochromic colorants. (Some applications



A and B are states of a compound which have different absorption characteristics in the visible region;
when X = light, photochromism is “P-type”
and when X = heat, photochromism is “T-type”

Fig. 5.1 General depiction of P- and T-type photochromism rely on the ability of particular photochromic molecules to react efficiently also to blue light of wavelengths around 410–420 nm.) Industrial dyes respond well to sunlight since UV-A makes up a significant proportion of the solar radiation incident at the Earth's surface: they become rapidly coloured and deliver pronounced photochromic effects in unfiltered sunshine outdoors. However, their effectiveness decreases markedly behind architectural glazing and automotive windows because these structures attenuate UV light. For example, laminated car windscreens block transmission of UV-A wavelengths very efficiently. On the other side of the coin, light sources that emit only a small proportion of their radiation in this region are, unsurprisingly, not very effective at activating commercial photochromic dyes. Consequently, artificial thermoluminescent illumination that radiates little energy within the near UV, such as tungsten filament light bulbs, is typically incapable of bringing about photochromism.

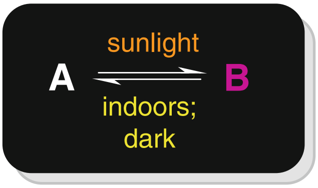
Industrial T-type colorants revert thermally to their colourless form in the absence of activating UV-A light as fast as design considerations and other performance aspects will allow. Not all dyes used commercially behave in a completely T-type manner. In these instances, certain wavelengths within the visible region also drive the back-reaction from coloured to colourless, conferring an element of P-type character on their photochromism. The presence of these visible wavelengths thus partly counteracts the effect of UV-A radiation by causing photobleaching. Consequently, the photochemical component of the back-reaction must remain inefficient.

Another way of classifying photochromic effects involves the nature of the colour change. The T-type dyes described above are said to exhibit "positive photochromism" [5]. This label means that the longest wavelength absorption band shifts from the UV upon irradiation to the visible region of the spectrum, i.e. moves from shorter to longer wavelengths and usually entails a transition from a colourless state to a coloured one through activation by UV. The opposite behaviour is "negative photochromism". This term does not refer to the absence of any photochromism! It typically applies instead to a coloured material becoming colourless upon irradiation with light, returning to its original coloured state in the dark, i.e. a shift of the longest wavelength band in the visible region to a shorter set of wavelengths in the UV. Examples of the latter type of switching are rarer than those of the former kind. As might be deduced from the preceding paragraph, industrial photochromism is overwhelmingly of the positive type.

The properties of commercially significant photochromic colorants outlined above thus represent only a small subset of the permutations under the general umbrella of possibilities covered by photochromism. The term "heliochromism" [7] accurately captures the specific characteristics of the photochromism typically exhibited by industrial dyes. This label, derived from the Greek word for sun, was coined to define a special type of photochromism where the response is dependent on the intensity of incident unfiltered sunlight. A "heliochromic" colorant is efficiently activated by near UV radiation, exhibits a moderately efficient thermal fade, and is photobleached with low efficiency by white light. While heliochromism is by far the most commercially important variant of photochromism, industry and academia usually apply the more general term "photochromic" when describing the behaviour of colorants and products which falls within the definition of heliochromic.

Industrial photochromism arguably takes the form of an even narrower definition (see Fig. 5.2). Economic considerations come into play in addition to technical criteria. Photochromic effects must meet consumer expectations of longevity and cost without infringing third party intellectual property. In addition to forming the basis for marketable products, industrial photochromism has to be economically viable as well as safe to remain a commercial proposition otherwise the phenomenon just reverts to being photochromism!

The relationship that industrial photochromism has with the other classes of photochromic behaviour is depicted in Fig. 5.3. The hierarchy as shown is a little



A reversible colour change induced in a dye, which:

(i) rapidly becomes coloured on exposure to a source of strong UV light and quickly becomes colourless when exposure to the source is stopped;

(ii) can be repeated over many cycles during a time period that is acceptable to the expectations of consumers;

(iii) is cost-effective and safe to implement.

Fig. 5.2 A definition of industrial photochromism

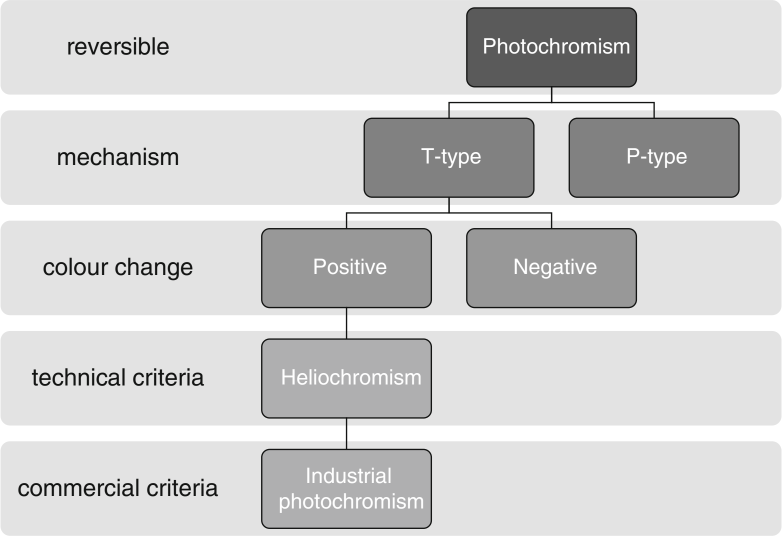


Fig. 5.3 A hierarchy of photochromic behaviour

simplistic in that many industrial dyes are not purely T-type and it refers only to commercialised mainstream applications. The introduction of significant new potential uses for P-type photochromic colorants mentioned in the following section would lead to major revision of Fig. 5.3.

As we shall see in the next section, although heliochromism forms the basis for a commercially successful global enterprise, the genesis behind the dyes upon which it is reliant may be traced back to efforts to develop materials by the military.

5.2.2 History, Current Status and Future Development of Industrial Photochromism

The roots of the industrial exploitation of photochromism lie in the first modern systematic efforts to study organic light-responsive materials in the mid-twentieth century. In its pioneering attempts to make use of photochromic colorants for the visual protection of its personnel, the US military synthesised the initial examples of a class of dye [8] that eventually became one of the most industrially important families. However, the first commercially successful outlet for industrial photochromism marketed to the consumer depended not on organic colorants, but on an inorganic system [9]. Photochromic glass lenses containing silver halide microcrystals [10] have been produced in their millions since the 1960s for prescription spectacles. Since then, polymer materials have largely replaced mineral glass in the fabrication of lenses because the former substances enable the construction of more lightweight and robust optics – but they are not compatible with silver halide systems. Consequently, the goal of producing photochromic plastic lenses grew from one of wishful thinking, when light-responsive glass spectacles were first introduced, into a real and unfulfilled need as the market share of plastic lenses grew. In order to plug this important gap in the market, industry searched for commercially viable alternative systems based on organic dyes during the 1970s and 1980s – it formed the primary driver for progress in industrial photochromic technology. These efforts, which focused not only on dye design, but also the material of lens construction and mode of colorant application, culminated in commercial success during the 1990s in the US, Europe and Japan [9]. Accounts of early developments in the US are available [11, 12]. Further advances to dye technology, application techniques and lens media have led to better performing and more robust products so that globally the majority of photochromic lenses worn today are plastic. Around 15–20 % of corrective lenses prescribed in the US and Australia are photochromic, whereas the proportion is lower in Europe and Asia (around 1 in 10 and 1 in 20 respectively) but nevertheless significant [13]. Their manufacture therefore has spread worldwide. The lens industry dominates the consumption of photochromic colorants, acquiring them by one or more of these means:

(i) Use of photochromic lens monomer mixtures that are marketed by companies with the expertise in dye and polymer chemistry to formulate them. This business model enables lens manufacturers who do not have in-depth knowledge of the intricacies of formulating to cast or coat photochromic lenses themselves. It also gives them freedom to operate where there is patented technology in place.
(ii) Purchase of colorants 'off-the-shelf' from specialised photochromic dye producers (such as Vivimed Labs Europe Ltd). This route allows lens manufacturers flexibility in creating their own formulations, but without having to concern themselves about colorant chemistry.
(iii) Synthesis by external contract manufacture or an in-house facility. Since this option demands substantial investment of resource as well as an in-depth knowledge of dye design, it tends only to be used by larger players within the industry.

The industry associated with the production of photochromic plastic lenses continues to account for a substantial proportion of the research taking place into photochromism. While it has achieved its overall goal of producing neutral-coloured photochromic eyewear based on plastic lenses with performance and robustness levels generally acceptable to the consumer, more remains to be done. The business still strives to improve properties like responsiveness and durability as well as develop new ways of introducing photochromism to lens materials that have proved resistant to it – more will be said about this aspect later. The improvements made in photochromic dye technology for lenses have crossed over into other avenues of use, such as coloration of plastics and surface coatings, from the perspective of colorant choice and performance. Nevertheless, what was said in a previous review [1] holds true: "*... achieving commercially acceptable performance is by no means a trivial matter for those unused to working with photochromic colorants. They tend not to be as robust or as easy to use as conventional dyes and pigments. In addition, they are more expensive, cost being of the order of thousands of dollars per kilogram of photochromic dye as opposed to merely dollars per kilogram for commodity colours.*" In order to create a product with satisfactory economics, behaviour and longevity, a commercial enterprise must take heed of numerous technical factors which are peculiar to industrial photochromism. As we shall see in the next section, various disparate applications have been envisaged for photochromic colorants. Some present technical challenges that remain beyond the reach of current dye technology. Others, however, have met with commercial success.

5.3 Focus on Important Applications of Photochromic Dyes

Significant investment has been sunk into research and development work over the past half century or so that has attempted to make a wide range of aesthetic and functional applications for light-responsive colorants a reality. This section looks at the various potential and actual uses for which photochromic dyes have been advocated.

5.3.1 Types of Application

So far, one main application – sun-responsive lenses – has dominated in terms of commercial success. Other diverse outlets have also been industrialised, but all rely on organic molecules exhibiting T-type photochromism. Each usage depends upon one or more of three aspects of photochromic behaviour [2, 14]:

(a) Reversibility
In the case of sun lenses for spectacles, the importance of reversible adaptation to varying ambient lighting levels of transmittance is self-evident. For these items to constitute useful products, they must automatically modulate the intensity of light received by eyes of the spectacle wearer on a repeated basis for a significant duration. More will be said about the ophthalmic exploitation of photochromism later, but for most uses of photochromic colorants, robust reversibility is crucial. The term is relative as light-responsive systems can be rather delicate – more so than conventional dyes and pigments. Nevertheless, even low-end aesthetic applications depend upon repeatable colour change effects to bring about variations in lighting levels without intervention by other means. Resilient switching is an essential requirement for potentially wide-ranging functional applications, such as adaptive windows and agricultural films, which are intended to spontaneously regulate transmitted light for the comfort and protection of the people and crops inside. These last two types of use are a highly sought after prize, but are beyond the reach of known photochromic colorant systems. Unfortunately, the durability of current materials fall far short of the minimum of a decade of working lifetime required for commercial success. It is unlikely that the types of industrial dye in circulation today can ever be modified to stand up to the levels of prolonged solar exposure which must be endured. Alternative solutions to the problem of furnishing sufficiently long-lasting reversible colour changes posed by glazing and related applications are being intensively researched. One active field attempting to tackle the issue of longevity centres on electrochromic materials, for windows [15] and even spectacle lenses [16].

(b) Sensitivity to radiation
As well as being essential to the above functional uses, this property forms the basis for the creation of arresting visual changes that are purely for aesthetic reasons. These encompass attention-grabbing promotional novelty items, toys and even pieces of jewellery as well as artwork. While there have been demonstrations of striking heliochromic effects in large structures, the aforementioned shortcomings in photostability prevent them becoming a commercial reality. For example, the concept of vehicles coated with T-type

photochromic materials was explored in the 1980s, but durability remains orders of magnitude too low for it to become anything more than a curiosity. Challenges of a different kind hold back the exploitation of photochromic compounds in cosmetics and personal care products. They are regulatory in nature: the business might not justify the cost of proving that use in such applications is safe, or be barred legally or ethically from doing so.

Photochromic colorants have, however, been employed commercially in textile coloration for many years. This usage firmly remains niche for a small market size where poor fastness, particularly photostability, is not critical. The usual technique for application is screen printing whereby a coating laden with photochromic colorant is applied to the surface of a garment and cured [17]. Photochromic detail may also be imparted to fabric by means of -commercially-available mass-coloured thread, such as poly(propylene) melt-spun with photochromic dye, being woven into it. Other conventional textile coloration techniques are not suited to the application of industrial photochromic colorants. For example, conventional commercial T-type dyes are not substantive to natural fibres, while treating them as disperse dyes in the exhaustion dyeing of important hydrophobic polymers such as polyester [18], nylon [19] and acrylic [20] leads to significant residual colour and/or weak photocoloration. This outcome lies with the fact that the dye molecules are relatively delicate and bulky. The conditions required to exhaustion dye these synthetic fibres degrade photochromic colorants. Additionally, the relatively large molecular size of photochromic colorants compared to conventional disperse dyes greatly hinders diffusion into the polymer. As will be discussed later, the nature of the polymers themselves tends to suppress photochromism. Durable, high-contrast photocoloration with acceptable kinetics will require specific development of new coloration processes and a re-think of dye design, moving away from current conventional T-types which are the product of research to find optimal colorants for ophthalmics. Steps have been made in this direction, such as conversion of commercial types to water-soluble acid dyes for silk [21] and wool [22] or fibre-reactive colorants for cotton [23, 24]. The viability of alternative means of delivery of industrial dyes has also been examined, for example, in conjunction with solvents [25–27] or supercritical carbon dioxide [28] as well as sol-gel coating [29] and nanoparticulate composites [30]. However, the above aims require radical advances to be made.

