The Photochemistry and Photophysics of Triphenylmethane Dyes in Solid and Liquid Media

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Contents

Debra Duxbury was born in Victoria, Australia, in 1957. She received a B.Sc. honors degree in chemistry from the University of Melbourne, Australia in 1980. Her Ph.D., awarded in 1986, is from the University of New South Wales, Australia for the study of the photochemistry of triphenylmethane dyes in wool and other substrates. She did postdoctoral research in the physical chemistry laboratory at Oxford University, U.K., where she investigated methods of shaping CO_2 laser pulses in order to study the multiphoton absorption of SF_6. Between 1987 and 1989 she had a dual appointment at Michigan State University, first as a postdoctoral researcher with Professor Thomas J. Pinnavaia and second as a X-ray specialist for the Center for Fundamental Materials Research. Currently, she is preparing for entry into medical school.

I. Abstract

This review examines the literature on the photochemical and photophysical properties of triphenylmethane dyes in solid and liquid media published up to the end of September 1991. It is intended to serve researchers interested in both the pure and applied aspects of this class of dye.

After an introduction discussing the importance and use of these dyes, the main aspects covered include the absorbance spectra of triphenylmethane dyes, photophysical deactivation of the excited states, and the photochemical reactions of these dyes with particular emphasis on photooxidation, deamination, and photoreduction processes. Other factors influencing dye fading such as temperature, humidity, gaseous reactants, dye concentration, the spectral distribution of the irradiating light, and the nature of the substrate in proximity to the dye are also discussed. In the final section consideration is given to the sensitized fading of triphenylmethane dyes in protein substrates.

II. Introduction

Triphenylmethane dyes form a very important class of commercial dye. They are among the first of the synthetic dyes to be developed[1a,2a,3a] and still find applications in many fields. These dyes are renowned for their outstanding intensity of color, their brilliant shades of red, blue, and green, and low lightfastness on many substrates. In fact, it is these features which enable the uses of triphenylmethane dyes to be divided into two categories namely situations where (1) low lightfastness is not a problem and intensity of color is advantageous and (2) where low lightfastness is of interest.

This review examines the literature on the photochemical and photophysical properties of triphenylmethane dyes in solid and liquid media up to the end of September 1991, and the majority of this is related to category two. Unfortunately it would be a formidable task, beyond the scope of this paper, to comprehensively

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review all the many uses of this class of dye. However, in order to underline the importance of triphenylmethane dyes and provide those interested with an indication of the available literature, a brief discussion on applications more pertinent to category one will follow, but not before noting that the many uses of triphenylmethane dyes have been extensively reviewed in the series of books edited by Venkataraman[4a,b,d] and by others.[1b-d,5a,6b,7]

Examination of the more recent analytical chemistry literature shows that numerous elements are able to associate with triphenylmethane dyes. This enables elements such as Sn(IV),[8,9] Be,[10-13] Ga,[13,14] Mg,[15] Co,[15,16] Zn,[15,17] P,[18,19] Gd,[20] Al,[21-24] B,[25-28] Cu,[29] Ti,[30], Sb,[27] V,[31,32] Rh,[17,33,34] Pt,[33-35] U,[36] Th,[37] Ni,[38] Fe,[39] and Ir[33] to be detected spectrophotometrically. Surfactants are frequently added to the sample solutions to enhance sensitivity.[20,40-42] The review by Sandell and Onishi,[43] on this topic, mentions many other metals that can be detected as do the works by Tikhonov[17] and others.[5c,41,42,44-47]

Triphenylmethane dyes have been used by Pan and co-workers to prepare carbon-coated poly(vinyl chloride) matrix membrane electrodes selective to IO_4^-,[48,49] $TlBr_4^-$,[48] $InBr_4^-$,[49,50] SCN^-,[49,51] ClO_4^-,[49,51] picrate,[49,51] I^-,[49] ReO_4^-,[49] and BF_4^-.[49] Similarly, other workers[52-54] have prepared electrodes using triphenylmethane dyes. While others have investigated using the dyes in solar cells[55,56] and as sensitizers for photoconductivity.[57]

In surface chemistry, the spreading of a drop of ethanol colored with basic violet 3 has been examined[58] as has the surface tension of an aqueous solution of basic green 1.[59]

By utilizing the energy transfer between a xanthene dye and a triphenylmethane dye, researchers determined the fractal dimension of vesicle surfaces[60b] and SiO_2 materials such as controlled-pore glasses[61-63] and silica gels.[61-64] The fractal dimension of a specially prepared sample of Vycor 7930 glass has also been determined.[65] However, Yang et al.[66] have questioned whether or not this value arises due to an excluded volume effect or due to true fractal structure of the glass. Nevertheless, fractal structures are an area of current interest in a wide range of scientific disciplines.

Triphenylmethane dyes have been extensively employed in the medical and related biological sciences. They exhibit antibacterial properties,[1d,67a,c,68-70] are used for the disinfection of post-operative wounds,[71] and are employed in tests which are useful for controlling diabetes.[72] The dyes acid blue 83 and acid blue 90 are frequently used to assay proteins,[73-77] and other members of this class of dye are used in cytology and histology to stain tissue.[78,79]

In addition, triphenylmethane dyes are employed as colorants in the photographical,[80] food,[81,82a] cosmetic,[81,82a] and stationery[1c,d,3c,83,84a] industries.

As a consequence of their many applications triphenylmethane dyes find their way into aquatic environments.[81,85] In view of this and the reports that certain triphenylmethane dyes may be toxic[1e,81,85-87] it is not surprising that research is directed toward assessing the extent of dye pollution[85,88-90] and finding better waste-water treatments,[81,85,90-94] particularly since some dyes from this class seem to present a health hazard to humans.[1e,87]

Also as a consequence of their many uses, and the fact that triphenylmethane dyes are available from several manufacturers, it is not uncommon to encounter more than one name describing a given dye. During the course of writing this review, it became apparent that triphenylmethane dyes are employed in a wide variety of scientific disciplines and that each area of interest in the dyes prefers one particular name over another. Since this review encompasses a variety of fields of study on the dye, a brief discussion on nomenclature seems beneficial to the reader before proceeding with the body of the review.

III. Nomenclature

Four predominant methods seem to be in current use for naming dyes.

The first method classifies the colorant according to its recognized use by issuing a C.I (*Colour Index*) Generic Name and also according to its chemical constitution by issuing a C.I Constitution Number. These classifications are listed in a series of books known collectively as the *Colour Index*.[82]

The second method, implemented by the Chemical Abstracts Service (CAS) in 1965, is to issue a unique number to each chemical substance. This number is known as a CAS Registry Number, and it includes up to nine digits which are separated into three groups by hyphens. Registry Numbers assigned by CAS are listed in the *Chemical Abstracts Service Registry Handbook Number Section*.[95] A CA Index Name accompanies each CAS Registry Number in the handbook.[95]

The CA Index Name may be derived by consulting the CA Index Guide, Appendix IV ¶ 101.[96]

The IUPAC naming method constitutes the third predominant systematic method of naming dyes. The extensive rules of this naming system may be found in the following references.[97-101]

To complicate matters, however, there is usually more than one nonsystematic name in existence, and they are frequently used to describe a particular colorant. Such names frequently take the form of a commercial or trivial name. Commercial and trivial names constitute the fourth predominant method of naming dyes. Many of these are listed in Volume 5 of the *Colour Index*.[82]

To facilitate ease of reading this review the C.I Generic Name, C.I Constitution Number, CAS Registry Number, and several (but not all possible) commercial names for many of the dyes mentioned in this review have been tabulated in Table I. For a more comprehensive list of commercial names the reader should consult the *Colour Index*.[82] The IUPAC names have not been listed in this table since they are quite lengthy and can be obtained from the CAS Registry Number via the CA Index Name as mentioned above. Furthermore, the structures for one form of some of the dyes and indicators, relevant to this review, are given in Chart Ia–c.

It is appropriate now to return to the major concern of this review, namely the interaction of light with triphenylmethane dyes.

