



Negatively photochromic organic compounds: Exploring the dark side



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ABSTRACT

The last few years have seen an explosion of interest in traditional photochromic systems not only for their applications in variable transmission devices, which continues to attract commercial interest, but also for the ability of these molecules to undergo structural and electronic reorganisation which has been seized upon by materials scientists for the development of switches, logic gates, photoinduced molecular motions such as rotors and fibrils, and photoregulation of drug availability. This comprehensive review examines, for the first time, the 'dark side of photochromism'; negatively photochromic systems which are coloured in their ground state and reversibly photobleach upon exposure to electromagnetic radiation with a wavelength over ca. 400 nm i.e. visible light responsive systems. This review is organised by structural class and examines their synthesis, structure, key spectroscopic data for coloured and bleached species, structure – switching relationships and applications. The usefulness of these negatively photochromic systems is only gradually coming to the fore with the advantages of low energy activation c.f. conventional Uv-activated switches, enabling the modulation of a plethora of useful optical and physical properties and the design of new materials with broad ranging applications.

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1. Introduction

The phenomenon of photochromism may be simply defined as:

'a light-induced reversible transformation of a chemical species between two states having different absorption spectra',

and was first noted in 1866 by J. Fritzsche who observed the reversible photodimerisation of anthracene [1]. Brown compiled the first major review of photochromism, in *Techniques of Chemistry*, volume III, entitled 'Photochromism' in 1971 [2]. Normal or positive photochromism is exemplified by the reversible development of an intense colour upon irradiation, typically with UV light, of the photochromic molecule. Colour fading, associated with return of the photogenerated species to its original state, either occurs thermally upon cessation of irradiation (T-type photochromism) or upon irradiation with an alternative wavelength of light (P-Type photochromism). Here the authors note that the originally conceived distinction between T- and P- type

photochromic systems is somewhat fuzzy since many photochromic systems originally described as T-type do indeed show some component of P-type behaviour with the reverse reaction responding to some extent to irradiation as well as temperature [3]. Studies on P-type photochromic systems are almost entirely dominated by switching applications of diarylethenes. T-Type photochromic behaviour is a common occurrence for wearers of ophthalmic sunlenses where the lens appears coloured in normal sunlight and fades upon being placed in the shade. To date photochromic sunlenses remain the major commercial application of photochromism and sunlenses invariably utilize combinations of naphtho- [4] and indeno- [5] pyrans and spiroindolinonaphthoxazines [6]. The absorption spectra of a simple T-Type photochromic dye, pre- and post-irradiation, are presented in Fig. 1.

Conversely, negative photochromism (sometimes referred to as reverse or inverse photochromism) is observed when the colour of a dye reversibly fades on exposure to electromagnetic radiation such as visible light or sunlight but the intensity of the colour recovers in the absence of visible light i.e. the intense colour of the dye develops in the dark. The term negative photochromism has also been extended to systems wherein the intensity of the long wavelength absorption band of a dye has decreased

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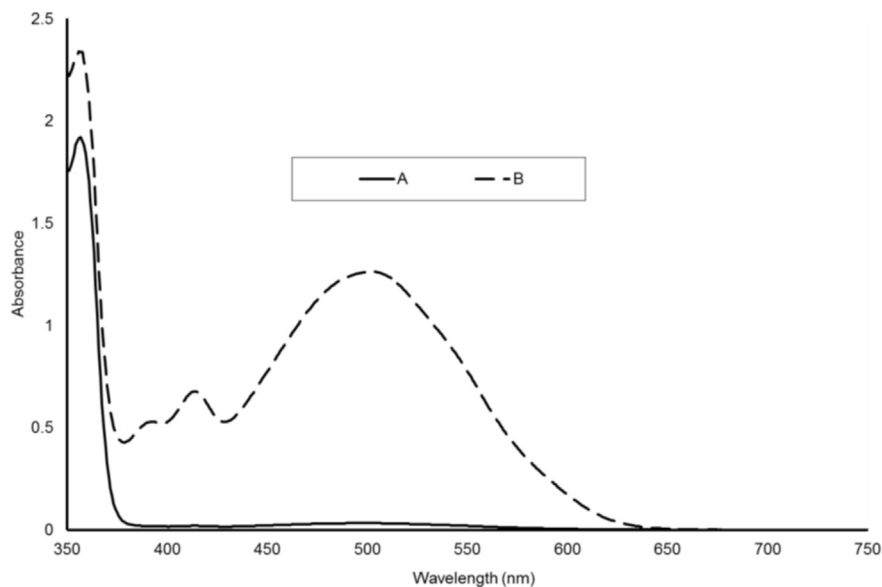


Fig. 1. Response of a typical T-type positive photochromic dye solution. (A pre-irradiated, B immediately after cessation of irradiation).