(c) Functionality

Light-sensitive ophthalmic lenses straddle the boundary between aesthetics and functionality: not only must their colours be appealing to consumers, but they must also be pleasant to wear and capable of modulating lighting levels without degrading visual acuity. However, many proposed applications exploit photochromism purely as a means to an end. In these outlets, colour is of little or no importance: the mere existence of a visually observed or machine-readable change is key. One example of this functional use of photochromic colorants is their incorporation into packaging in the form of security markings. Their light-driven property changes make possible the overt or covert authentication or validation of goods [31]. Variations on this approach that have been investigated range from the discrete marking of currency to the hidden labelling of fuel [32]. However, the durability and cost of the dyes hampers the commercialisation of these applications. An interesting niche functional use of photochromism to reach the market relates to angling. The inclusion of a photochromic colorant in fishing line enables anglers to keep track of the cast line whilst hiding its presence from their prey. Water shields the line from UV, so below the surface the line remains colourless and inconspicuous to fish. In contrast, above the surface of the water, solar UV photoactivates the dye in the line, so it becomes coloured and readily visible.

5.3.2 Applications of P-Type Dyes

A large proportion of the research effort into photochromism expended over the past decade concentrated on highly functional applications. Most of them tend to lie within the realm of information technology, optoelectronics and nanotechnology. All of these hi-tech uses require tightly controlled reversible switching of optical properties between states that do not decay [33, 34]. P-type colorants are suited to these sorts of task [35], whereas T-types are not owing to their thermal fading. For example, optically-switchable molecules have been at the heart of efforts to develop next generation memory technologies because they can in theory offer much greater data storage densities than existing systems [36–39]. Many instances of novel materials that can act as light-activated switches have been created by covalently linking P-type dyes to non-photochromic systems so that the fluorescence [40, 41] or electrical [42, 43] properties of the latter can be photo-regulated. Another area that has attracted great interest is full or partial replacement of electronic circuitry with that based on photons, for example in computer processors, leading to step changes in speed and power consumption [44]. Consequently, P-type dyes have been the focus of work to create optical equivalents to electronic components, such as switches and logic gates [45, 46]. Other avenues of investigation include therapeutic uses, such as the photo-control of drug activity, as well as the development of light-responsive constructs intended as components for machinery at the macro [47] and nano scale [48].

The most well studied P-type colorants present a marked contrast to T-type dyes not only in their photochromic properties, but also in their synthesis and the mechanism behind their light responsiveness. Compounds displaying pure P-type behaviour are rare: just two classes are known [49]. The first, diarylethene, is a relative newcomer and continues to receive the greatest attention, although to date, just a small number of such dyes are listed for sale in lab supply catalogues. The second class, made up of fulgides and their derivatives, is older and comprises examples that were commercialised for a time, but remains of minor importance in an industrial context. These two types will now be reviewed briefly along with another chromophore, azobenzene, which is very familiar to industry. Its P-type photochromic tendencies have led to a surge of interest in teaching this old dog new tricks.

5.3.2.1 Fulgides

Since fulgides were first synthesised a century ago, they and their derivatives attracted attention because of their unusual chromic properties [50, 51]. These include piezochromism (colour change with pressure), tribochromism (colour change with mechanical grinding) and photochromism [52]. Interest in their photochromic properties grew during the early 1980s following the finding that some derivatives, such as derivative **1** shown in Fig. 5.4 [53], exhibited purely P-type photochromism [54], making them candidates for the functional applications listed above [55].

Fulgides and their derivatives are capable of spanning the gamut of the visible spectrum, and even into the infra-red, when photoactivated with UV light [52], which leads to a ring-closure reaction. Figure 5.4 illustrates such a transformation for dye **1** which was once commercially available as Aberchrome 540 for use in chemical actinometry [56]. The low spatial requirements for the isomerisation mean that these compounds are photochromic as solids as well as in solution. However, a major drawback of this class is poor fatigue resistance.

Fulgimides (imido analogues of fulgides) were used commercially for producing lenses in Japan during the early 1990s [57]. Fulgides themselves have been the subject of investigation for conventional textile and printing ink applications [58]. While fulgide derivatives are still available from laboratory chemical

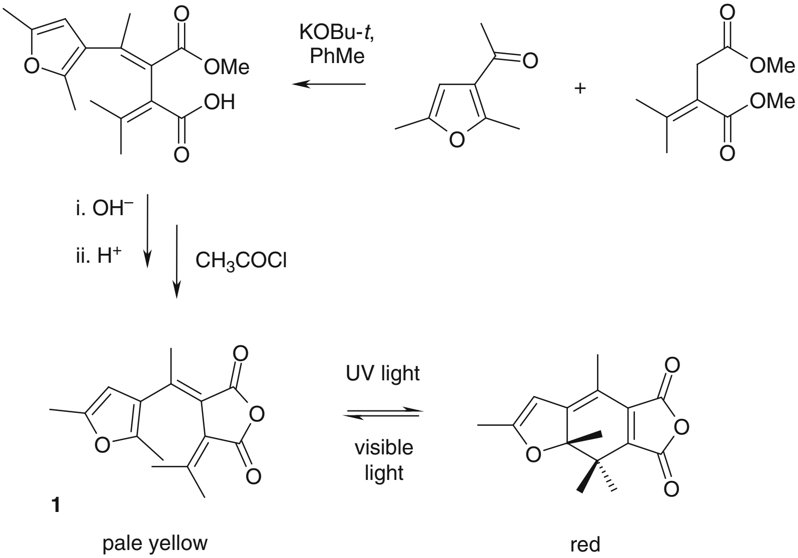


Fig. 5.4 Synthesis and photochromism of a furyl fulgide **1** [52]

suppliers in research quantities, their industrial renaissance awaits the development and commercialisation of an optical switching technology to which they suited.

5.3.2.2 Diarylethenes

This class of compounds remains the most intensely researched group of P-type dyes over the past two decades [54]. Great interest surrounds their potential use as elements in high density memory systems, optical switches for photonic circuitry and light-triggered components in nanomechanical devices as well as for many other applications [59, 60]. The subclass of dithienylhexafluorocyclopentenes (or dithienylethenes, DTE) is arguably the most deeply investigated. An example of the synthesis and photochromism of a generalised symmetrical DTE is shown in Fig. 5.5 [61]. A halothiophene is lithiated, then reacted with perfluorocyclopentene, which is a low boiling (27 °C) liquid, to create a colourless compound **2**. This material undergoes a ring-closure reaction, either in solid form or in solution, upon exposure to UV, generating a thermally stable coloured species. Irradiation of the coloured ring-closed form with particular wavelengths of visible light leads to reversion through ring-opening back to the colourless isomer **2**.

As well as symmetrical DTE, asymmetric compounds can be created by sequential exposure of the cyclopentene to different lithiated heterocycles rather than just two equivalents of the same one [59]. By appropriate design, one can synthesise a range of dyes that spans the visible spectrum. In one elegant proof-of-concept study, three different types of DTE units were linked together to give a 'trimer' that was capable of being switched between yellow, red and blue colours by particular combinations of UV and visible light for potential use as a multiple state memory element [62]. Crystals of DTE undergo pronounced shape changes on irradiation [63, 64], making them of interest as actuators in nanotechnology. Despite the significant effort which continues to be expended on diarylethenes, no applications for these colorants have yet become a commercial reality.

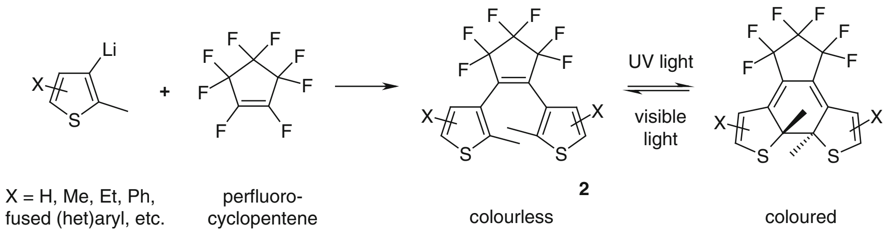


Fig. 5.5 Synthesis and photochromism of a dithienylethene **2**

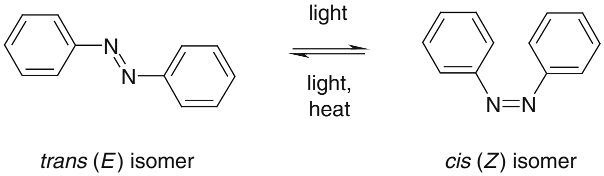


Fig. 5.6 Photochromism of azobenzene

5.3.2.3 Azobenzenes

Although not a pure P-type photochromic material and despite being a very well-known chromophore, azobenzene (and more correctly compounds derived from it) has been receiving much attention recently as a means to create functional materials. Through structural modification, its P-type character can be strengthened, such that the *trans* to *cis* photoisomerisation is effected with one set of wavelengths and the *cis* to *trans* conversion brought about with another range of wavelengths as shown in Fig. 5.6 [65].

As with the other two classes discussed above, azobenzene-based systems have been investigated in connection with optical switching and storage of data. Of particular note is the incorporation of azobenzene units into polymers to produce light responsive materials with novel properties. The geometry changes in azobenzene brought about by photoisomerisation produces deformation: contraction occurs upon irradiation with UV light whereas exposure to visible light leads to expansion. This phenomenon made possible a proof of concept study in which a light-driven motor was demonstrated: the design centred on an azobenzene-containing belt which acted as a photomobile material, transforming light energy into controlled motion that turned the motor [47].

It is remarkable that the azo chromophore, despite being almost as old as the field of synthetic dye chemistry itself, is finding new uses at the cutting edge of material science. However, like the outlets being sought for P-type fulgide derivatives and diarylethenes, its commercial exploitation is likely to be some distance away. However, industry is already exploiting T-type colorants – we shall now look at the ways in which they are being utilised.

5.3.3 Non-ophthalmic Applications of T-Type Dyes

To get the best out of commercial T-type dyes, they must be incorporated into the right media using suitable techniques. One cannot simply treat them like conventional dyes and then expect to obtain photochromism of the desired colour with useful kinetics and sufficient resilience. The properties of the medium are hugely important – they can make the difference between obtaining the desired photochromic effect and failing to generate any photochromism at all. For it to perform in the intended manner, care must be taken to ensure that the photochromic colorant ends up in the correct physical state in an appropriate environment without exposing it to conditions that can degrade it during or after application. This section will illustrate this necessity by looking initially at the incorporation of photochromic dyes into polymeric media through mass coloration in which the coloration is mixed and dissolved in molten polymer. It will point out where the limitations of the colorants lie in addition to ways in which these shortcomings can be overcome.

5.3.3.1 Thermoplastics

Injection moulding is an effective means of mass-colouring thermoplastics with industrial T-type dyes. Irrespective of whether the colorant is introduced in the form of neat dye or a masterbatch (i.e. plastic containing a high concentration of dye), the outcome must be a monomolecular dispersion of dye in the polymer because conventional T-type colorants do not furnish observable photochromic effects as solids – they must be in solution. The chemical and physical nature of both colorant and polymer dictate the photochromic properties of the system. The rigidity of the polymer matrix and the free volume it makes available to the dye strongly influence the thermodynamics and kinetics of the photochromism. Typical commercial T-type colorants perform best in polymer matrices, which consist of flexible polymer chains, such as those of polyolefins – these matrices are characterised by high free volume as well as low flexural moduli and glass transition temperatures (T_g). All these factors alter rates and extents of activation and fading because commercial T-type colorants change molecular shape substantially when they switch between colourless and coloured states [66]. Consequently, a host matrix with high rigidity and crystallinity either elicits a poor photochromic response or none at all. A reasonable rule of thumb is that polymers with a flexural modulus of greater than 2GPa, like polycarbonates and styrene–acrylonitriles, should be avoided. Care must also be taken when applying the dye to ensure that it can tolerate the temperature and time required to melt the polymer and mix the components uniformly. Exposure to temperatures above 250 °C causes degradation of conventional commercial photochromic dyes, leading to discoloration and loss of light-responsiveness. Polymers which require high processing temperatures, like nylon, are thus out of the reach of such colorants.

The nature of the polymer influences the lifetime of the photochromic effect. The cumulative dose of incident UV radiation determines the amount of photodegradation that occurs, not the number of cycles the plastic is switched between colourless and coloured states. While dye structure and polymer type are key factors in governing the rate of deterioration with UV exposure, the inclusion of additives can make an enormous difference to the working life of the photochromic system. These materials are typical of those employed in non-photochromic systems but, when employed in the right concentration and combination, can extend lifetimes by an order of magnitude, for example in polyolefins [67, 68]. The following types of additives are often used:

- UV absorbers – such materials can be very effective through the capture of high energy photons, which might otherwise destroy dye; it is crucial that they are selected so that absorption within the window of UV wavelengths which activates the dyes is minimised and responsiveness is not diminished.

- Hindered amine light stabilisers and antioxidants – these compounds scavenge free radicals to prevent them attacking colorants.
- Triplet state quenchers – these additives impede photochemical pathways that do not contribute to photochromism and which can lead to formation of non-photochromic side products, thus preventing dye degradation and often discoloration. They do so by harmlessly dissipating the energy of reactive excited states of the dye arising from absorption of UV, thereby inhibiting photochemical side-reactions.

The usefulness of additives varies from dye to dye: what works well for one colorant–polymer combination is not necessarily beneficial for another [68]. To complicate formulation further, significant interactions between additives may occur. In some cases, additives harm dye performance by adversely affecting kinetics or increasing unactivated system colour. However, many industrial photochromic systems owe their commercial existence to judicious use of stabilising packages of additives.

Through a suitable combination dye, polymer, additives and application technique, pronounced photochromic effects with commercially acceptable lifetimes can be produced. The intensity of the activated forms of industrial dyes enables them to be achieved with relatively low loadings of colorant. These concentrations vary typically within the range of just 0.01–0.30 %w/w depending on the colorant and medium. For example, in the case of poly(ethylene), an inclusion level of only 500 ppm dye is typical. Less is sometimes more in the case of photochromic colorants: application at too high a concentration can diminish or destroy any photochromism. A common mistake made by those who are new to handling photochromic dyes is to assume that the remedy for weak photocoloration is simply to add more dye to the system rather than pay attention to other aspects.