Table I. Some Dyes Mentioned in the Review

C.I. generic name	C.I. constitution number	CA registry number	some of the possible commercial or classical names
acid blue 1	C.I. 42045	129-17-9	brilliant blue GS, carmine blue VF, xylene blue VS
acid blue 7	C.I. 42080	3486-30-4	acid turquoise blue A, D and C blue no. 3, patent blue A
acid blue 15	C.I. 42645	5863-46-7	brilliant milling blue BA, optanol blue B, xylene milling blue BC
acid blue 20	C.I. 50405	8004-99-7	induline 5B, aniline blue 2B (biological stain)
acid blue 83	C.I. 42660	6104-59-2	coomassie brilliant blue R, eriosin brilliant cyanine 6B
acid blue 90	C.I. 42655	6104-58-1	brilliant acid blue J, coomassie brilliant blue G 250
acid blue 104	C.I. 42735	6505-30-2	acilan brilliant blue FFR, xylene brilliant blue FFR
acid blue 109	C.I. 42740	7253-35-2	brilliant wool blue FFB
acid blue 123	C.I. 44510	6661-40-1	coranil blue HEF, wool fast blue FBL
acid violet 17	C.I. 42650	4129-84-4	amacid violet 3B, hidacid wool violet, solar violet 4BN
acid violet 19	C.I. 42685	3244-88-0	acid fuchsine S, acid magenta, acid rubin
acid green 9	C.I. 42100	4857-81-2	brilliant acid green B, merantine green B, xylene fast green 6B
basic dye	C.I. 45010	2150-48-3	pyronine B
basic blue 7	C.I. 42595	2390-60-5	aizen victoria pure blue BOH, calcozine pure blue BO, Victoria pure blue BO
basic blue 9	C.I. 52015	61-73-4	methylene blue, ext. D and C blue no. 1, methylene blue I (medicinal)
basic blue 20	C.I. 42585	82-94-0	double green SF, light green, methyl green
basic violet 1	C.I. 42535	8004-87-3	methyl violet, gentian violet
basic violet 3	C.I. 42555	548-62-9	crystal violet, methyl violet 5BO
basic violet 4	C.I. 42600	2390-59-2	ethyl violet, ethyl violet AX
basic violet 14	C.I. 42510	632-99-5	magenta, fuchsine, fuchsin
basic green 1	C.I. 42040	633-03-4	brilliant green, diamond green G, fast green JJO
basic green 4	C.I. 42000	569-64-2	malachite green, Victoria green B
basic red 1	C.I. 45160	989-38-8	rhodamine 6G, rhodamine F5G, groundwood red
basic red 9	C.I. 42500	569-61-9	parafuchsin, paramagenta, pararosaniline

IV. The Photochemistry of Triphenylmethane Dyes

The photoprocesses of triphenylmethane dyes are not only complicated but intrinsically interesting, and researchers have strived to understand them more clearly in order to solve several practical problems. Two of these come to mind.

The first is encountered in the field of textile chemistry. Textile chemists have a need for bright, fast colors for natural fibers to compete with those available for acrylic fibers. Initially, it would seem that triphenylmethane dyes are promising candidates by virtue of their brilliant colors (ranging from pink, green, blue, and violet) and high tinctorial strength, but unfortunately they are often extremely fugitive to light, particularly on natural fibers such as silk, cotton, and wool, and only show moderate lightfastness on acrylic fibers based on poly(acrylonitrile).[1b,4a,e] Such systems can invoke quite complex photochemical reactions since both the dye and the substrate are photochemically active. Hence, many studies have been performed using model systems of dyed polymer films to represent the dyed natural fiber substrate. To date, most research has been confined to understanding the photochemical reactions of basic triphenylmethane dyes, with little attention being paid to the acid subclass, despite the fact that they are equal in tinctorial strength, potential commercial applicability, and fundamental interest.

The second problem arises in the field of laser spectroscopy where there is a need to produce intense light pulses of short duration in order to probe very fast photophysical and photochemical changes of various molecules. The technique called mode locking is one method of generating pulses of such duration. It may be accomplished in a number of ways, but the method most pertinent to this discussion is known as passive mode locking. It commonly employs a dye known as a saturable absorber which is placed inside the laser cavity. A saturable absorber has an absorption coefficient which is smaller for high-intensity radiation than for low-intensity radiation. Thus, high-intensity light (or peaks) within the laser cavity suffers less loss than lower intensity peaks. This leads to the generation of high peak powers, provided the saturable absorber is able to rapidly repopulate its ground electronic state. Because of their low fluorescence yield and accompanying fast nonradiative decay (section IV.B) triphenylmethane dyes have been suggested to be suitable saturable absorbers for mode locking.[102,103] In particular, basic green 4 has been studied[104,105] and has enabled pulses of sub-picoseconds to be generated when employed in conjunction with another saturable (nontriphenylmethane) dye, known as DODCI (3,3'-diethyloxadicarbocyanine iodide).[104,105]

It is clear, then, that in order to understand such complex systems it is essential to have a clear understanding of the photochemistry and photophysics of triphenylmethane dyes at the fundamental level. In the following sections both the pure and applied aspects of light interacting with triphenylmethane dyes are examined.

A. The Absorbance Spectra of Triphenylmethane Dyes

Triphenylmethane dyes exhibit many interesting spectral features which are a direct consequence of their structure and their interaction with the surrounding environment. These spectral features are often closely related to the photochemical behavior of the dyes and thus it is worthwhile achieving an understanding of how they arise.

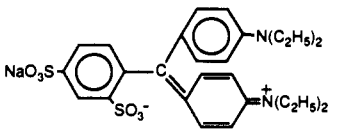
1. The Relationship between Dye Structure and Spectra

It was first pointed out by Lewis and Calvin[106] that in a planar or nearly planar molecule, there should be two types of absorption bands. These are called x and y bands since the absorptions are polarized along the

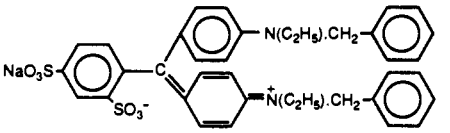
Chart I

A. Some Relevant Acid Dye Structures

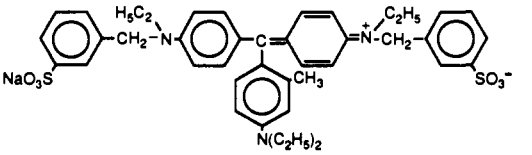
Acid Blue 1 C. I. 42045



Acid Blue 7 C. I. 42080



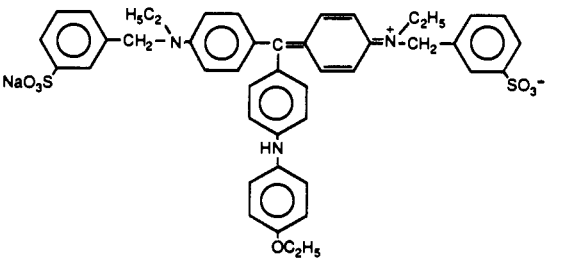
Acid Blue 15 C. I. 42645



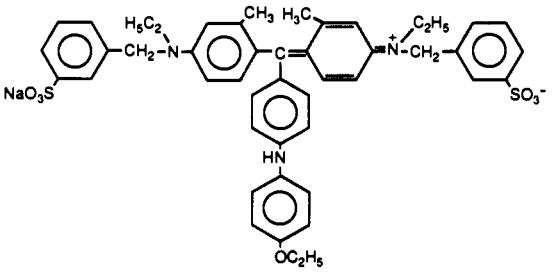
Acid Blue 20 C. I . 50405

No structure is given in the colour index. To produce this colourant sulfonate the various brands of C.I. Solvent Blue 7 (C.I. 50400) and convert the products into sodium salts.