(hypochromism) upon irradiation with the emergence of a new band at shorter wavelength in the visible region of the electromagnetic spectrum.

There have been several academic reviews concerning photochromism and photochromic systems following on from the initial comprehensive volume edited by Brown [2]. In 1998 a two volume set in the series Topics in Applied Chemistry was edited by Crano and Gugliemetti; volume 1 dealt with the synthesis and properties of the 'Main Photochromic Families' [7] and volume 2 with 'Physicochemical Studies, Biological Applications and Thermochromism' [8]. Irie edited a complete issue of Chemical Reviews dedicated to the application of photochromism in memories and switches, though much valuable general information on photochromic systems was included [9]. Perhaps as a consequence of the appearance of the latter two reviews and a general increase in interest in the subject Dürr and Bouas-Laurent revised their original book, 'Photochromism Molecules and Systems' [10], and included much more material in the 2003 revision [11]. The most recent addition to major works on photochromism entitled 'Photochromic Materials' was edited by Tian and Zhang in 2016 [12]. An English translation of a more obscure multi-authored Russian work entitled 'Organic Photochromes' edited by El'tsov appeared in 1990 [13]. Whilst many of the foregoing reviews focus on more academic aspects of photochromism one major work, edited by McArdle in 1992, 'Applied Photochromic Polymer Systems', is devoted to the behaviour and application of photochromic polymers [14], though due to the relatively recent activity in the area of photochromic polymer systems, see for example work by Evans et al. [15–17], 'McArdle' is probably due an update.

Other general reports and reviews featuring photochromism have appeared [18–22] and more specific reviews dedicated to individual photochromic systems have been published, noteworthy amongst these are those on diaryl benzo- and naphtho-pyrans [23], diarylethenes [24–28], spiropyrans [29–31], spiropyran-based materials [32], spiroindolinonaphthoxazines [33,34], photochromic compounds as ligands [35], photoswitching transition metal complexes [36,37], photochromic systems containing crown ether units [38,39] and azobenzenes [40–42]. A notable recent review by Jacquemin et al., examines highly functional materials

which contain more than one photochromic switching moiety [43]. Photochromic systems also feature in reviews concerned with the control of molecular architecture [44], molecular switches [45,46], devices and machines [47], photoswitchable bio-materials and biomolecules [48] and in reversible optical data storage devices [49]. Special issues of Molecular Crystals, Liquid Crystals [50–56], Dyes & Pigments [57] and also Advanced Optical materials [58] containing papers and abstracts from the International Symposia on Photochromism (ISOP) have appeared. In spite of such activity on positive or normal photochromic systems there remain relatively few articles concerning negative photochromism, indeed the phenomenon was summarised in only a few lines by Brown [59]. A short account of the reverse photochromism of spiropyrans was authored by Barachevsky in the Russian language in 1997 [60].

Of the many photochromic systems described in the foregoing reviews very few exhibit negative photochromism. This review primarily divides the phenomenon of negative photochromism into T- and P- type systems and thence subdivisions based on the molecular system and where there are sufficient examples further division into substituent and matrix effects.

2. Systems that exhibit predominantly T-Type negative photochromism

2.1. Spirobenzopyrans (spiro[2H-[1]-benzopyran-2,2'-indolines])

The spirobenzopyran system is perhaps historically the best known positive photochromic system. UV irradiation of the colourless pyran (1',3',3'-trimethylspiro[2H-[1]-benzopyran-2,2'-indolines]) **1** results in cleavage of the 1'–2' (O – spiro-C) bond to afford the zwitterionic (Z)-2-(2-(1,3,3-trimethyl-3H-indol-1-ium-2-yl)vinyl)phenolate **2A** which isomerises to the (E)-2-(2-(1,3,3-trimethyl-3H-indol-1-ium-2-yl)vinyl)phenolate **3B** (Scheme 1). It is generally accepted that quinoidal forms of **2B** and **3B** may also be present and the ratio between these and the zwitterions is dependent upon substituents and the nature of the matrix [61,62]. Additionally the possibility of various rotamers of **2** and **3** should be noted.

However, there are several examples of 'spiropyrans' bearing

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