The influence of matrix and difficulties with dye concentration can be avoided by using colorants in forms which enables them to be processed like pigments. One means is microencapsulation in which a solution of the dye in a non-polar solvent is enclosed within a polymer shell of only 1–10 μm in diameter. The resultant microcapsules can be dispersed in a similar manner to a conventional pigment, although higher loadings are needed than in the case of neat colorant. In addition, greater care must be taken during application to ensure that the microcapsules are not ruptured, for example, by shear stress during mixing. Since the dye is present encased in a solvent solution, microencapsulation presents two benefits: the first is that the colour and performance of the dye is independent of the polymeric matrix into which microencapsulate has been dispersed. Thus, even if the matrix is not favourable to photochromism, microencapsulation makes possible a satisfactory photoresponse. Secondly, because it is dissolved in a solvent, the kinetics of the dye will be superior to that typically observed in polymer matrices: not only will activation be more rapid, but thermal fading will occur more quickly too. Microencapulate is available commercially in powder form as well as an aqueous slurry. The subject remains the subject of industrial and academic study [69]. A related approach entails micronising a solid solution of photochromic dye in a polymer and dispersing the resultant photochromic pigment into the medium. One means of preserving the integrity of the dye/polymer system and attaining acceptable photochromic performance is to prepare core-shell particles [70]. The dye is incorporated into a relatively low T_g polymer, such as poly(2-ethylhexyl acrylate) which forms the core. Around it is fashioned a shell of a rigid high T_g polymer, like poly(styrene), conferring the particles with good mechanical properties to enable their application, for example in coatings or thermoplastics by mass coloration.

Other approaches to providing T-type photochromic molecules with localised environments which enable them to exhibit photochromism in media that are hostile to them include doping them into porous materials, such as silicas, zeolites and metal-organic frameworks [71]. The pores give sufficient free volume for the spatial reorganisation needed for interconversion of T-type dyes. An alternative and commercially successful strategy is to attach oligomeric chains to conventional industrial T-type dyes [72]. These chains, which may be primarily silicon- or carbon-based, e.g. polydialkylsiloxane, create a micro-environment for the colorant that enhances its photochromism in polymeric systems which are conventionally used with commercial dyes, and even makes possible colour changes in polymers that are off-limits for oligomer-free colorants [73, 74]. The difference that the oligomeric substituents make to kinetics runs counter to the usual rule of the thumb for conventional dyes that faster thermal fade equates to weaker photoactivated colour: when in a polymeric matrix, the kinetics of a dye substituted with oligomer are more like those of the corresponding chain-free dye dissolved in a solvent, i.e. faster to activate and to thermally fade than in a polymeric matrix, yet without any detriment to intensity of colour when one allows for the difference in molecular mass. These properties are usually mutually exclusive. The technology represents an advance in that it allows those working with photochromic colorants to create more responsive effects without sacrificing depth of photoactivated colour. In the case of ophthalmics, this translates to lenses that are faster to react to changes in light intensity, but which still achieve satisfactorily low levels of transmittance when activated. (One study manipulated the kinetics of three individual dyes by means of adjusting chain length on each to create a set of matched colorants for the production of a grey lens [75].) Another consequence is that successful application to substrates which are too challenging for conventional dyes becomes possible. For example, the production of photochromic effects in rigid thermoset plastics can be achieved by attachment of low T_g polymer chains to naphthopyran dyes [76]. A further benefit is that the oligomer appears to be protective of the chromophore. Polymers whose processing temperatures are too high for conventional dyes, like polyamides, thus become accessible. Conventional industrial photochromic dyes get severely damaged during mass coloration of nylon, leading to unacceptable base colour and ultimately a lack of photochromism. On the other hand, the application to such media of colorants whose structure contains oligomeric chains has been commercially successful. Industrial colorants bearing oligomeric chains are thus also capable of producing commercially acceptable photochromic effects in polymeric media that conventional colorants cannot.

Industry has taken advantage of these techniques for the application of photochromic colorants to polymers to produce a plethora of light-responsive products. For example, a diverse array of items have been fashioned from poly(ethylene) and plasticised poly(vinyl chloride) coloured by means of photochromic masterbatch or microencapsulate, including bottles, hair accessories, mobile phone case and toys. The encapsulation approach has even been claimed for use in lenses [77].

5.3.3.2 Surface Coatings

Photochromic colorants have found their way into inks and varnishes. While products like nail varnish reached the market (in which photochromic dyes are dissolved in organic media), their colour-change properties have been exploited for more functional applications, such as security printing. The simplest means of applying photochromic dyes in a coating form is to dissolve them in a commercially available solvent-based gloss varnish – this approach tends to work well with industrially available dyes owing to their solvent solubility and good photoresponsivity in non-polar solvents. As is the case with other media, photochromism will be suppressed if the concentration of colorant is too high. Steps must be taken to ensure that the colorant does not get damaged during formulation or application and it is provided with the right environment to function once the surface coating has been applied to a substrate. Consequently, because industrial photochromic dyes are not water soluble, alternative approaches must be taken for aqueous systems [78]. As is the case with thermoplastics, one approach is to disperse photochromic microencapsulates into surface coatings in a similar fashion manner to that for conventional pigments. One cannot simply add conventional industrial T-type dyes in neat form since the colorants are water-insoluble, yet must be in solution in order to furnish photochromic effects. Clearly, inclusion levels of colorant are dependent on the form in which the dye is added as well as the purpose of the application. Lithography, flexography and gravure are all printing techniques that produce relatively thin films of ink (2–7 μm thick when dry). Typically therefore, they require more neat colorant (1–3 % w⁄w dye in the ink) than techniques such as conventional screen printing, which produce thicker films (~12 μm when dry) and call for lower loadings (0.5–1 % w/w dye).

Since ophthalmic lenses are by far the most important commercial application of photochromism, the remainder of this review will concentrate on the properties demanded of industrial photochromic dyes for this use. It will describe the characteristics needed for commercial success and how colorants fulfilling these requirements are designed. In doing so, a flavour of the ways in which the molecular features of industrial colorants influence their photochromism will be given together with an outline of the means of their introduction during dye synthesis.

5.3.4 Ophthalmic Applications of T-Type Dyes

This section outlines the demands placed upon industrial T-type colorants by the lens sector and the ways in which they are applied.

5.3.4.1 Key Properties for Ophthalmic Applications

Commercial success demands compliance with numerous stringent requirements. Lenses must possess the following attributes:

(i) Show high transmittance in their unactivated state
This property is often termed low 'residual' or 'base' colour, which demands that the dyes themselves do not absorb appreciably in the visible region of the spectrum before exposure to sunlight.

(ii) Respond rapidly to exposure to sunlight
Lenses must change ('activate') as swiftly as possible from a colourless state to a strongly coloured one in response to an increase in ambient light intensity. Commercial lenses typically approach their peak darkness, i.e. minimum transmittance, after only a minute or two of exposure to strong sunlight at 20–25 °C. In order to do so, the dyes employed must switch from their colourless to coloured forms efficiently, the latter being strongly absorbing, so that only a relatively low concentration of activated colorant produces a pronounced colour change effect.

(iii) Fade quickly in the absence of sunlight
Once light levels drop, lenses should lose their colour rapidly to prevent impairment of vision. The initial fall in intensity tends to approximate first-order decay so a measure of rate of fade that is often used is 'half-life' ($t_{1/2}$), which is the time taken for absorbance to halve following removal of the activating light. Commercial lenses typically exhibit half-lives at 20–25 °C of a minute to a minute and a half. Short half-lives and high observed intensities tend to be mutually exclusive, therefore a balance usually has to be struck between attaining sufficient depth of shade and ensuring bleaching is acceptably quick. Since lens systems based on combinations of industrial dyes, polymers and additives do not always give idealised first order decay in absorbance, other means of capturing behaviour are sometimes employed when comparing kinetics to give a more rounded view of performance, e.g. $t_{3/4}$ – the duration over which absorbance falls to 25 % of its initial value.

(iv) Retain their photochromism
Photochromic dyes are notoriously delicate compounds compared to conventional colorants, especially with regard to photostability. However, it is possible through the inclusion of additives to create lenses that retain sufficiently pronounced photochromic behaviour over a commercially acceptable period, typically around 2 years – this behaviour is usually expressed in terms of minimum transmittance in an activated state and maximum transmittance in an unactivated state, particularly in regard to photoyellowing.

(v) Exhibit relatively little dependence to temperature in their photochromic response.
Given that the reversion of photoactivated commercial colorants back to their colourless forms is primarily driven thermally, higher ambient temperatures promote faster fade-back and thus lower intensities at steady state activation.

For changes in photochromic performance to remain sufficiently small across a range of ambient temperatures in which the spectacles will be worn so that they are not obvious to the wearer, this dependence must ideally be low.

In addition to being capable of satisfying the above criteria, there are other considerations which are vital to successful use of industrial dyes in lens manufacture. Generally T-types must be in solution to exhibit photochromism, i.e. dyes must be sufficiently soluble in the lens medium. There are isolated examples reported of T-type compounds related to families from which commercial derivatives are drawn undergoing colour changes in solid form [79]. However, the stipulation that dyes must be monomolecularly dispersed in solution to generate observable effects is certainly true of industrial colorants: too low a solubility in the medium, be it monomer, polymer or a solvent, will be deleterious to dye performance. Since commercial T-type dyes typically show positive solvatochromism (i.e. their absorption maxima shift to longer wavelengths as the polarity of their environment increases), then one has to allow for the fact that the nature of the lens medium into which the dye is incorporated will not only affect the kinetics of the colorant but also its colour.

5.3.4.2 Methods of Dye Application to Ophthalmic Lenses

The would-be manufacturer of photochromic lenses is faced with a number of choices when deciding how to incorporate dyes. However, these options are restricted by the considerable patent protection that still exists and which claims particular techniques for applying colorants. Additionally, the physical characteristics and optical properties demanded of a lens may dictate its constituent materials, which in turn often narrow down the application methods available. Consequently, in terms of imparting an economic, resilient and high performance effect to a lens, the dye is just one part of the story. The other two important determinants are the lens matrix and the production technique. These factors contribute to the environment which the lens manufacturer provides for the colorant: this is crucial, hence the build-up of intellectual property and the need for different techniques. For a review which provides a useful, albeit dated, insight into photochromic lens manufacturing, see [9]. A brief overview of the main techniques follows:

In mass: Where the lens medium is compatible with the photochromic dyes, then the two can be mixed along with additives, such as stabilisers, in order to give a lens in which the dye is dissolved uniformly throughout. One of the simplest techniques for manufacture in this manner is injection-moulding a mix of thermoplastic and dye. A commonly used current method is dissolution of dye in a monomer or resin system at a concentration of roughly 300–500 ppm which is then thermally or UV-cured into a semi-finished lens that can be ground to the desired prescription. While this methodology is quite heavy in its use of dye and is restricted to polymer types in which the dye exhibits satisfactory photochromism, such as acrylates, the technique is relatively simple technically, especially when the manufacturer buys in a monomer/dye/additive package as a pre-mix. There is considerable scope for expertise in optimising dye performance by blending different monomers and/or achieving a particular level of cure to supply an environment that favours responsive, intense photochromism.

Coating: This manufacturing technique involves applying photochromic dye in a coating to the front or the back face of a lens in solution along with a resin by a technique like spin- or dip-coating. While the coating must contain a relatively high concentration of dye to achieve a satisfactory photochromic effect because the coating is thin, less colorant overall is used compared to in-mass casting. The use of a coating also enables photochromic effects to be achieved with lens materials, like polycarbonates, in which dyes traditionally will not work when applied in-mass. However, since the colorant concentration is high, the dye must possess a low base colour and also good photostability since, unlike in an in-mass lens, there is no reservoir of dye lying deeper into the lens to replace degraded colorant.

Lamination: While technically challenging, this technique offers advantages similar to those for coating. It involves bonding a film containing photochromic dyes to the surface of one half of a lens; the film is then enclosed by being sandwiched between the other half of the lens.

Imbibition: This process is proprietary to Transitions Optical [13]. Dye is applied to the lens surface by spin-coating. The lens is then baked to enable the dye to diffuse from the coating into the polymer matrix. A photochromic layer around 150–200 μm thick is created. The dye remains trapped in the lens surface upon cooling. The spent coating is then washed off.

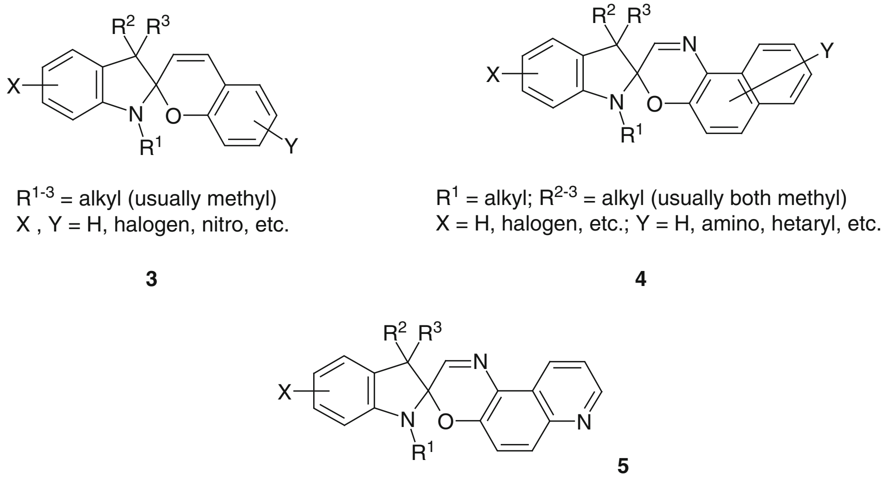
5.4 Industrially Important T-Type Photochromic Dyes

During its endeavours since the mid-twentieth century to meet the technical and commercial challenges of creating marketable lenses as well as developing other photochromic systems, industry scrutinised many thousands of T-type dyes. In order to identify suitable colorants for this application and others, industrial, governmental and academic laboratories synthesised large numbers of colorants drawn from a variety of photochromic dye classes. However, only a tiny proportion survived to the stage of commercial exploitation. To get that far, these colorants not only had to demonstrate acceptable performance in their targeted end-use – as illustrated for lenses above – but also be practical and economic to make. Consequently, just a select few of the numerous families of T-type dye have been industrialised.

The first modern attempts to develop commercial outlets for organic photochromic materials centred on spiropyrans. This kind of dye still forms the focus of many studies into developing new technologies (for a good recent review, see [80]). However, only two classes of T-type photochromic colorant are currently of industrial importance: spirooxazines and naphthopyrans. This section will therefore describe these two classes in more detail in terms of their general characteristics and preparation.