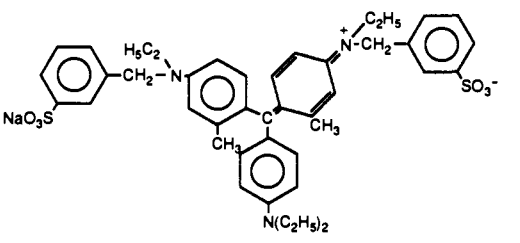
Acid Blue 83 C. I. 42660



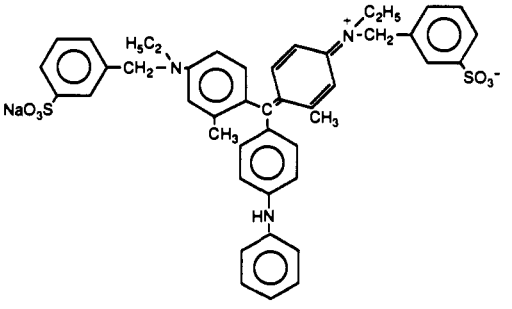
Acid Blue 90 C. I. 42655



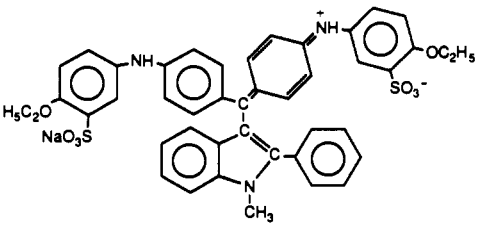
Acid Blue 104 C. I. 42735



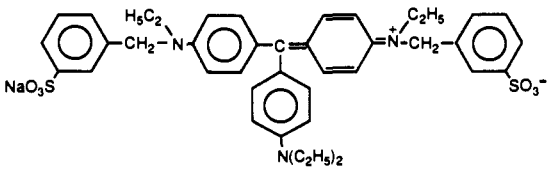
Acid Blue 109 C. I. 42740



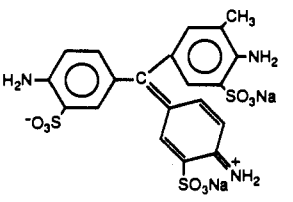
Acid Blue 123 C. I. 44510



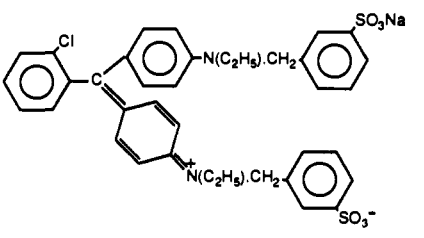
Acid Violet 17 C. I. 42650



Acid Violet 19 C. I. 42685

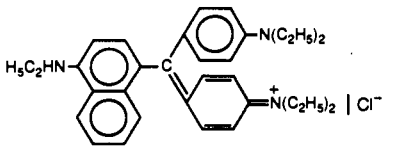


Acid Green 9 C. I. 42100

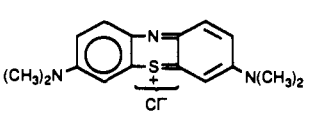


B. Some Relevant Basic Dye Structures

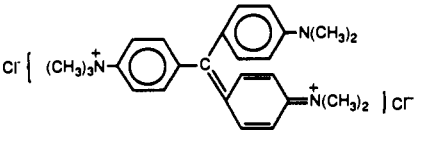
Basic Blue 7 C. I. 42595



Basic Blue 9 C. I. 52015



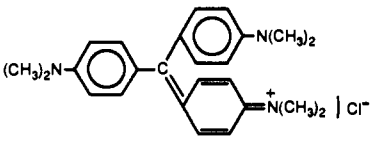
Basic Blue 20 C. I. 42585



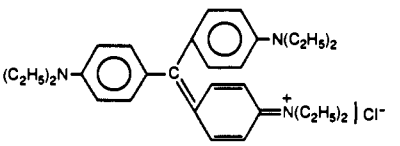
Basic Violet 1 C. I. 42535

No structure is given in the colour index as this is a mixture of the hydrochlorides of the more highly methylated pararosanilines.

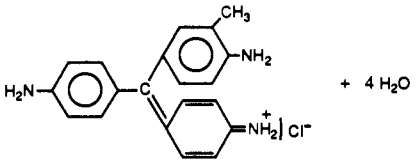
Basic Violet 3 C. I. 42555



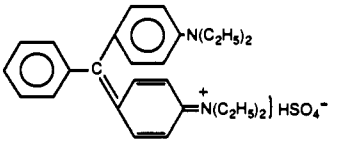
Basic Violet 4 C. I. 42600



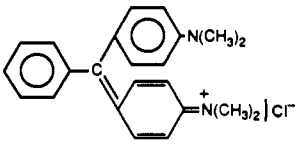
Basic Violet 14 C. I. 42510



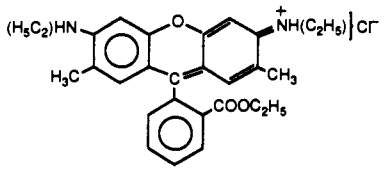
Basic Green 1 C. I. 42040



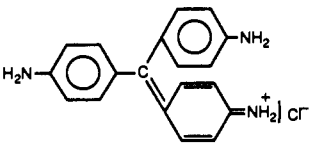
Basic Green 4 C. I. 42000



Basic Red 1 C. I. 45160

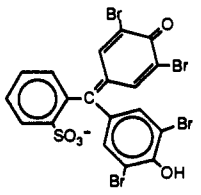


Basic Red 9 C. I. 42500

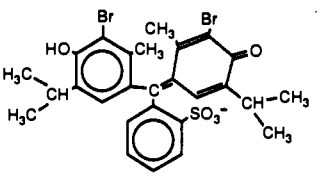


C. Related Sulfphonephthalein Indicator Structures

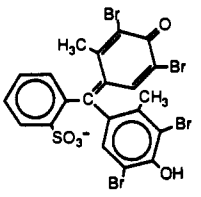
Bromophenol blue [5, 396]



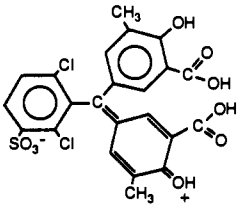
Bromothymol blue [5]



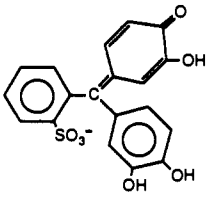
Bromocresol green [5, 43, 396]



Chromazurol S [5, 397, 419, 446]



Pyrocatechol violet [5, 47, 398]



mutually perpendicular x and y directions in the molecule. For triphenylmethane dyes this has been substantiated using polarization[107-120] and Raman[112] measurements. It has also been shown in studies of the dyes in stretched poly(vinyl alcohol) films[114,115] that there is a contribution to the absorbance in the visible and ultraviolet regions from a z-polarized transition. Figure 1 shows the x and y directions for the two triphenylmethane dyes, basic green 4 and basic violet 3, and related compounds. The z direction is directed out of the page.

Charge migration accompanying the x-band transition of basic green 4 is essentially confined to the central carbon atom and the two phenyl rings bearing the R_1 and R_2 groups (Figure 1).[121] This corresponds to the promotion of an electron from the nonbonding molecular orbital (NBMO) to the lowest antibonding orbital and produces an excited state with a high electron density on the central carbon atom.[121,122a] On the other hand, the y-band transition involves migration of electrons from the phenyl ring, bearing the R_3 group, into the rest of the system. The y band arises from excitation of an electron from the second highest occupied bonding orbital (i.e. the orbital below the NBMO) to the lowest vacant orbital.[122a] (Here, it is important to distinguish between NBMOs which are essentially delocalized π-orbitals and nonbonding atomic orbitals, which are localized on a heteroatom.[122b] The former orbitals, unlike the latter, may occur in molecules which do not contain heteroatoms,[122c] e.g. 1,3-pentadienide anion.) The maxima of the x and y bands are more widely separated the greater the optical asymmetry in the molecules.[113] This is reflected in the absorption spectra of basic green 4 and basic violet 3 in 98% acetic acid.[123a] In this solvent the x and y bands coincide (λ_{max} = 589 nm) for the symmetric dye basic violet 3 and absorb maximally at 621 and 427.5 nm, respectively,[123a] for the asymmetric dye basic green 4. In certain solvents (e.g. toluene), however, there is a pronounced splitting of the x and y bands for the symmetric dye basic violet 3. This results in a shoulder on the main absorption band in the visible region of the spectrum and this feature has been the subject of much debate. It has been attributed to two overlapping electronic transitions[107,119,120,124-129] as implied above, to the vibrational structure of a single electronic state[130] and also to the existence of two ground-state isomers[129,131-136] as discussed below. Other factors influencing the shape of the main absorption band are discussed in sections IV.A.2.a and IV.A.2.b.

Examination of molecular models reveals that the six o-hydrogen atoms, in basic violet 3 and basic green 4, are subjected to steric hindrance. In order to reduce this effect, the simplest assumption that can be made about the shape of a symmetrical dye, such as basic violet 3, is that it assumes a propeller shape. Lewis and Calvin[106] predicted that such phenyl ring rotation would give rise to two isomers A and B (Figure 2). These would result in the splitting of the main absorption band into two components α and β which correspond to the A and B isomers, respectively. Lewis, Magel, and Lipkin[135] claim to have observed the β-band in dilute solutions of basic violet 3 (10^{-4}–10^{-6} M) and low temperature (T = 114 K) solutions of basic green 4.

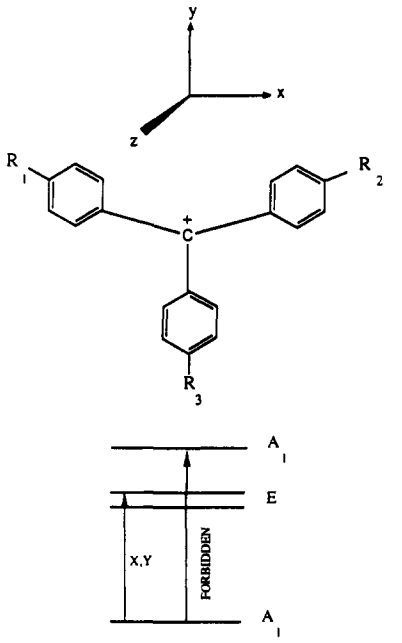


Figure 1. Structures of various triphenylmethane dyes and the x and y dichroic axes of the molecules, along with the energy level scheme for basic violet 3 according to Adam and Simpson,[107] where $R_1 = R_2 = R_3 = N(CH_3)_2$ for basic violet 3; $R_1 = R_2 = N(CH_3)_2$, $R_3 = H$ for basic green 4; $R_1 = R_2 = R_3 = H$ for the triphenylmethyl cation; $R_1 = R_2 = N(CH_3)_2$, $R_3 = OCH_3$ for methoxy basic green 4; $R_1 = R_2 = N(CH_3)_2$, $R_3 = O^-$ for 4,4′-bis-dimethylamino fuchsone. (Reprinted from ref 107. Copyright 1959 Academic Press Inc.)

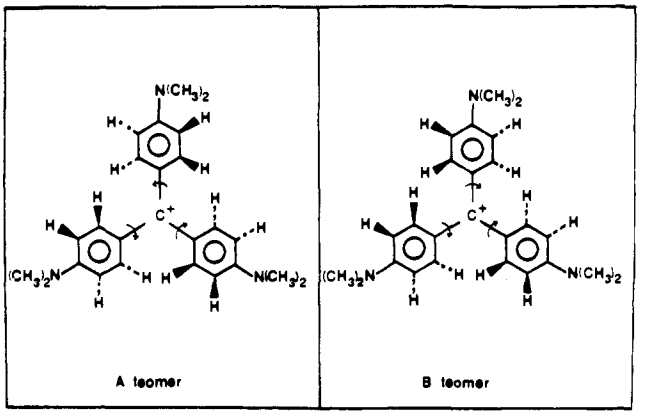
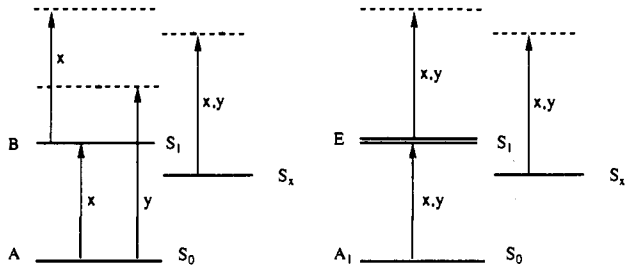


Figure 2. The rotational isomers of basic violet 3 predicted by Lewis and Calvin.[106] In the A isomer all the rings are twisted in the same direction. The A isomer has D_3 symmetry. In the B isomer, one ring is twisted in the opposite sense to the other two. The idea of phenyl ring rotation was invoked to relieve steric hindrance between the six ortho hydrogen atoms. (Reprinted from ref 106. Copyright 1939 American Chemical Society.)

However, this spectral assignment was subsequently challenged by Looney and Simpson,[126] Barker et al.[137] and more recently by Korppi-Tommola et al.[124,125] Also resonance Raman,[130,138,139] magnetic circular dichroism,[140] and X-ray[141] studies suggest that only one conformer of basic violet 3 exists in both solution and solid media. It has been refuted that the α- and β-bands arise from vibrational structure of one electronic band, as suggested by Angeloni et al.,[130] since there is a lack of structure in the fluorescence spectrum of basic violet 3.[127] Also the observation that the short wavelength shoulder of the visible absorption band tends to diminish at lower temperatures while the long wavelength portion of the peak is enhanced[135] also denies the possibility that the band structure arises from partially resolved vibrational structure of a single electronic state, as this is just the opposite of the predicted result. Furthermore, this hypothesis may be rejected on the basis of the mathematical band-shape analysis, of the absorbance spectra of basic violet 3 and basic green 4 in methanol and glycerol, performed by Menzel and Kessler.[128] This treatment revealed that when the absorbance spectra of the dyes was deconvoluted into a minimum of two subbands, each subband exhibited a different halfwidth, which is also contrary to expectation based on a vibrational progression. Hückel molecular orbital calculations predict an energy level scheme (for C_{3v} symmetry) that suggests that the α- and β-bands arise from the absorptions from one ground state (A_1) into two neighboring excited electronic levels (E)[107] (Figure 1), rather than as implied by Lewis et al.[135] that the absorptions can be attributed to two different ground states. Such an interpretation is also in accord with HMO calculations,[142] and PPP-SCF-CI calculations[140] based on D_3 symmetry (where the weak z-polarized transition to the A_2 state is neglected).[114,143] The possibility that the higher energy state of the doublet is a twisted intramolecular charge transfer state (TICT) has been considered.[124] However, this alternative was considered unlikely since it was unable to explain (a) why the β-band of basic violet 3 in toluene is blue-shifted relative to that in alcohol[124,125] and (b) why basic violet 3 exhibits temperature dependent absorbance spectra,[124,135,144] whereas the triphenylmethyl cation does not.[140] Interestingly, work[144,145] on the viscosity-dependent radiationless relaxation of triphenylmethane dyes also considers the involvement of a TICT state. However, unlike the above suggestion, the energy of this state is lower than the initial state prepared by absorption. Nevertheless, the hypothesis by Lewis and Calvin[106] of the existence of two isomers of basic violet 3 provoked numerous studies (of which only a few are indicated)[110,119,120,130,141,146-161] which attempted to determine the configuration of triphenylmethane and related compounds, in both the excited and ground states. Several of these favor the propeller-shaped D_3 geometry for the ground-state triphenylmethyl cation.[141,154,162] The configuration in which one of the phenyl rings is twisted out of the plane more than the others, pseudo-C_{2v}; the pyramidal structures, C_3 and C_{3v}, and the D_3 propeller configuration, have been suggested for basic violet 3 and basic red 9 ground-state conformers.[107,110,114,117,126,138] Several of the most recent studies[119,130,138] suggest only one ground-state conformer, with D_3 symmetry for basic violet 3, with the phenyl ring rotated 32° from the central plane.[141]

Mokhtari et al.[120] point out that their recent time-resolved transient excited-state absorption results, for basic green 4 and basic violet 3 in water (λ_{ex} = 620 nm and λ_{probe} = 390 nm), fail to account for the ratio of the amplitudes of the photoinduced absorption recovery signals obtained using parallel and crossed pump–probe polarizations, as predicted by polarization analysis. The results do, however, support the research discussed above, that the molecular symmetries of the dyes are close to a D_3 point group for basic violet 3 and a C_2 point group for basic green 4. The polarizations for the transitions applicable for these symmetries are shown



Basic green 4 for C_2 symmetry

Basic violet 3 for D_3 symmetry

In both cases s_x has unknown symmetry.