5.4.1 Spirooxazine Class of Photochromic Dyes

From an industrial perspective, spiropyran dyes were the class of principal interest during the 1950s–1970s. Readily synthesised from accessible starting materials, they furnish intense photocoloration that decays over useful timescales [81]. A particularly well explored set of compounds was the indolino-spirobenzopyrans **3** as shown in Fig. 5.7. However, in the 1970s, isolated reports appeared in the open and patent literature of studies that replaced a methine carbon of the pyran ring with a nitrogen atom to give spirooxazines, for example the indolino-spironaphthoxazines **4**. When industry realised that members of the spirooxazine class were much more photostable than their spiropyran counterparts [8], interest in the latter for use in lens materials waned (although they are still much utilised in academic studies as probes or for the creation of photocontrolled systems [82]). The focus shifted to spirooxazine-based systems, leading in the early 1980s to the launch of the first plastic photochromic lenses into the US market by American Optical [8]. This initial effort failed commercially because the look, performance and lifetime of the product did not fulfil customer expectations [11]. An attempt by PPG Industries using a closely related type of blue oxazine-based dye **5**, which the company started working on in 1983 [11], was also short-lived [12]. However, further developments meant that polymer-based lenses, which employed the



$R^{1\text{-}3}$ = alkyl (usually methyl)
X , Y = H, halogen, nitro, etc.

3

R^1 = alkyl; $R^{2\text{-}3}$ = alkyl (usually both methyl)
X = H, halogen, etc.; Y = H, amino, hetaryl, etc.

4

5

Fig. 5.7 General structures of typical industrial spiropyrans and spirooxazines spirooxazine class in their manufacture, did ultimately taste commercial success in the 1990s. At this time, PPG Industries marketed the Transitions® lens, while Rodenstock distributed Colormatic® and Photocolor® lenses produced using this dye class in the US [9]. In Japan, Tokuyama also made use of oxazine colorants [57]. This family of photochromic dye remains of industrial interest, but is now of secondary importance to the naphthopyran class. In 1992, the TransitionsPlus® lens was brought to market with a mix of oxazine and naphthopyran dyes, while the Transitions 3 lens launched in 1996 was formulated with an all-naphthopyran combination [83] since such dyes offer less temperature-dependent behaviour [84].

Given their structural similarity, it should be no surprise that the spiro-pyran and -oxazine classes **3–5** share the same general mechanism of photochromism and that their methods of synthesis are closely related.

Their photochromic properties arise from the ability of the colourless form of the compound to undergo a reversible molecular rearrangement in which the pyran or oxazine ring-opens to generate a coloured photomerocyanine dye in contrast to the mechanisms of the P-type colorants outlined earlier. Figure 5.8 illustrates the transformation for a simple spiropyran. This reaction is sparked by UV irradiation (although in the case of commercial dyes, short wavelength visible light can also be a trigger). Energy is absorbed, leading to a photochemical sequence of events that includes cleavage of the bond between the spiro carbon atom and the pyran/oxazine ring oxygen atom, ultimately leading to the formation of a mixture of coloured photomerocyanine isomers [85]. Many academic studies have investigated the nature of the photochemistry behind this isomerisation; they have been recently summarised [82].

It is important to remember that the equilibrium shown in Fig. 5.8 is dynamic. At any given time, there is constant interconversion between the ring-closed and -opened forms. The balance between these two sides of the equilibrium determines the intensity of the coloured state of the system. When irradiated with UV light, the concentration of dye in its photomerocyanine form rises because of the resultant increase in rate of the ring-opening reaction. In other words, the balance of the equilibrium shifts from the ring-closed side, leading to an intensification of colour. Cessation of the UV irradiation causes the opposite effect. The rate of ring-opening relative to the rate of ring-closure falls, so that the concentration of the colourless

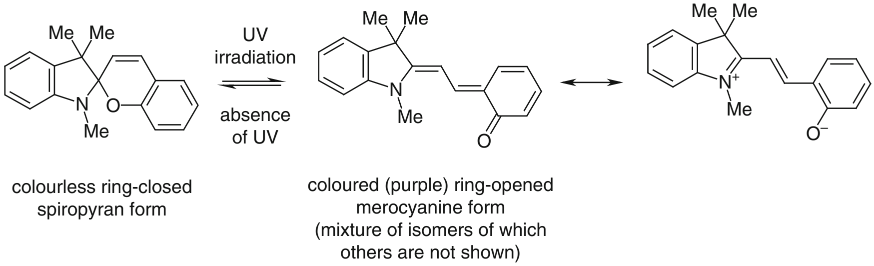


Fig. 5.8 Photochromism of a simple spiropyran

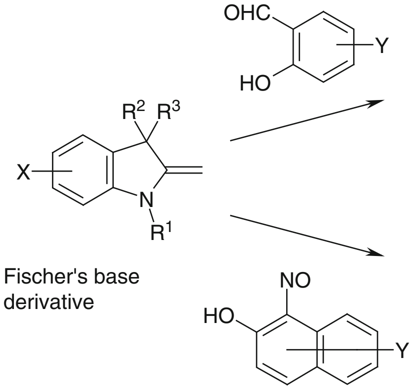
form of the dye rises relative to the photomerocyanine form. Observers see this overall switch in the equilibrium as fading of colour.

The goal of industrial dye design is create colorants that show little tendency to ring-open under low levels of ambient lighting, i.e. the equilibrium is far towards the pyran/oxazine side, so residual colour is minimised and transmission is at its maximum. Conversely, at high ambient lighting levels, the aim is to achieve an equilibrium shifted as far as possible to the photomerocyanine side in order to maximise the intensity of photocoloration. Reality involves compromise. High photoactivated colour strength can be achieved but at the expense of a slower thermal fade and a tendency to exhibit residual colour. Speeding up the rate of fade is one means of lowering base colour but the trade-off is a weakening of photocoloration. As we shall see later in this Chapter, there are ways to modify structure and environment to achieve the better of both worlds.

Because the ring-closure reaction in commercial spirooxazine dyes is essentially entirely thermally driven, the ambient temperature affects the position of the equilibrium with important consequences for commercial products. A rise in temperature speeds up decay of the photomerocyanine dye to the colourless spirooxazine form. At a given intensity of irradiation, more thermal energy therefore leads to the equilibrium shifting away from the coloured ring-opened side in the case of both spiropyrans and spirooxazines. The overall result is thus a perceived reduction in intensity of colour at higher ambient temperature. While more rapid fading back to a colourless state upon removal of UV irradiation accompanies this effect, such temperature dependence is generally undesirable. It can complicate the formulation of dye mixtures and leads to differences in performance that are noticeable to the consumer: pronounced changes in response are perceptible at 5 °C, 20 °C and 35 °C. Consequently, the photochromism of lenses based on spirooxazines is thus less effective in hotter climates: they work better on winter ski-slopes than on summer beaches.

As discussed elsewhere in this Chapter, factors other than temperature influence the photochromism of a given dye, such as the substrate into which it has been dissolved, by affecting the position of the equilibrium between the ring-closed and ring-opened forms as well as the ease of interconversion between them.

A commonly employed synthetic route to non-ionic indolino-spirobenzopyrans **3** involves condensation of Fischer's base (or an analogue) with a salicylaldehyde (see Fig. 5.9), typically in equimolar amounts, in refluxing alcohol. The hot solvent readily dissolves the starting materials while the spiropyrans tend to have limited solubility in cold alcohols, so they can often be isolated following cooling of the reaction mass. However, variations in reaction stoichiometry and solvent choice, e.g. toluene, can bring about improvements in yield and quality. Depending upon the particular materials involved and the intended application for the dye, the product may be sufficiently pure without requiring subsequent clean-up by recrystallization. Reference [81] gives an excellent overview of the important practical considerations involved in spiropyran preparation, including quality of starting materials, reaction conditions and purification. Oxazine analogues are synthesised in an analogous manner as discussed shortly below. Studies aimed at optimising the



3

4

Fig. 5.9 Commercial synthetic routes to indolino-spirobenzopyrans and -spironaphthoxazines

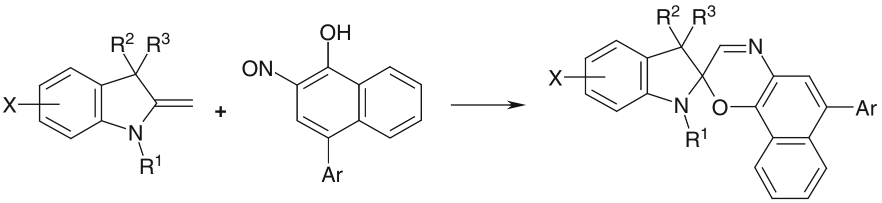
conditions of spirooxazine synthesis do not often appear in the open literature, but a good example is [86].

There are two sub-classes of spirooxazine which are of particular commercial interest. The first type has already been mentioned: naphth[2,1-*b*][1,4]oxazines **4**. These colorants are useful for producing bluish-red, violet and blue photochromic effects. They are generally prepared from a 1-nitroso-2-naphthol derivative in refluxing alcohol. As is the case with spiropyrans, alternative conditions may be beneficial, such as use of toluene as solvent. However, for most purposes, purification of the isolated product is accomplished by recrystallization. An effective means of doing so is to use an alcohol as a non-solvent in combination with an aromatic hydrocarbon, like toluene, an ester or an ether, such as tetrahydrofuran, in which the dyes tend to have good solubility. Column chromatography is sometimes utilised commercially, but only as a last resort because of the relatively high cost of this technique.

Use of a 5-nitroso-6-hydroxyquinoline derivative as the “naphthol” component furnishes indolino-spiropyridobenzoxazines **5**. This type of dye garnered industrial attention in the 1980s for the coloration of plastic lenses [11] and went on to become part of the successful commercialisation of the technology early in the next decade [12].

The second sub-class of spirooxazine is a source of industrially useful greenish-blue colorants: naphth[1,2-*b*][1, 4]oxazines **6**. The synthetic strategy is very similar to their [2,1-*b*] counterparts (see Fig. 5.10), the main difference being a switch to the use of 2-nitroso-1-naphthol synthons [87, 94].

Upon activation with UV light, the parent compounds **4** (R^{1-3} = methyl; X, Y = H) and **6** (R^{1-3} = methyl; X, Ar = H) are relatively fast-fading dyes that produce weak blue photocoloration. Industry has realised the potential of this class to produce intense reddish-blue to turquoise photochromic effects with commercially interesting half-lives by means of judicious selection of substituents. This Chapter covers these design aspects in more detail later.



$R^{1\text{-}3}$ = alkyl ($R^{2\text{-}3}$ usually methyl); X = H, halogen, etc.; Ar = H, aryl

6

Fig. 5.10 Synthetic route to commercial naphth[1,2-b][1, 4]oxazines

Table 5.1 Typical solubilities (g/L) of industrial indolino-spironaphthoxazines in organic solvents

Class	Toluene	Ethyl acetate	THF	Acetone	Methanol
4	60–120	20–80	100–300	10–30	2–5
6	200–300	25–50	300–500	10–30	1–3

Industrial naphthoxazines do not exhibit photochromism in their solid state. While they may show changes in absorption upon irradiation, these are not visible to the naked eye. The colorants tend to be in the form of weakly coloured powders, although certain dyes have sufficiently extended conjugated π-systems in one or both halves of their ring-closed forms to give them an intrinsically yellow physical form. Commercial derivatives **4** and **6** are relatively high melting (typically >150 °C and >100 °C respectively) with some oxazine derivatives possessing more than one melting range as a consequence of polymorphism. Their solubility varies widely (see Table 5.1), but all are essentially water-insoluble. Particularly good solvents are aromatic hydrocarbons, such as toluene and xylene, in contrast to alcohols like methanol or ethanol. Both classes of oxazine dissolve very readily in ethers, while common esters and ketones act as reasonably good solvents, exemplified in Table 5.1 by tetrahydrofuran (THF), ethyl acetate and acetone, respectively. The ranges tabulated are only guidelines, for example, certain [2,1-*b*] oxazines have much lower solubilities in particular solvents. When stored in the dark, sealed at ~20C away from moisture, industrial naphthoxazines are stable for years. They are also non-toxic: LD_{50} values are typically >2,000 mg/kg (oral, rat).

Indolino-spironaphthoxazines remain a popular option in commerce for the production of photochromic effects. Industry continues to take advantage of their responsive and intense heliochromism for plastics and coatings. However, where higher end performance is required or greater compatibility between components of dye mixtures is desired, particularly in the case of photochromic ophthalmic lens manufacture, then as we shall see in the next section, naphthopyrans have assumed greater industrial significance.

5.4.2 Naphthopyran Class of Photochromic Dyes

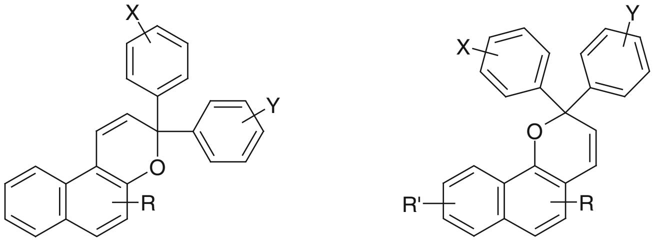
Naphthopyrans are the most commercially important class of photochromic molecule. All the major manufacturers of plastic photochromic lenses make use of naphthopyrans. Their chemistry allows ready and cost-effective adjustment of structure, enabling great control of kinetics and colour by appropriate selection and location of many different types of functional group. Different permutations bring into reach colours that span the visible spectrum from yellows through to oranges, reds, purples and blues. In addition, commercial naphthopyrans generally have stability properties that are as good as any other known class. Another reason for their importance is the lower sensitivity of their photochromism towards variations in temperature when compared to spirooxazines. The versatility of the naphthopyran class in providing colorants across the visible spectrum means that formulators can create mixtures from this single class to produce neutral shades. An advantage of doing so is that properties, such as temperature dependence, are likely to be better matched than when working with mixtures of dyes drawn from different families [84].

This class of dyes were initially neglected by industry for many years owing to misinformation and lack of clarity concerning properties published in the academic and patent literature [88]. However, once their potential was recognised as colorants for lenses, these dyes became the subject of intense study over the past three decades [88, 89]. Initially, they were introduced in the early 1990s as hypsochromic components in conjunction with blue oxazine-based colorants to generate neutral shades [90]. As more was learnt about manipulating their colour and kinetics, naphthopyrans displaced oxazines as the bathochromic constituents in such mixtures and thus became the dominant type of industrial photochromic dye.

Of the three possible naphthopyran subclasses, only two are commercially useful: 3*H*-naphtho[2,1-*b*]pyrans **7** and 2*H*-naphtho[1,2-*b*]pyrans **8** (see Fig. 5.11).