Figure 3. The polarizations of several transitions frequently probed in photophysical studies of basic violet 3 and basic green 4, assuming D_3 and C_2 symmetry, respectively. (Adapted from ref 120. Copyright 1987 The American Institute of Physics.)

in Figure 3 along with the corresponding first three singlet states (S_0, S_1, and S_x) frequently discussed in the literature concerning the photophysical deactivation of triphenylmethane dyes (see section IV.B). While these schemes may be suitable for explaining results from Raman spectroscopy,[130,138,139] they are perhaps best considered as a starting point in any explanation of the complex photophysical deactivation dynamics observed for triphenylmethane dyes. Instead, as Mokhtari et al.[120] note, in a consideration of such dynamical properties, this class of dyes is more reasonably treated as an inhomogeneous set of thermally twisted molecules distributed around the initial symmetry.

The reorientational correlation time of the phenyl groups of triphenylmethane in carbon tetrachloride solution has also been examined, by Raman line-shape analysis, in order to examine the interaction between the phenyl groups within the molecule.[163] This study found that the reorientational correlation time of the phenyl groups of triphenylmethane in carbon tetrachloride was 18.6×10^{-12} s^{-1}, which is approximately six times larger than that found for toluene in the same solvent (2.88×10^{-12} s^{-1}). Nomura et al.[163] ascribed this difference to the fact that the rotational motion of the phenyl groups of triphenylmethane, in carbon tetrachloride, is more strongly hindered than that of the phenyl group in toluene. Strong interactions among the phenyl groups of triphenylmethane arising from steric hindrance and π-coupling were said to be responsible for the restricted motion.

On the basis of steric effects alone, ortho substituents are expected to modify the spectra of triphenylmethane dyes by increasing the departure from molecular planarity. The resultant spectral shift however, will be a superimposition of the steric effect and the electronic effect caused by the ability of the substituent to withdraw or donate electrons. This idea provoked Barker, Hallas, and co-workers[137,164-166] to perform studies on numerous triphenylmethane dyes. Also see references reviewed by Fabian and Hartman.[167]

The theoretical treatment by Dewar[123b] predicts that the steric response of the symmetrical dye basic violet 3 to an ortho substituent should be bathochromic (shift to longer wavelengths), with a reduction in intensity of the x band. Theory[142] also predicts that an electron-donating ortho substituent will cause a hypsochromic shift (shifts to shorter wavelengths), whereas an electron-withdrawing group would cause a bathochromic shift. Thus, as noted by Barker et al.[123a,137] when an *o*-methyl group (a bulky, electron donor) is introduced into basic violet 3, the steric and electronic effects are opposed. The net effect, however, is a reduction in intensity and a bathochromic shift.[123a,137,168]

The steric substituent effects induced in the asymmetric dye, basic green 4 (where one of the phenyl rings may undergo most of the rotation), represent a more complex situation due to lower molecular symmetry. Introduction of an ortho substituent into the unsubstituted phenyl ring (R_3 = H in Figure 1) of basic green 4 is expected to produce a hypsochromic shift and a decrease in the intensity of the y band. The x band is expected to show a bathochromic shift and a decrease in intensity (due to enforced bond rotation). Although the y band is observed to behave this way, the x band exhibits an increase in intensity, and no satisfactory explanation is available yet.[122d]

Further discussions on this effect and the electronic effects of substituents in the unsubstituted phenyl ring of basic green 4 are found in review articles by Hallas,[169] Gordon and Gregory,[2b] and Fabian and Hartman.[167] These authors also discuss spectral changes caused by other types of variations in triphenylmethane dye structure, as do Ferguson and Hallas.[170]

In general, alkylation of the amino groups of these dyes produces a bathochromic shift in the principal absorption band; this reflects the degree of merging of the lone electron pair on nitrogen with the π-electron system of the benzene ring. This interaction is greater for methyl substituted dyes:[171] Upon alkylation, Doebner's violet (a salt of 4,4'-diaminotriphenylmethanol) is converted to basic green 4 (malachite green). Similarly, basic red 9 (paramagenta, pararosaniline, or parafuchsin) (bluish red) is converted to basic violet 3 (crystal violet), which can further be methylated to give basic blue 20 (methyl green),[1b,172] and the commensurate bathochromic shift.[1b,171,172]

Current research is directed toward examining the absorbance spectra of monoethynologues of triphenylmethane dyes.[173-177] These compounds, by virtue of an ethylenic bond between the central carbon atom and an aryl group of the dye structure, are planar unlike the classic triphenylmethane dyes. Although this results in a new resonance system involving an allene–quinoid structure, it releases steric congestion between *o*-hydrogen atoms of the phenyl groups, allowing a clearer indication of the electronic effects of various para substituents to be observed.[176,177] It also produces dyes which absorb further into the infrared than the classic triphenylmethane dyes.[173,174,176]

2. The Effect of Environment on Dye Spectra

a. The Effect of Changing the pH. The absorbance spectra of triphenylmethane dyes are also greatly dependent upon the pH value[3b,6a,9,42,47,106,178-193,194a,195-203] (Figure 4). Use has been made of this by Cigén and co-workers[204-208] in spectroscopic studies on the protolytic equilibria of basic triphenylmethane dyes. Other workers have also studied this behavior.[75,181,209-220] Also see references reviewed in several other articles.[44a-e,69,221,222]

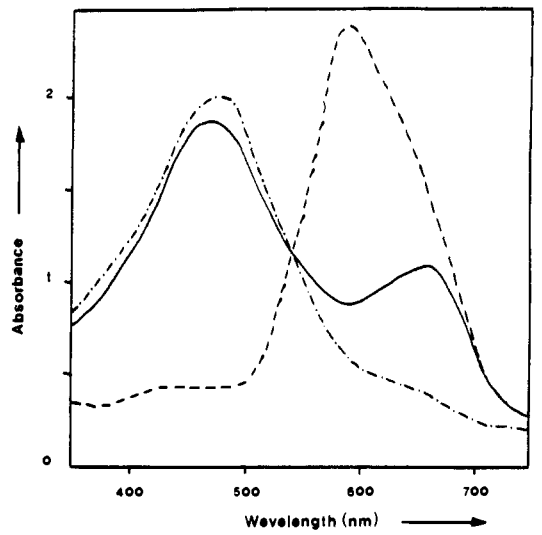


Figure 4. pH-dependent changes in the spectrum of acid blue 90: (—) acid blue 90; (- - -) acid blue 90, pH = 1.25; (- · -) acid blue 90, pH = 0.3. (Adapted from ref 75. Copyright 1985 Academic Press Inc.)

Several groups[223,224] have examined dye indicator equilibria in water solubilized by surface-active agents in benzene. It was suggested that for dyes which are uncharged prior to protonation and therefore partitioned in the bulk benzene, H^+ transfer occurs either across the micelle hydrocarbon barrier or by an encounter of reactants upon dissociation of the dodecylammonium propionate aggregate, since water is contained in the surfactant aggregate. Otherwise, when a dye is charged in both the protonated and unprotonated states, the dye exists within the surfactant trapped water, which is also the location of the hydrogen ions. Other groups have studied the surface pH of micelles using bromophenol blue (α,α-bis[(3,5-dibromo-4-hydroxyphenyl)-α-hydroxy-o-toluenesulfonic acid γ-sultone) and bromocresol green (α,α-bis(3,5-dibromo-4-hydroxy-o-tolyl)-α-hydroxy-o-toluenesulfonic acid γ-sultone).[225]

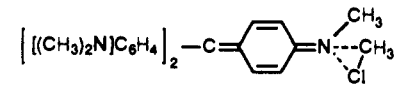
The associative and aggregative reactions between the organic triphenylmethane dye cation and anions in ionic solution affect protonation.[214,215]

The observation that alkaline solutions of the basic dyestuffs are totally decolorized has led to further studies on kinetic solvent effects where carbonium ions derived from various triphenylmethane dyes react with nucleophiles either added to various solvents or from various protic, aprotic, and dipolar aprotic solvents.[222,226-236] This phenomenon is sometimes referred to as alkaline fading.[210,226,232,237-243] Alkaline fading of cationic triphenylmethane dyes in aqueous solution can be accelerated by cationic polyelectrolytes[241,242] and cationic surfactants[226,237,238,242,244] usually in the form of micelles.[226,242] Conversely, anionic polyelectrolytes and anionic surfactants can retard the alkaline fading of such dyes[237,238,241,242] as can nonionic surfactants.[226] It has been observed that these effects are greatest when the dyes, polyelectrolytes, and surfactants[226] have large hydrophobic groups. For the related sulfonphthalein indicators the rate of fading is virtually unchanged in the presence of anionic surfactants[238] and retarded by cationic surfactants.[225,238] It should be noted that these references do not rigorously review the kinetic solvent effects. Rather they are mentioned here firstly to point out that triphenylmethane dyes may be decolorized not only by the action of light but also by chemical processes and secondly to direct those that are interested in the direction of more detailed literature.

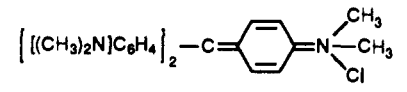
b. The Influence of Dye Concentration, Simple Salt Concentration, Solvent, Temperature, and Pressure. A particularly interesting feature of the absorbance spectra of this class of dye is the splitting of the main absorption band into two absorption bands (α and β mentioned previously in section IV.A.1) (Figure 5). It is observed in solid[183,245-247] and liquid media[124,133,135,183,246,248-262] and is more pronounced for triaminotriphenylmethyl dyes (e.g. basic violet 3) than the diaminotriphenylmethyl type (e.g. basic green 4).[135,183,251,257,260] The relative intensity of the α- and β-bands has been frequently observed to change with variations in the (a) dye concentration,[133,135,183,246,249,251,253-255,257,258,261-264] (b) simple salt concentration,[135,258] (c) solvent,[135,183,249,258,258] (d) temperature,[124,135,144,255] and (e) pressure[131-133] of the system.

When the dye concentration is increased, the spectral changes observed are an enhancement of the β-band and diminution of the α-band. As the dye concentration is increased further, both the α- and β-bands are depressed and replaced by γ- or μ-bands, which appear on the short wavelength side of the α- and β-bands (Figure 5).[79]

One early study on basic violet 3 attributed this phenomenon to dye tautomerism.[252] At high dye concentration, basic violet 3 was believed to adopt an addition type product structure (red colored) in which methyl chloride is bound to the nitrogen atom by partial valencies, while at low dye concentration the dye formed an ammonium salt type structure (blue colored). These two forms were depicted as shown in eq 1:

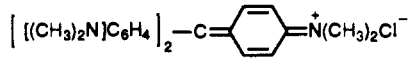


believed to be red



believed to be blue (1)

However, at high dye concentrations, a more likely possibility is that the chloride ion covalently binds to a site on the aromatic ring. In the blue form the nitrogen to which the chlorine is attached is depicted as being pentavalent. This is not possible and a better representation would be to represent the structure as



Other studies[133,183,248,255,259,262-265] have attributed this phenomenon to dye aggregation, the α-band being attributed to the monomer, the β-band being attributed to the dimer, and higher polymeric forms of the dye being associated with the μ- and γ-bands. Similar spectral behavior is observed in the photocurrent spectrum of basic violet 3 adsorbed onto the surface of an oriented ZnO(0001) single-crystal electrode[133] and the visible absorbance spectrum of basic violet 3 adsorbed onto CdS.[263] In addition, a study[268] of solid solutions of triphenylmethane dyes has revealed that

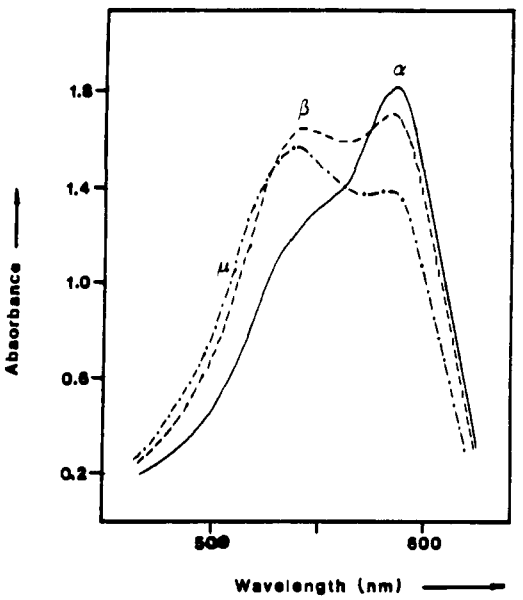


Figure 5. The absorbance spectra of aqueous solutions of basic violet 3:[302a] (—) 2×10^{-5} M; (- - -) 5×10^{-4} M; (- · -) 2×10^{-3} M. The α-band occurs at 590 nm, the β-band occurs at 550 nm, and the μ-band occurs at 510 nm. (Reprinted from ref 302a. Copyright 1980 Elsevier Applied Science Publishers.)

dye–dye interactions can produce an additional spectral band (the L-band) on the long wavelength side of the α-band. The band was not observed in solution spectra.

It has been suggested that an increase in the degree of sulfonation, or more symmetrical sulfonation in a dye or an increase in the number of benzene rings or amino group substituents, enhances dye aggregation.[183,267,268]

Dye aggregation is a well-established phenomenon[269-271] and many other studies have been performed on triphenylmethane dye aggregates.[252,272-260]

Lewis, Magel, and Lipkin[135] observed the β-band in dilute solutions of basic violet 3 (10^{-4}–10^{-6} M) and low temperature (T = 114 K) solutions of basic green 4. While they were aware of the effect of aggregation on the absorbance spectra of this class of dye, they considered that the α- and β-bands arose, respectively, from the A and B isomers previously predicted by Lewis and Calvin[106] (Figure 2). As indicated previously in section IV.A.1 of this review, this spectral assignment was subsequently challenged.

Clark and Drickamer[133] have dispersed triphenylmethane dyes in polymeric[131,281] and aqueous media[131-133,281] to probe the effects of local environment on the rotational isomerization process of the dye molecules. Optical absorption spectroscopy was used to monitor the isomerization process in all media at room temperature as a function of pressure. In general the α- and β-absorption peaks shift to lower energy with increasing pressure, which is characteristic of π–π^* transitions. However, the β-peak of basic violet 4 shifted to the blue with increasing pressure.[132] Similar shifts have been observed in the photocurrent spectra of basic violet 3 adsorbed to the surface of an oriented ZnO-(0001) single-crystal electrode with increasing pressure.[133,281] It is worthwhile noting here that variable-temperature studies on basic violet 3 in alcohol solution showed that the β-peak red-shifted with decreasing temperature while the α-peak remained unchanged.[124] This latter study argues against conformational isomerism in triaminotriphenylmethane dyes; however, the idea that triphenylmethane dyes exhibit conformational isomerism has recently been invoked, by some researchers, to explain the mechanisms by which these dyes undergo radiationless transitions (section IV.B).