Dyes of structure **7** are a source of industrially important yellow, orange and red colorants, whereas colorants based on **8** furnish red, purples and blues. As we shall see later, the latter class also supplies dyes with relatively neutral shades, simplifying the formulation of mixtures to produce brown or grey coloration. Like spiropyrans and -oxazines, the photochromism of naphthopyrans relies on light-induced ring opening. Figure 5.12 illustrates the transformation in the case of a simple naphthopyran. As with the analogous transformation for spirooxazines, a mixture of several photoisomers results. The ground states of the photomerocyanines feature increased charge density on the oxygen atom (from contributions by zwitterionic canonical forms such as that shown in Fig. 5.12). In addition, the charge densities of first excited states involve transfer of electron density to the oxygen. Substitution patterns favouring this transfer, e.g. electron donors on the aryl rings such as the amino group in the [1,2-*b*]naphthopyran shown in Fig. 5.12, therefore lead to bathochromic shifts in absorption. Relationships between colour and constitution of industrial dyes will be covered in a later section.

As is the case with spiropyrans and spirooxazines, the position of the photostationary state equilibrium between ring-opened and -closed forms and the



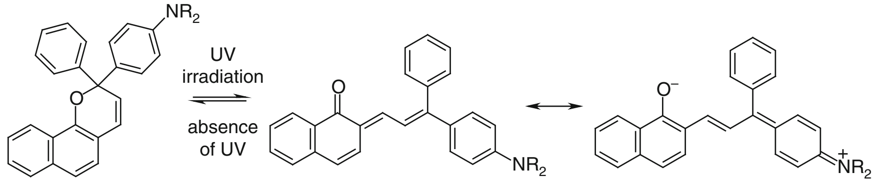
X, Y = H, alkoxy, amino, alkyl, etc.
R = H, amino, alkoxy, etc.

7

X, Y = H, alkoxy, amino, alkyl, etc.
R, R' = H, alkyl, aryl, ester, amino, etc.

8

Fig. 5.11 General structures of typical industrial naphthopyrans



colourless ring-closed
naphthopyran form

coloured (red) ring-opened
merocyanine form
(mixture of isomers of which
others are not shown)

Fig. 5.12 Light-induced photoisomerisation of a simple [1,2-b]naphthopyran

rate of thermal fade can be readily manipulated by modification of dye structure. The flexibility available stems from the synthetic accessibility of naphthopyrans by combination of naphthols (and corresponding analogues) with diarylalkynols as illustrated for [2,1-*b*]naphthopyrans in Fig. 5.13.

While only one of several pathways to such materials, that shown in Fig. 5.13 is a general and important manufacturing route for large-scale production. The medium is often a non-polar solvent, such as toluene or xylene, in the presence of an appropriate acidic substance, for example, an aromatic sulphonic acid or an aluminium oxide. The reaction sometimes benefits from the azeotropic removal of water generated during the reaction (or introduced from the acid). Occasionally, chemical dehydration by means of a reagent such as a trialkyl orthoformate is advantageous. The goal industrially is to isolate a product of sufficient purity directly from the reaction mass since it is the cheapest option. While this is sometimes possible, recrystallisation, or as a last resort column chromatography, of the obtained product is typically needed to obtain the desired product quality. A very good overview of the synthesis (and properties) of naphthopyrans is provided by [91].

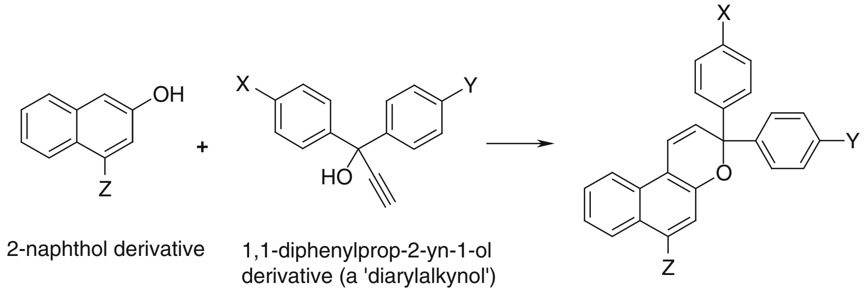


Fig. 5.13 A commercial synthetic route to naphthopyrans using general [2,1-*b*] derivatives as an example

Table 5.2 Typical solubilities (g/L) of industrial naphthopyrans in organic solvents

Class	Toluene	Ethyl acetate	THF	Acetone	Methanol
7	20–100	10–30	10–200	10–30	1–10
8	15–200	10–30	30–400	10–30	1–5

When not provided as solutions in pre-formulated monomer mixtures, industrial naphthopyrans are supplied as powders, typically of m.p. >150 °C, whose appearance is often highly dependent upon purity and method of isolation. With a few exceptions, they have shelf-lives of years when kept in cool, dark, dry conditions. Industrial naphthopyrans are generally classified as non-hazardous for transport and tend to be non-toxic. All commercial dyes are water-insoluble with poor solubility in alcohols. They dissolve far more readily in solvents of moderate to low polarity (see Table 5.2). As is the case with spirooxazines, aromatic hydrocarbons like toluene and xylene function as good solvents whereas aliphatic hydrocarbons like hexane do not. Naphthopyrans tend to have reasonable solubilities in common ethers, esters and ketones, which is reflected in the figures given in Table 5.2 for THF, ethyl acetate and acetone, respectively. However, these ranges are only indications: the solubility of a particular dye–solvent combination might fall outside of them.

5.5 Designing in the Properties: Structural Influences in Industrial Dyes

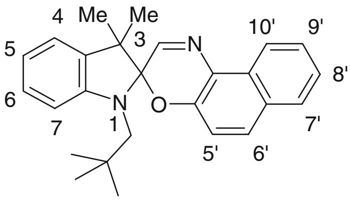
This section looks in depth at how structural features of industrial dye types influence their photochromic properties. Use of commercially important molecular substitution strategies to manipulate the colour and intensity of the photochromism of indolino-spironaphthoxazines and naphthopyrans receives particular emphasis. These rules of thumb continue to prove helpful in the design of valuable colorants for ophthalmic use, but they are also worth bearing in mind when attempting to employ these types of colorant in other applications. It is often the case that academic studies base an active molecule on a simple pyran or oxazine but report only weak light-responsive behaviour. Researchers should be able to use some of the design rules outlined below to their advantage when constructing novel photochromic materials intended for use as functional dyes in many different spheres of activity.

As mentioned earlier, modifications to the molecular structure of the parent spirooxazines and naphthopyrans successfully led to the creation of industrially useful photochromic dyes with appropriate kinetics and absorption characteristics. As we shall see, the impact of such changes on colour and photochromic behaviour is not usually mutually exclusive. While it is possible to alter structure in ways that minimally affect hue but make a pronounced difference to equilibrium intensity and thermal fade rate, it is often the case that decisions concerning the types of substitution pattern to introduce when targeting a particular set of performance criteria involve compromise.

5.5.1 Substituent Effects in Indolino-Spironaphthoxazines

Industrial indolino-spironaphthoxazine dyes depend upon structural modifications in one or both of the indoline or naphthalene moieties of their parent compounds to slow their thermal fading to useful rates, to improve the efficiency of their interaction with UV light, to reduce fatigue as well as to adjust colour and intensity advantageously.

Commercial [1,2-*b*][1, 4]oxazines **6** tend to be more bathochromic and slower as a class than [2,1-*b*][1, 4]oxazines **4**. For example, dye **9** is a commercial blue dye with an absorption maximum at 600 nm in toluene solution with a half-life of 31 s at 20 °C whereas the industrially useful dye **10** gives turquoise photocoloration in toluene with a longer λ_{max} (618 nm) and $t_{1/2}$ (20 °C) of 120 s. Both dyes feature an *N*-substituent that lengthens their half-lives (and activated intensity) to a suitable duration. We shall now consider this aspect in detail as well as other types of structural modification employed to create dyes of industrial interest.



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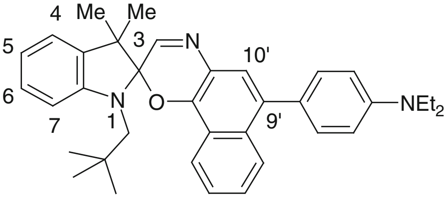

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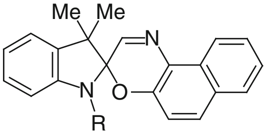
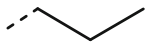
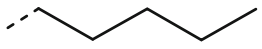
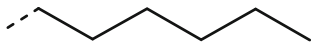
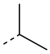
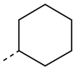
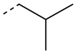
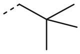
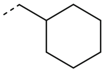
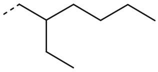
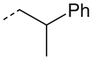
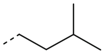
Substituents on the indoline fragment exert considerable influence over dye kinetics with varying degrees of effect on colour. Increasing the bulk of the *N*-

substituent is a relatively well-known means of slowing down the fade of indolino-spironaphthoxazines without significantly shifting their absorption maxima. Simple colorants derived from Fischer's base (i.e. **4** where R = Me) tend to give only weak photocoloration owing to rapid rates of thermal reversion by which the coloured photomerocyanine forms revert back to their corresponding colourless ring-closed form. Replacing the *N*-methyl group of a dye with a bulkier alkyl chain of an appropriate kind retards the thermal fade rate of the colorant and increases photostationary state absorbance, while red-shifting its absorption maximum by just a few nm. Dyes modified in this way thus develop a similar colour when photoactivated but are more intensely absorbing. Table 5.3 testifies that the

Table 5.3 Effects of varying substituents at the 1-position of indolino-spironaphthoxazines on absorption maximum and half-life



R		Relative intensity[a]	Residual photo-coloration[b]
	Et	0.9	0.9
	*n*-Pr	0.9	0.9
	*n*-Am	0.9	0.9
	*n*-Hx	0.7	0.9
	*i*-Pr	0.7	0.8
	Cy	0.7	0.9
	*i*-Bu	1.4	1.2
	Np	1.7	1.3
	CH_2Cy	1.3	1.2
	2-EtHx	1.5	1.2
	2-PhPr	1.5	1.2
	*i*-Am	1.0	1.0

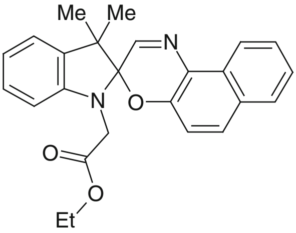
[a] Absorption intensity at photostationary state relative to that for $R = CH_3$

[b] Residual photocoloration 10s into thermal fade relative to that for $R = CH_3$

relationship between chain structure and enhancement of photochromism is not a straightforward one. The presence of branching slows the speed of thermal fade and improves intensity of photocoloration, but only when located at the right point in the alkyl group (see Table 5.3). A branch on the carbon adjacent to the indoline nitrogen (R = *i*-Pr or Cy) actually speeds up rate of thermal fade and weakens the dye. A lack of any branching has a similar effect. However, a branch beta to the nitrogen atom brings about pronounced increases to strength of the photocoloration, for example, R = 2-EtHx compared to R = *n*-Hx. This beneficial effect is lost upon shifting the branching to the gamma carbon (R = *i*-Am). Switching alkyl functions has little effect on fatigue (or activated colour) so tuning properties by appropriate selection of the indolino *N*-substituent is an effective design strategy. Groups such as neopentyl, isobutyl and methylcyclohexyl are introduced readily in an economical manner during synthesis of the requisite Fischer's base intermediates, hence their appearance in industrial dyes like **9** and **10**. The impact of bulky 1-substituents on half-life does not relate to enhancements to the extinction coefficients of the colourless or coloured forms of the dyes since they remain largely unaffected. Nor do they appear to increase the quantum efficiency of photoisomerisation, i.e. the generation of coloured species [92]. Instead, their influence is rooted in the steric crowding they introduce which hinders the ring closure reaction whereby the oxazine C-O bond re-forms, leading to restoration of the spiro geometry. A reduction in the rate of thermal fading, as pointed out earlier, means that for a given intensity of incident UV, the equilibrium concentration of photomerocyanine increases, which results in stronger photocoloration.

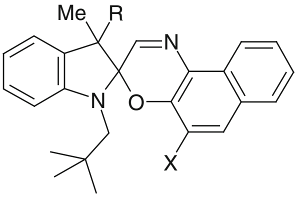
Branched *N*-alkyl groups tend to offer another advantage: reduced temperature sensitivity. As discussed earlier, the photochromism of spirooxazine and naphthopyran dyes exhibits an undesirable dependence on temperature. For example, the photochromic performance of conventional N-methyl oxazine-based dyes drops away in hotter environments. However, switching the alkyl function can reduce the rate by which photocoloration weakens as temperature rises. For example, over the temperature range 10–40 °C and for a given intensity of incident light, the photocoloration of the dye in Table 5.3 where R = Np decreases less rapidly than when R = Me.

Strongly inductive electron-donating and -accepting functions may markedly affect colour as well as kinetics when located onto an *N*-alkyl residue in a way that does not insulate their effects from the indoline nitrogen. For example, the ester functionality in **11** produces a hypsochromic shift of 15 nm in absorption maximum to 575 nm compared to the *N*-methyl analogue (toluene solution), presumably through inductive lowering of electron density on the indoline nitrogen.



11

Table 5.4 Effects of varying substituents at the 3-position of indolino-spironaphthoxazines on absorption maximum and half-life in toluene solution at 20 °C [94]

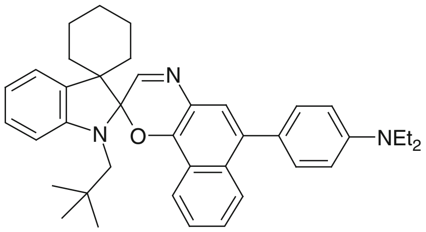


R	X = H		$X = CO_2Me$	
	λ_{max} (nm)	$t_{1/2}$ (s)	λ_{max} (nm)	$t_{1/2}$ (s)
Me	600	31	620	12
Et	600	52	620	20

Another means of tuning dye kinetics without causing a substantial shift in λ_{max} is to make changes to the 3,3-dialkyl motif of the indoline residue. Many commercial oxazine dyes comprise 3,3-dimethyl substitution purely for reasons of synthetic expediency: they are derived from cheap and readily available Fischer's base, or easily-accessible close analogues, all of which possess this substitution pattern. Variations on it, however, have been explored industrially [93] and exploited successfully to slow down thermal fade and thus increase photoactivated intensity. Just a small change can, when coupled with crowding at the 1-position, have a substantial effect on half-life without appreciably altering hue (as illustrated by the data in Table 5.4) to produce strong blue dyes.