The spectral changes shown in Figure 5 have also been interpreted in terms of the influence of the counterion on the π-electron system of the dye. Triphenylmethane dyes are resonance stabilized and under conditions which are conducive to dye–counterion interactions, the counterion may preferentially stabilize one of these resonance structures. In a dye molecule such as basic violet 3 (Figure 1), the counterion may either stabilize the form of the dye in which the central carbon atom bears the positive charge or one of the resonance structures in which a terminal amino group is positively charged. McKay and Hillson[258] have suggested that dye–counterion attraction causes the absorption spectrum to shift to shorter wavelengths, irrespective of whether the interaction occurs at a terminal amino group or at the central carbon atom. In addition, they suggest that the greater the loss in energetic symmetry caused by such an interaction, the greater the loss in the molar extinction coefficient of absorption. A similar idea has been discussed in ref 282. Lomonosov and Nikolaev[282] note, as discussed in a series of papers,[214,283-285] that it was shown that association of a triphenylmethane dye cation with an anion occurs via the part of the cation bound by the two most basic groups, where the resonance structures have their greatest localization of positive charges. Since in triphenylmethane dye cations the association area is on the outside of the main conjugation chain, they argue that the association of basic violet 3 with an anion will create a hump on the short wavelength side of the main absorption band. It is to be noted, however, that the study by Lomonosov and Nikolaev[282] does not consider the effect of varying the dye concentration. It is interesting to note here that early X-ray crystallographic data[286] on hexamethyl violet [$[(CH_3)_2NC_6H_4]_3$-CCl] suggest that the halogen is located on the central carbon atom.

McKay and Hillson[258] claim that an increase in dye concentration or addition of salt to a dye solution (prepared from a dye in which the characteristic charge is an integral part of the chromophoric system) increases dye–counterion attraction. Similarly, it has been proposed[107,135,249,250,258] that solvents of low dielectric constant support the formation of ion pairs. It has also been shown that for a constant concentration of triphenylmethane dye in aqueous solution, addition of salt can result in an alteration of the shape of the main absorption peak.[258,265]

A study by Feichtmayr and Schlag[250] draws attention to the fact that both dye–counterion interactions and dye aggregation effects may occur simultaneously. They interpreted their spectral data for several triphenylmethane dyes in solid and solution, in terms of an equilibrium between three forms of the dye salt: (1) dissociated ions surrounded by solvent, (in the case of their solution studies), or by residual solvent within the solid polymer films employed or by polar groups of the polymers (in the case of their studies in solid substrates); (2) ion pairs; and (3) dimers or higher

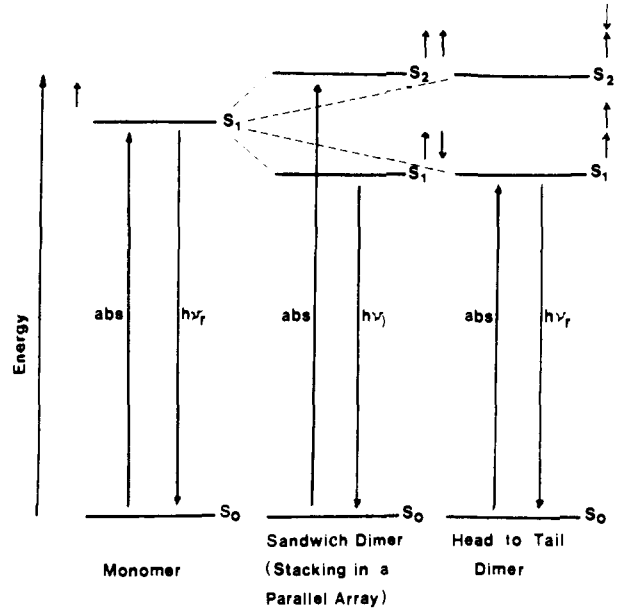


Figure 6. The effects of aggregation on the absorption and fluorescence emission of dye molecules.[299,302a] The arrows represent transition dipole moments, abs represents the absorption of light, and $h\nu_f$ represents the fluorescence emission. (Reprinted from ref 302a. Copyright 1980 Elsevier Applied Science Publishers.)

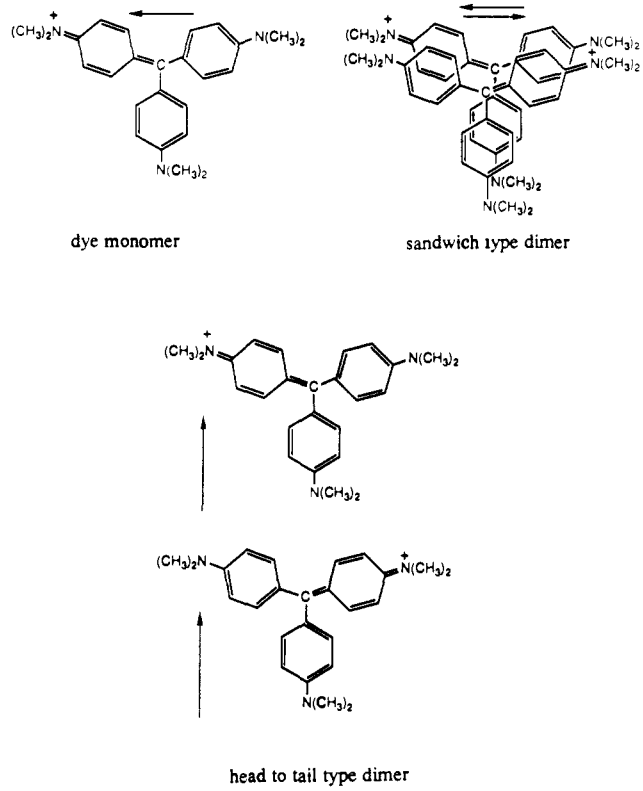


Figure 7. The relative geometry of the monomeric components in two types of basic violet 3 dimer. The arrows represent the approximate direction of the transition dipole moment for the absorption polarized along the x direction of the dye (refer to figure 1). (Adapted from ref 362. Copyright 1980 The Chemical Society of Japan.)

polymeric forms. They argued that in solutions that have a high dielectric constant (except water which is unable to 'solvate' organic molecules)[258] the dye would exist in form 1, whereas in solutions that have a low dielectric constant forms 2 and 3 would be more stable. Thus, the presence of an α-band in the dye spectra in either solid or solution, indicated the presence of dissociated ions. Similarly, the presence of a β-band indicated the presence of either ion pairs or aggregated dye molecules. However, later work by Blandamer et al.,[287] using electron spin resonance and absorbance spectroscopy, presents strong evidence that the spectral changes, observed by varying the dye concentration, are caused by dye aggregation rather than dye ion–counterion pairing. Levshin and Slavnova[288] also discount the proposal by Feichtmayr and Schlag[249] that counterion pairing is responsible for the spectral changes. Although they acknowledge that anions have a very strong effect upon the association of dye molecules.[279] More recently, it was observed[289] that addition of NaCl (up to 10 mM) to a 10 μM solution of basic violet 3 in 90% isopropyl alcohol essentially left the dye spectrum unchanged. Addition of 10 mM of NaBr resulted in a slight enhancement of the absorption band centered at 302 nm and addition of 10 mM of NaI caused the appearance of a broad absorption band at 353 nm. No comments were made regarding the alteration of the shape of the main absorption peak in this paper. However, the spectral changes noted were attributed to ion pairing and the consequent appearance of a charge-transfer type transition, the charge-transfer absorption frequency being dependent on the ionization potentials of the halide counterion i.e. $I^- < Br^- < Cl^-$.