Even more pronounced increases in activated strength are possible by switching one of the 3-alkyl functions for an ester group, or both with a lactone ring. The latter change is at the cost of a moderate hypsochromic shift in absorption to give slower-fading reddish-blue dyes.

Replacement of the *gem*-dimethyl fragment with 3,3-spirocyclohexyl substitution is another piece of molecular engineering utilised by industry. The end-result is strongly dependent upon dye structure. The presence of the spiro-aliphatic ring in certain colorants causes substantial reductions in $t_{1/2}$ and losses in photocoloration intensity when compared to those properties for analogues with the 3,3-dimethyl motif. Such dyes are weaker but feature a modest bathochromic shift in absorption maximum. For example, the cyclohexyl [1,2-*b*]oxazine **12** is greener and faster (λ_{max} 626 nm and $t_{1/2}$ 26 s in toluene at 20 °C) than the *gem*-methyl analogue **10** ($\Delta\lambda_{max}$ −6 nm and $\Delta t_{1/2} + 94$ s) [94]. The same effect is manifest in some blue [2,1-*b*]oxazines of structure **4** ($R^1 = Np$, $R^2R^3 = -(CH_2)_5-$). However, the impact of introducing a spirocyclohexyl ring may be favourable in other cases: the (now obsolete) industrial colorants **13** (X = N, Y = CH) and **13** (X = CH, Y = N) incorporated this aliphatic system [57].



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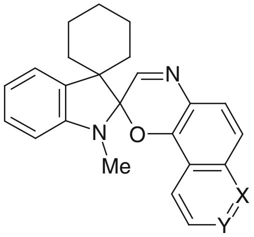

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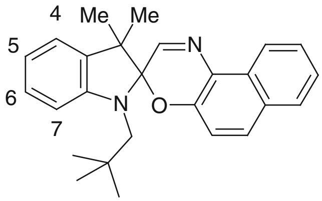
Owing to the complex interplay of steric influences that 1- and 3-substituents exert within photomerocyanine species, the impact of modifying 3,3-functionality varies significantly, as noted above. The influence of *N*-substituents was first recognised during the late 1970s [95]. The ability to tune kinetics by means of replacing groups at the 3-position was noted a few years later [96]. Both remain powerful tools with which to manipulate dye kinetics. Nevertheless, academia often overlooks these design strategies as a means of increasing photochromic response. Many studies that attempt to exploit simple indolino-spironaphthoxazines (or more commonly their pyran analogues) achieve limited success because of the weak, fast-fading nature of the dyes involved. Consequently, the focus prematurely moves on to other photochromic systems. Appropriate structural change at the 3-position (and/or at the indolino nitrogen atom) brings about much more intense photocoloration and would potentially yield better photochromic materials with which to undertake investigations and demonstrate proof of concept. The potential enhancements to photochromism that appropriate substitution of the five-membered ring of the indoline moiety can confer are thus well worth taking into consideration when attempting to exploit spirooxazines (or spiropyrans) as light-responsive units in novel applications.

While the aforementioned adjustments in spirooxazines predominantly affect the kinetics of their photochromism rather than their colour, numerous means of manipulating the absorption characteristics of such dyes exist. However, none can do so in isolation from the photochromic properties. Consequently, one must consider the overall impact of making a particular change and perhaps try to mitigate any undesired effects with other modifications, bearing in mind that these may have implications relating to synthesis and economics.

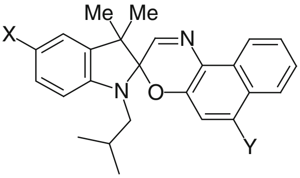
For example, one can fine-tune colour and kinetics by addition of electron-donating and -accepting groups on the 4- to 7-positions of the indoline ring system (see Table 5.5). Donors produce bathochromic shifts, i.e. λ_{max} becomes longer and colour becomes greener, since they facilitate transfer of electron density from the nitrogen heterocycle towards the keto-naphthalene end of the photomerocyanine. The strength, number and position of donors not only affects absorption maximum, but also half-life, as illustrated in Table 5.5 for the [2,1-*b*] class. Similar behaviour is observed for [1,2-*b*]naphthoxazines [94].

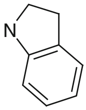
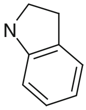
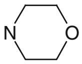
Table 5.5 Effect of donor substitution within indoline moiety on spirooxazine properties in toluene solution at 20 °C



Substitution	λ_{max} (nm)	$t_{1/2}$ (s)
Unsubstituted	600	31
5-methyl	608	21
4,6-dimethyl	605	20
5-methoxy	615	10

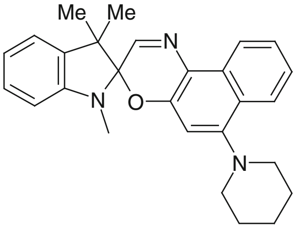
Table 5.6 Effects of donor substitution at the 6′-position of spirooxazine properties in toluene solution at 20 °C



X	Y	λ_{max} (nm)	$t_{1/2}$ (s)
H	H	599	9
H		590	25
OMe		608	9
H		576	33
H	NMe_2	564	32

The introduction of electron donors onto the naphthalene system generally has the opposite effect to their placement on the indolino fragment. As pointed out above, a donor on the indoline ring causes a bathochromic shift: Table 5.6 gives an example of how 5-methoxy substitution produces a bathochromic dye with a faster thermal fade (X = methoxy, Y = indolin-1-yl). In contrast, electron donor functionality on the naphthalene system causes an increase in intensity of photocoloration accompanied by a hypsochromic shift. An important motif of this type is an amine group at the 6′-position, i.e. Y = amino in Table 5.6, because this substitution pattern not only expands the gamut of commercially useful spirooxazines from the blue towards the red, but also confers enhanced photochromism. Industry has exploited it for around a quarter of a century [97]. The size of hypsochromic shift and increase in half-life correspond with a rise in the basicity of the 6′-amino function [98], i.e. indolin-1-yl < *N*-piperidino < *N*-morpholino < dimethylamino (see Table 5.6 for some examples).

Industry has manufactured dyes of this type for over two decades [99], for example **14**, which is available commercially as Reversacol Plum Red [100]. Its 6′-piperidino group transforms a weak fast-fading blue colorant into a much stronger magenta dye (λ_{max} 565 nm and $t_{1/2}$ 23 s in toluene solution at 20 °C). Dyes of this type photoisomerise with greater quantum efficiency to merocyanine forms that intrinsically absorb more intensely [92, 101]. Another reason put forward for better performance is that the 6′-amino function modulates the absorption profile of the photomerocyanines so that they do not compete as effectively for activating UV wavelengths with the ring-closed form, improving photochromic response [97]. While the absorption of their ring-closed forms tends to bleed a little into the visible region, leading to more pronounced residual yellowness (and greater sensitivity to activation by blue light), their augmented photochromism results in deep coloration even at relatively low usage levels. Industry has therefore exploited all of the amino functions shown in Table 5.6 to create colorants that react rapidly to incident UV and short wavelength visible light by developing strong purple and bluish-red photocoloration. Indolinospiro[2,1-*b*][1,4]oxazines containing a 6′-amine function can be prepared in the conventional manner from reaction of a Fischer's base derivative with a 2-nitroso-1-naphthol having the corresponding amino substitution. It is also possible to use a one-pot method to build up the dye from three separate components (Fischer's base, nitrosonaphthol and amine), although yield and quality depend strongly on how the process is executed, e.g. stoichiometry, reaction conditions, order and duration of addition, etc.



14

Converse rules of thumb hold for electron acceptors: when located on the indoline fragment, they cause hypsochromic shifts in λ_{max}, i.e. a shortening of wavelength of absorption, leading to the photoactivated form becoming redder. In contrast, electron-withdrawing functions placed on the naphthalene system shift absorption maxima to longer wavelengths. As an example, Table 5.4 indicates the impact of locating a (moderately electron-withdrawing) ester group at the 5′-position, i.e. X = CO_2Me. In addition to a moderate red-shift in absorption

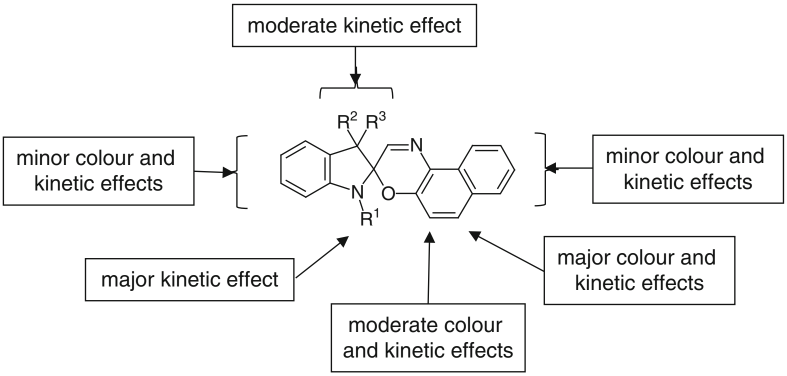


Fig. 5.14 Summary of substituent effects in naphth[2,1-*b*][1,4]oxazines

compared to the corresponding unsubstituted (X = H) analogue, the 5′-ester dyes produce weaker photocoloration as indicated by significantly reduced $t_{1/2}$ values.

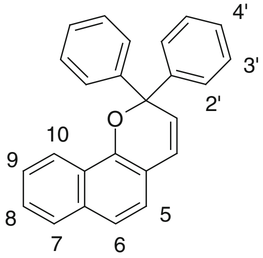
Figure 5.14 summarises in a very general way the tools at the disposal of the dye designer to adjust the properties of spirooxazines of the [2,1-*b*]-type. As ever with photochromic colorants, exceptions crop up depending upon the exact nature of the alterations and the structures under modification. For example, increasing the bulk of 3,3-dialkyl fragment on the indoline system leads to pronounced differences in $t_{1/2}$ in certain instances but not others. The rules illustrated apply in an analogous manner in the case of the isomeric [1,2-*b*]-class of oxazines, for example, enlarging the *N*-alkyl function tends to lead an increased half-life whilst making little impact on the position of the absorption maximum of the activated form.

It should also be borne in mind that the long wavelength absorption bands of photomerocyanine species induced from typical commercial spirooxazines are often not clean peaks but exhibit shoulders like those of many other colorants owing to bands arising from a complex array of electronic transitions and the presence of isomeric photoproducts. Consequently, it is dangerous to assume that simple relationships exist between absorption maxima and changes to molecular structure across the spirooxazine class since alterations to band shape may dictate the wavelength of maximal absorption. As has previously been pointed out, environment exerts a substantial influence on dye colour and kinetics. When one also takes in account that appearance is strongly sensitive to subtleties in absorption band shape, it is perhaps no surprise that rules of thumb remain more effective design guides than current computational methods. Consequently, when fine-tuning the performance of photochromic systems based upon spirooxazines, there is no substitute for the preparation of candidate structures for evaluation of their photochromism in terms of colour, kinetics and longevity. The same is true of the naphthopyran class, especially when constructing derivatives that produce complex absorption patterns upon photoactivation in order to generate neutral colours. However, before jumping straight into such intricacies, we will look next at some of the general relationships governing the photochromic properties of the two types of commercial naphthopyran dye and strategies employed in controlling their colour and kinetics.

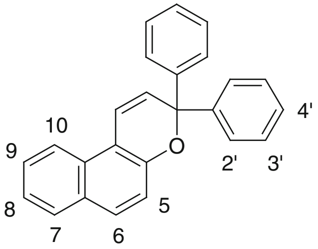
5.5.2 *Substituent Effects in Naphthopyrans*

Just as is the case with spirooxazines, many ways exist of adjusting the photochromic properties of naphthopyran derivatives through modification of molecular structure. Qualitative rules derived from observations of structure–property trends generally serve as reliable guidelines. They are often helpful in a quantitative sense too. This section illustrates this point by examining some molecular design strategies employed by industry to create naphthopyran colorants with commercially useful performance. While rules associated with specific changes to structure usefully inform decisions on which approaches to take, there are plenty of exceptions where the impact of transformations in structure does not quite match with expectation. Given the many factors that influence the photochromism of organic colorants other than dye structure, nothing can replace synthesising and testing compounds of interest when fine-tuning colour, kinetics and performance.

The parent [1,2-*b*]naphthopyran **15** produces very slow fading red-orange photocoloration (λ_{max} 508 nm and $t_{1/2}$ >400 s in toluene at 20 °C) and is of no commercial significance in its own right. However, appropriate substitution at positions 5–10 and 2–4′ has proven a very powerful means of adjusting colour and kinetics to generate dyes of great industrial importance. The parent [2,1-*b*] naphthopyran **16** is more hypsochromic and much faster fading (λ_{max} 429 nm and $t_{1/2}$ 14 s in toluene at 20 °C) than its isomer **15**. While it is an industrial dye and available commercially as Reversacol Rush Yellow [102], the relatively fast thermal fade leads to somewhat weak photocoloration.



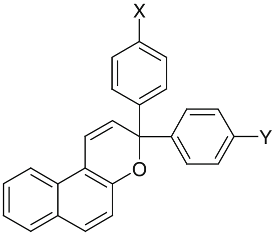
15

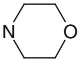
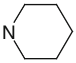
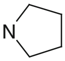
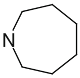
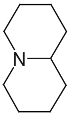
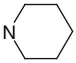
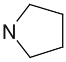
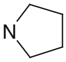


16

However, augmentation of structure **16** (Table 5.7, X = Y = H) enables the achievement of much more. Placing electron-donor groups such as alkoxy and amino functions into positions X and Y (i.e. the 4′- and 4″-positions *para* to pyran ring link) leads to

Table 5.7 Impact of varying 4′,4″-groups on absorption maximum and half-life in toluene (20 °C)



X	Y	λ_{max} (nm)	$t_{1/2}$ (s)
H	H	429	14
OMe	H	460	5
OMe	OMe	472	2
	H	501	4
	H	515	3
	H	542	2
NEt_2	H	544	2
	H	549	3
	H	581	2
CF_3	H	421	18
CF_3	OMe	446	7
CF_3		510	4
NEt_2	NEt_2	576	1
		577	1

significant bathochromic shifts in absorption, creating orange and red colorants. Unfortunately, they are too weak to be of much industrial interest. Generally, as overall donor strength at these two positions rises, $t_{1/2}$ falls so strength diminishes. A single methoxy or amino group thus produces marked red shifts in absorption, but at the expense of intensity of photocoloration. These effects grow in size as the electron-donating character of the substituent increases, i.e. H < methoxy < morpholino < piperidino ≈ dimethylamino < diethyamino ≈ pyrrolidino < homopiperidino < julolidino. Addition of a second donor function further enhances the bathochromic shift in λ_{max}, although to a lesser degree than that brought about by introduction of the first group. The same holds true of the reduction in half-life resulting from the presence of the second donor. For example, a single methoxy group (Table 5.7, X = OMe, Y = H) induces a significant red shift of ~30 nm with a substantial shortening in $t_{1/2}$ from 14 s to 5 s; a second methoxy function (X = Y = OMe) gives a fast-fading orange dye as a consequence of a further 12 nm red-shift in λ_{max} and drop in half-life to just a couple of seconds. Placing one amine function into the parent structure (i.e. Table 5.7, X = amino, Y = H) leads to both large bathochromic shifts (~70–120 nm) and decreases in half-life giving fast-fading, weak red dyes. A second amine group of the same type typically pushes absorption maxima another ~20–30 nm longer and further speeds up thermal fade – Table 5.7 shows several examples of such mono- and di-amino pairings. An extreme case is the action of two powerful donors in concert (Table 5.7, X = Y = pyrrolidino or diethylamino). They shift absorption sufficiently to give bluish-purple photocoloration. However, since strong donors also shorten half-life, the dipyrrolidino dye and its diethylamino analogue are only weakly photochromic at ambient temperatures ($t_{1/2} = <1$ s) despite these groups being likely to increase the intensity of absorption of the merocyanine form [103].

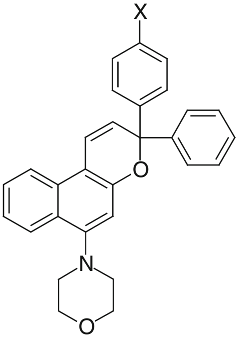
Electron acceptors tend to have the opposite effect, i.e. hypsochromic shifts in absorption of photoactivated dye to shorter wavelengths accompanied by an increase in activated intensity and duration of $t_{1/2}$. Table 5.7 exemplifies this relationship with trifluoromethyl groups: placing one of these acceptors onto the parent dye creates a colorant (Table 5.7, X = CF_3, Y = H) that has a slightly slower thermal fade (18 s cf.14 s) and which is modestly blue-shifted (421 nm cf. 429 nm). Given the big influence that it has on absorption and kinetics, substituent choice on the aryl rings of [2,1-*b*]naphthopyrans (as well as [1,2-*b*]naphthopyrans) is therefore a crucial aspect of dye design. The relationship between colour and rate of thermal fade means that the [2,1-*b*]naphthopyran class is restricted to being a source of commercially important yellow, orange and red dyes only. However, many of these dyes rely on additional design features.

One such industrially useful design tactic is the incorporation of a strong electron donor onto the naphthalene moiety in an analogous fashion to spirooxazines. An amino or alkoxy function located at the 6-position boosts the strength of photocoloration, mitigating the kinetic effects of strong donors introduced onto the 3-aryl groups to red-shift absorption (see Table 5.8).

Industry has been utilising this means of creating valued orange and red colorants for more than 20 years [104]. For example, when one compares the figures for 6-morpholino derivatives in Table 5.8 with those in Table 5.7, the addition of the 6-amino group leads to a substantial decrease in rate of thermal fade (accompanied by a large jump in intensity of steady state photocoloration) along with a moderate hypsochromic shift: several commercial naphthopyrans make use of this substitution pattern.

Substitution with an alkoxy group is also effective. For example, swapping the 6-morpholino residue of the derivative in Table 5.8 (X = morpholino) with a methoxy group leads to a minor bathochromic shift (2 nm) and a substantial further increase in half-life from 42 to 92 s. The same switch in the case of the analogue in

Table 5.8 Absorption maxima and half-lives of 6-morpholino derivatives of [2,1-*b*]naphthopyrans in toluene solution at 20 °C



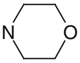
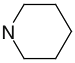
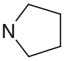
X	λ_{max} (nm)	$t_{1/2}$ (s)
H	418	103
OMe	433	54
	470	42
	488	33
	518	29
NEt_2	516	23

Table 5.8 with X = piperidino brings about a minor hypsochromic shift (2 nm) and an increase in $t_{1/2}$ from 33 to 84 s. These derivatives are prepared by reaction of diaryl alkynols as per Fig. 5.13 with 4-morpholino-2-naphthol (Z = morpholino) and 4-methoxy-2-naphthol (Z = methoxy). These two naphthols are readily prepared from 2-naphthol [88].

Placing an electron donor onto the 8-position gives a similar, albeit less pronounced, effect as 6-donor functions. All else being equal, an 8-methoxy group leads to greater bathochromism of photoactivated colour as well as a slower thermal fade and greater photostationary state intensity compared to corresponding substitution at adjacent 7- and 9-positions. An explanation for this observation is that the presence of a donor at the 8-position makes possible an additional zwitterionic canonical form like a 6-donor (see Fig. 5.15). Given that this form involves destruction of the aromaticity of the naphthalene system whereas it is partly preserved in the case of the 6-donor [88] means that the impact of the 8-donor is more limited.

Another well-used approach to enhance photocoloration is the inclusion of a substituent on one of the 3-aryl rings *ortho* to the C3 carbon, i.e. at the 2′-position as shown in Table 5.9. Generally, the imposition of a fluoro function at this location leads to a modest shift in absorption maximum. Far more remarkable is the increase in half-life and intensity of photocoloration. For example, when

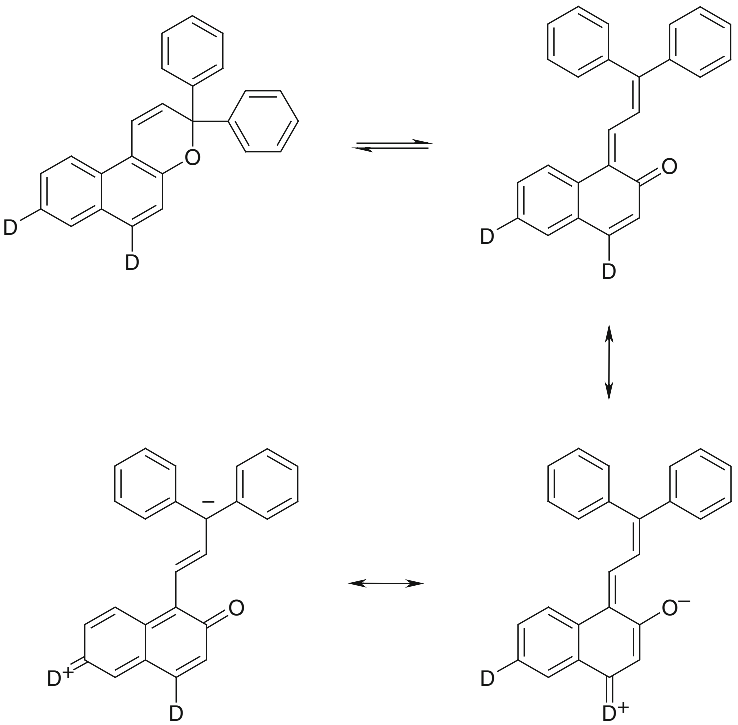
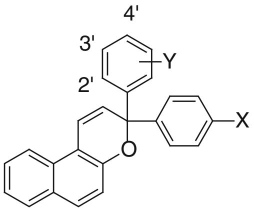
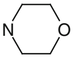
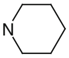


Fig. 5.15 Donor effects at 6- and 8-position of [2,1-*b*]naphthopyrans

Y = 2′-F, the dyes produce stronger photocoloration and are slower to fade (i.e. $t_{1/2}$ is much longer) following activation compared to dyes in which Y = H. This is illustrated in Table 5.9 for the corresponding pairs of dyes where X = H, methoxy, morpholino or piperidino. The more sterically demanding o-methyl and -methoxy groups, i.e. Y = 2′-Me or 2′-OMe, generate even more pronounced effects. While their donor character leads to rather small bathochromic shifts, these substituents greatly lengthen half-life as can be seen from the data shown in Table 5.9. Such patterns are thus of interest for slowing down the rate of fading (and increasing the intensity of photocoloration) of relatively fast and weak [2,1-*b*]naphthopyrans while retaining their hypsochromism. For example, $t_{1/2}$ is increased by two orders of magnitude in dyes where X = alkoxy or X = amino through the introduction of an *ortho* methyl or methoxy group (see Table 5.9). In contrast, their absorption maxima see no more than a 10 nm shift. This strategy has been used commercially for many years, although it is often used in conjunction with other features to adjust kinetics because the change it produces is so marked. The *ortho* substituent is believed to be a source of steric hindrance to ring closure [105], thus increasing the lifetime of the photomerocyanine species, leading to slower thermal fading and increased photostationary intensity. Even more bulkier *ortho*-groups lead to longer half-lives, for example, $t_{1/2}$ 2′-Cl < $t_{1/2}$ 2′-Br < $t_{1/2}$ 2′-I.

Table 5.9 Effect of 2′- and 3′-substitution on absorption maxima and half-lives of [2,1-*b*]naphthopyrans in toluene solution at 20 °C

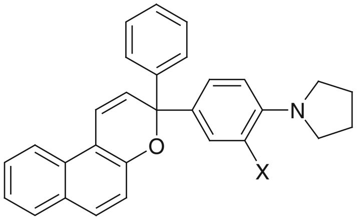


X	Y	λ_{max} (nm)	$t_{1/2}$ (s)
H	–	429	15
	2′-F	421	108
OMe	4′-OMe	472	2
	2′-F-4′-OMe	463	36
	2′-Me-4′-OMe	470	400
	2′,4′-DiOMe	476	320
	3′,4′-DiOMe	482	3
	–	501	4
	2′-F	503	87
	2′-OMe	508	1,500
	4′-OMe	505	2
	–	515	3
	2′-F	525	75
	2′-OMe	525	880
	3′-OMe	520	6
	4′-OMe	519	2
NMe_2	4′-NMe_2	538	1
	4′-NMe_2-2′-Me	549	99
CF_3	4′-OMe	446	7
	2′,4′-DiOMe	437	600

Notice in the data of Table 5.9 how a 3′-substituent does not bring about a large increase in half-life: a methoxy function in this position confers a bathochromic shift as would be expected of an electron donor, but no large increase in half-life as it does not bring about the hindrance typical of 2′-OMe substitution.

However, a 3′-substituent is capable of usefully producing steric hindrance but for different reasons to 2′-groups. Crowding of a 4′-amino substituent is a tactic sometimes exploited in industrial dye design to adjust colour with relatively little impact on kinetics as illustrated in Table 5.10. Locating a group *ortho* to the pyrrolidino nitrogen (i.e. at the 3′-position) leads to twisting of the amine function out of the plane of the aryl ring, resulting in diminished participation of the amino group in the molecular π-system. Consequently, when X = Me or halogen, significant hypsochromic shifts result because the effectiveness of the amino group as an

Table 5.10 Influence of 3′-substituent on absorption maximum and half-life of 4′-amino functionalised [2,1-*b*]naphthopyran in toluene solution at 20 °C [106]



X	λ_{max} (nm)	$t_{1/2}$ (s)
H	538	5
Me	517	3
OMe	557	5
F	529	4
Cl	513	4
Br	493	4
I	494	5

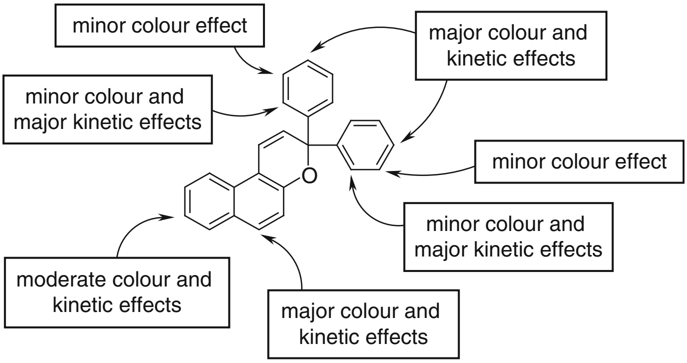


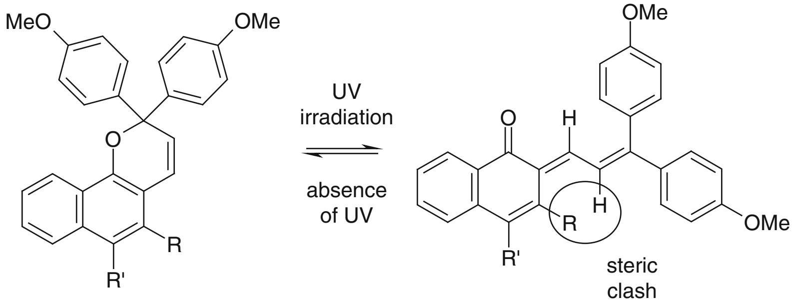
Fig. 5.16 Summary of substituent effects in [2,1-*b*]naphthopyrans

electron donor is reduced through losses in conjugation. A 3′-methoxy function (i.e. Table 5.10, X = OMe) bucks this trend: its capacity as a donor is sufficient to outweigh any steric hindrance caused, producing bathochromism.

A summary of the relationships outlined above regarding the position of a substituent on the [2,1-*b*]naphthopyran system and its potential impact on the colour and kinetics of the colorant is shown in Fig. 5.16.

Some of the relationships given in Fig. 5.16 also hold true for the [1,2-*b*] naphthopyran system. These include substitution on the 2-phenyl rings: for example, introduction of strong donors at the 4′- and 4″-positions leads to bathochromism accompanied by an increase in rate of thermal fade, whereas *ortho* groups, i.e. at 2′- and 2″-positions bring about pronounced lengthening of half-life. As previously mentioned, the parent compound **15** fades too slowly thermally to be of commercial use. Industry overcomes this drawback by the

Table 5.11 Influence of 5- and 6-position on kinetics of [1,2-*b*]naphthopyrans [109]

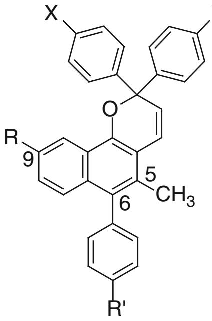


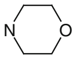
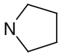
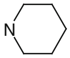
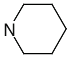
R	R′	$t_{1/2}$ (s)	λ_{max} (nm)
H	H	>1,800	508, 412
Me	H	178	496, 416
Me	Me	65	492, 418
Ph	Ph	20	508, 418
CO_2Me	H	2	492
CO_2Me	Me	4	492, 416
CO_2Me	Ph	7	506, 416

location of functional groups onto the 5- and 6-positions (i.e. Table 5.11, R and R′) to impose steric crowding on the photomerocyanine, reducing stability and prompting a greater tendency for thermal reversion to the ring-closed form of the dye. Replacing the hydrogen at the 5-position with a methyl group (i.e. R = Me, R′ = H) is sufficient to bring the half-life down by an order of magnitude to a length that is approaching commercially utility, yet makes only a small impact on colour. Addition of a methyl group to the structure at the 6-position further shortens half-life to an industrially useful duration while retaining its red colour when activated. The resultant colorant (R = R′ = Me) is available on the market as Reversacol Berry Red [107, 108].

Imposition of even bulkier groups at the 5-position (i.e. R = Ph or CO_2Me) further speeds up thermal fade, giving dyes that are too weak. However, a substitution pattern of 5-Me-6-aryl is commercially valuable. It not only permits the creation of intense bathochromic colorants with suitable half-lives, but also furnishes relatively neutral-coloured dyes with prominent double absorption peaks (see Table 5.12). Donor groups placed into the 9-position and 6-phenyl ring cause bathochromism and increased intensity through longer half-life. In certain cases, two distinct peaks appear, giving duller and more neutral colours. The effect is more pronounced for alkoxy groups compared to alkyl groups, e.g. where X = pyrrolidino and Y = H. Subtle differences in substituent effects can make a substantial impact on colour. For example, when X = Y = piperidino, the gap between the two absorption peak maxima widens to around ~100 nm compared to ~80 nm for dyes with just one amine function, producing a more neutral

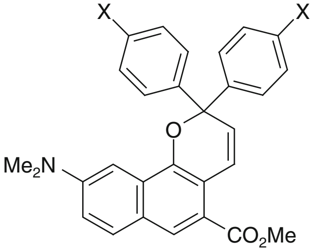
Table 5.12 Influence of donor groups in 5-methyl-6-phenylnaphth[1,2-*b*]pyrans in toluene solution at 20 °C



X	Y	R	R′	λ_{max} (nm)	$t_{1/2}$ (s)
OMe	OMe	H	H	498, 419	32
		OMe	OMe	528, 427	53
		Me	Me	506, 422	59
	H	H	H	514	63
		OMe	OMe	532, 461	99
	H	H	H	550	42
		OMe	H	559, 488	44
		OMe	OMe	560, 485	52
		Me	Me	549	54
		H	H	551	14
		OMe	H	560, 466	17
		OMe	OMe	560, 465	22
		Me	Me	549, 448	22

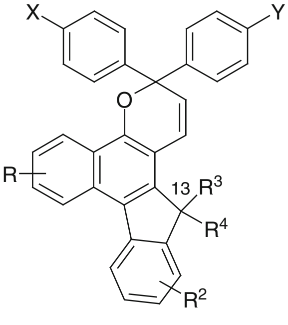
appearance. A consequence of the presence of two amino groups is that thermal fade is more rapid, leading to weaker steady-state coloration.

Locating stronger donor functions on the 9-position is a strategy that has proved commercially successful for producing colorants with multiple broad absorption bands, simplifying the formulation of neutral grey lens formulations. Derivatives of general structure **17** have been marketed over the past 15 years featuring 9-amino groups, giving grey [110] and brown [111] photocoloration. The substituent enhances intensity of absorption in the short wavelength region of the visible spectrum when photoactivated. Colour and kinetics can be further adjusted using the rules of thumb already discussed above to fine tune the position of these absorption bands while also trying to keep a reasonable balance of photocoloration intensity and rate of thermal fade. In the case of **17** (X = OMe), brown coloration results as photoactivation gives two peaks (λ_{max} 556 nm and 454 nm in toluene at 20 °C). Increasing donor strength in the aryl rings shifts these bands bathochromically in line with expectation. For example, **17** (X = piperidino) is purplish-grey since the absorption maxima are shifted to 581 nm and 490 nm in toluene. These bands are affected in slightly different ways by the medium in which the dye is applied so colour may be subtly affected by solvatochromism. Nevertheless, this strategy was innovative by enabling formulators to minimise the amount of shading components required to produce a lens of neutral colour.

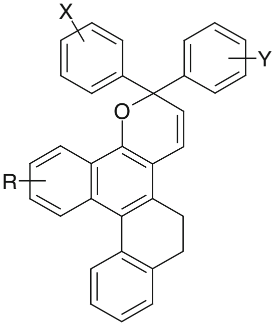


17

Another commercially important class are indeno-fused dyes of general structure **18**, which have been used in lens manufacture for the past 20 years [12, 112]. In the case of these colorants, industry made further use of crowding by fusion of ring systems at the 5- and 6-positions of the [1,2-*b*]naphthopyran system to manipulate kinetics whilst simultaneously tuning absorption to give blue and green colorants with multiple broad absorption bands for neutral shades. Changes at the 13-position enable adjustment of kinetics while the indeno skeleton holds the fused phenyl ring in plane with the rest of the π-system, creating a chromophore of enhanced intensity and bathochromism. Analogues with other fused systems appear in many patents, but only a few have been commercialised, e.g. derivatives with a 6-membered ring **19**. In this field, the existence of a very large proportion of structures in the patent literature owes itself not so much to the supposed technical advantages claimed, but to efforts aimed at skirting round existing patents.

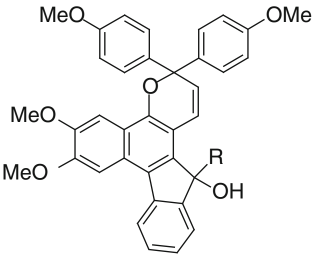


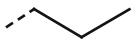
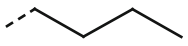
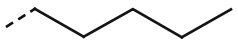
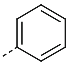
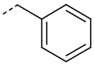
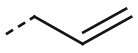
18



19

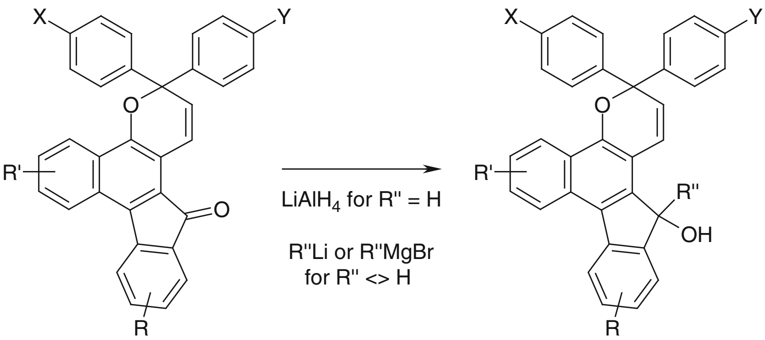
Table 5.13 Influence of 13-substituent in indeno-fused [1,2-*b*]naphthopyrans in methacrylate-based polymer at 23 °C



R		$t_{1/2}$ (s)	λ_{max} (nm)
	H	351	460, 570
	Me	230	455, 575
	Et	146	455, 580
	*n*-Pr	115	460, 580
	*n*- Bu	116	455, 580
	*n*-Am	157	460, 570
	Ph	260	460, 580
	Bzl	258	460, 580
	Vinyl	325	460, 575
	Ethynyl	171	460, 575
	Allyl	186	460, 575

Substituents at the 13-position of **18** strongly influence kinetics with a minor impact on colour (see Table 5.13). Small variations in the position of the two main absorption bands of the dyes in the visible region occur, but significant differences in half-life are apparent. In line with findings from 5- to 5,6-substituted [1,2-*b*] naphthopyrans, locating bulkier groups into the 13-position tends to lead to increased fade-speed. However, the relationship is complex. For example, when R = Me, thermal fading is more rapid than when R = H. Increased crowding results in shorter half-lives as shown in the data for R = Et and R = *n*-Pr. As we saw earlier in the case of *N*-alkyl functions in indolino-spironaphthoxazine dyes, geometry as well as size plays a part. For example, increases in chain length (R = *n*-Bu or *n*-Am) or introduction of aryl groups (R = Ph or Bzl) fail to decrease $t_{1/2}$ further. In addition, there are significant differences between the kinetics of the sets of dyes where R = Et, R = vinyl and R = ethynyl as well as the pair of dyes where R = *n*-Pr and R = allyl. The data demonstrate that once again, when developing industrial colorants, it is difficult to make exact predictions and that, even when one has developed rules of thumb, the adjustment of dye properties remains an exercise in trial and error.

The indeno-fused derivatives can be prepared by several means, two of which are shown in Fig. 5.17 where coloured non-photochromic ketone derivatives are



X, Y = H, alkoxy, amino, etc.; R, R' = H, alkyl, alkoxy, etc.; R'' = H, (un)saturated alkyl, aryl

Fig. 5.17 A commercial synthetic route to 13-substituted indeno-fused naphthopyrans

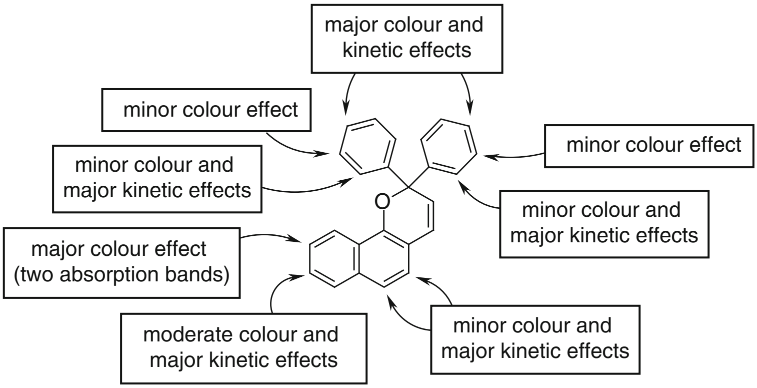


Fig. 5.18 Summary of substituent effects in [1,2-*b*]naphthopyrans

either reduced, or reacted with an organometallic compound, to furnish photochromic products.

This section has given a flavour of the relationships that govern photochromic properties of the [1,2-*b*]naphthopyran system. A summary of them is provided above in Fig. 5.18.

5.6 Conclusions

Heliochromism is a good starting point for the current definition of the most commercially successful kind of industrial photochromism. While P-type photochromic colorants have been the focus of intense efforts to develop new technologies in the areas of optoelectronics, data storage and nano-engineering, the principal commercial use of industrial dyes is to put T-type photochromism to work in ophthalmic lenses. The light-sensitive silver halide-based glasses of half a century ago have largely given way to all-organic polymeric systems. Breakthroughs in colorant chemistry and dye application, whose roots lay in the late 1960s and 1970s, made the switch to more lightweight, more responsive materials possible. These advances included the identification of two broad and versatile classes of colorants with relatively high intrinsic photostability. They came into their own in the 1990s as chemists learnt how to manipulate structure to fine-tune dye colour and kinetics. Formulators and polymer technologists complemented their efforts by finding new ways of enhancing colorant performance through use of additives and providing dyes with right environment in which to function best. Consequently, the industrial usage of photochromism for ophthalmic lenses blossomed, driving the development of more sophisticated dyes. Their structures have been carefully designed to balance the often mutually exclusive demands of colour, speed, strength and stability. This Chapter has attempted to enlighten the reader with some background behind these advances, providing insight into the synthesis, design rules and limitations of these colorants. Even now, over half a century since the first serious modern efforts to develop organic photochromic molecules for real world applications, much remains to be learnt. Considerable progress continues to be made in improving upon the properties of existing T-type molecules for commercial use. By appropriate structural design, one can obtain dyes with multiple absorption bands in the visible region when activated, thereby simplifying the task of the formulator because mixtures of fewer dyes are needed to obtain neutral colours. Other modifications reduce the compromise between speed and strength with, in certain cases, minimal impact on activated hue. Trial and error still plays a part. . .and is likely to continue to do so. Many influences interact in too complex a manner to allow precise predictions of behaviour. Fortunately, there are rules of thumb to help one navigate through this maze. This Chapter outlined some of them.

Numerous applications, either new or old in terms of their inception, await the creation of photochromic entities with the right set of technical properties, economics and, in particular, robustness. Of the many thousands of light-responsive colorants subjected to industrial scrutiny, only a very small proportion have made it through to commercialisation. One could argue that with just a tiny fraction of the design space of photochromic molecules explored, the potential to discover improved variants within existing dye classes, as well as truly novel types of light-responsive colorant, is enormous. Just how much of this space is economically accessible remains to be seen. While the existing industrially significant types of T-type dye will probably retain their dominance in the immediate future, it is conceivable that the rise of another technology reliant upon photochromism might alter the landscape of industrial dye usage radically. If one of the high-tech applications described in this Chapter that make use of P-type dyes became commercially successful, then it could be expected to dwarf the market for T-type colorants. Such a development would redefine industrial photochromism and necessitate a complete re-write of this Chapter. However, efforts in this direction not only need to see off competing technologies that do not utilise photochromic materials, but also surmount substantial technical challenges, which may prevent them seeing the light of day – either literally or metaphorically…

Acknowledgements Thousands of people working during this century and the last within industry, academia and elsewhere in countries across the globe can take a share of the credit for making industrial photochromism what it is. However, the author wishes to acknowledge the contribution to the knowledge, as well as the previously unpublished data, contained within this Chapter of the numerous members of technical staff of Vivimed Labs Europe Ltd (and James Robinson Ltd as was), particularly Dr. D.A. Clarke and Dr. S.M. Partington. In addition, mention must be made of the fruitful collaboration between the organisation with the research groups of Prof. J.D. Hepworth, Dr. B.M. Heron and Dr. C.D. Gabbutt, leading to the creation of insights into the properties of photochromic dyes and its realisation in the form of industrial photochromism.

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