Levshin and co-workers[255,272,288,290,291] have determined the forces which are responsible for dye aggregation. They found that triphenylmethane dyes dissolved in aqueous solution, or in binary mixtures of polar and nonpolar solvents, associate mainly via hydrogen bonding.[255,272,288,290,291] The formation of hydrogen bonds can take place among the dye molecules themselves or with the help of the solvent which links the dye molecules with hydrogen-bond formation. Furthermore, they claim that London dispersion forces play a minor role in enabling the dyes to associate. In the latter papers discussed,[290,291] they note that the concept of hydrogen bonding is insufficient to explain all the spectral effects observed for solutions of dyes, since hydrogen-bonding interactions between dye and solvent, in dilute dye solutions, do not produce spectral changes of the same magnitude as those observed for concentrated dye solutions. In order to explain these effects they rely on the theories by Davydov[292,293] and Förster.[294] This theory treats the resonance interaction of excited states of weakly coupled composite systems. Essentially it points out that, when two molecules are linked close together by weak intermolecular forces (hydrogen bonds, van der Waals forces), the dispersion or resonance interaction is greatly increased and this produces splitting of the electronic levels and deformation of the electron spectra. The exciton model has been advanced by McRae and Kasha[295–299] and more detailed accounts of its development are available in several articles.[271,300,301]

For a more pictorial explanation the reader is referred to Figure 6. This diagram shows that dye aggregation causes the excited singlet levels of the aggregate to split relative to those of the monomer, but essentially leaves the ground state unchanged. Furthermore, the wavelength of absorption depends on the relative geometry of the monomeric components in the dimer as shown

in Figure 7. In this figure, one of the resonance structures of basic violet 3 is shown along with the approximate direction of the transition dipole moment for the absorption polarized along the x direction of the molecule (see section IV.A.1 and Figure 1). When this monomer combines with another dye monomer to form a sandwich-type dimer the dipole moments for each monomeric component of the dimer will be opposed, in order to minimize the energy of the complex. Therefore, for this type of dimerization, the transition dipole moments for each monomeric component of the dimer will also be opposed and this results in the $S_0 \rightarrow S_1$ transition being forbidden. The opposite is true for the $S_0 \rightarrow S_2$ transition, and so the absorbance of this dimer is blue-shifted relative to the monomer transition. In the case of head-to-tail stacking the $S_0 \rightarrow S_1$ transition is allowed since the individual transition dipole moments of the monomeric components do not cancel. Consequently, for this type of dimerization the absorption is red-shifted relative to the monomer transition.[299,302,303a] Spectral changes consistent with the formation of aggregates are frequently observed for many organic dyes. In particular, the absorbance spectra of basic dye (C.I. 45010),[259] basic blue 9,[245] and basic red 1[279,291] etc., show that these compounds, like triphenylmethane dyes, also form dimers from a parallel arrangement of dye monomers.

As a brief summary to this subsection it is noted that current thought recognizes that at constant ionic strength, dye aggregation, and either rotational isomerism or ground-state absorption into two neighboring excited electronic states lead to the splitting of the main absorption peak, but it refutes that counterion pairing is responsible (except in the sense that counterion pairing may aid dye aggregation).[279] Basic violet 3 illustrates this behavior, as reported in refs 133 and 262. For this dye it would seem that at aqueous dye concentrations less than 5×10^{-5} M and at 1 atm of pressure, the A and B isomers (Figure 2) absorb maximally at 595 and 549 nm, respectively. Whereas, for aqueous dye concentrations greater than 5×10^{-5} M and 1 atm of pressure, the dimer absorbs maximally at 540 and 625 nm. The latter band, however has a small transition moment and is not usually observed.

c. *The Effect of Adding Other Organic Species.* Complex formation between cationic triphenylmethane dyes and organic anions also results in changes in the absorbance spectrum of the triphenylmethane dye. Gicquel et al.[304] have shown that charge transfer complexes are formed between the triphenylmethane dye (which acts as the acceptor) and the sulfonated azo dye (which acts as the donor). They have also shown that both the SO_3^- group and the N=N group must be present in the azo dye for the phenomenon to be observed. Owen et al. have also studied complexes between cationic triphenylmethane dyes and disazo dyes[305] and xanthene dyes.[306] Interestingly, several studies report that cationic triphenylmethane dyes are also able to complex with basic red 1 which is a cationic xanthene dye[306,307] and cationic acridine dyes.[308]

Hamai[309] observed spectral changes in basic violet 3 upon addition of either 1-naphthaleneacetate, 1-naphthalenesulfonate, 2-naphthalenesulfonate, or 2-anthracenesulfonate and ascribed these to the formation of 1:1 complexes between the dye and the monoanion. Frequently the term metachromasy is used to describe the color change observed when an organic cation (such as a dye) is mixed with an organic anion[304,305] or the color changes observed upon changing the dye concentration.[258] Sometimes, however, it is treated separately[309] and reserved for the color change described below, which occurs when a polyelectrolyte is added to a dye solution.

d. *The Influence of Polyelectrolyte on Triphenylmethane Dye Spectra.* Similar spectral changes to those induced by increasing the dye concentration can be observed when a dye binds to a polyelectrolyte. Unlike spectral changes observed when a dye aggregates, those induced when a dye binds to a substrate can be observed when the dye concentration is low. Addition of appropriate polyanions in approximately equivalent amounts, produces a spectrum similar to that of the dye at its highest concentration in aqueous solution, i.e. with a prominent μ-band and depressed α- and β-bands. This phenomenon is known as metachromasy (the appearance of more than one color) and was first documented in the works of V. Cornil, L. A Ranvier, R. Jürgens, and R. Heschl in 1875 (according to Bergerson and Singer[310]). It can be subdivided into two types, one called simple metachromasy and the other called compound metachromasy. In simple metachromasy, solutions containing two metachromatic dyes and a polyanion have spectra almost identical with the sum of the spectra of solutions of the separate dyes, each in the presence of the polyanion. This is attributed to dye ions which occupy adjacent sites on a polyelectrolyte chain and interact such that their spectral behavior is analogous to that which is observed when they form aggregates in more concentrated solutions.[311] In compound metachromasy, deviations from additivity of spectra are large, and it is believed that heteropolymers are formed from pairs of dyes, each stabilized by the polyelectrolyte.[311] The polyelectrolytes employed in most studies are macromolecular; however, this need not be the case. It has been shown that certain inorganic compounds like ammonium molybdate[312] and mercuric chloride[313] can induce metachromasy in aqueous solutions of basic violet 3. Similarly, the highly negatively charged inorganic colloids, sodium and potassium silicates, can alter the absorbance spectrum of basic violet 3.[314]

Unlike the spectral changes observed when a dye dimerizes, those induced when a dye interacts with a polyelectrolyte do not always show an enhancement of the β-band. As an example, addition of polymethacrylic acid to a solution of basic violet 3 causes the β-band to disappear,[315] whereas addition of the appropriate amount of mucopolysaccharide chondroitin sulfate enhances the β-band.[261,302a] Other reports on basic violet 3, in the presence of various polyelectrolytes, reveal that a metachromatic band (called the L-band) can occur on the long wavelength side of the principal absorption peak.[316-319] In several studies on basic green 4,[320,321] a band appeared on the long wavelength side of the α-band when poly-α-L-glutamic acid was added to a solution of the dye. The appearance of this band was very sensitive to the experimental conditions, such as the temperature of the solution,[320] and standing time after mixing the solution[320] in addition to other con-

ditions discussed later. This band was only observed for an aqueous dye concentration of 2×10^{-5} M when the pH and the dye/polymer ratio were between 4.5 and 5.5 and 20 to 100, respectively, with the minimum amount of salt present in solution.[321] It was attributed to the formation of a dye–poly-α-L-glutamic acid complex, but interestingly, it was not observed when basic violet 3 was examined.[320] In some instances, however, interaction with a substrate may induce a dye to obey the Beer–Lambert law at a concentration where the free dye does not.[322] Also consult references quoted in the review by Bellin.[322]

Numerous studies[73,191,209,213,248,261,314-319,321,323-354,362] have been performed on a variety of triphenylmethane dye–polyelectrolyte systems and early works on the subject (in general) have been reviewed in several articles.[252,310,355-358] It is clear from many of these studies that metachromasy is a complex phenomenon and is more pronounced for triaminotriphenylmethane dyes than diaminotriphenylmethane dyes.[314,328,329,335,338,343] Metachromasy is exhibited only by dyes in which the characteristic ionic charge is an integral part of the chromophoric system and is distributed throughout the system by resonance.[270,359] Many of the above-mentioned studies reveal that the relative intensity and/or wavelength position of the α-, β-, γ-, and μ-bands in the observed dye spectrum (i.e. the experimentally obtained spectrum indicating the absorbance of both the bound and unbound dyestuffs) are dependent upon the experimental conditions e.g. the ionic strength of the solution,[248,261,333,335,341,360] although exceptions are known,[318] dye to polyelectrolyte ratio,[209,261,316,318,319,327,333,334,341,348,360-362] pH,[319,327] dye concentration,[261,350,360] and the nature of the polyelectrolyte[248,316,318,319,330,335,344,348,350,352,360] (including its overall or local conformation,[248,318,319,320,327,341,362] functional or ionizable group(s),[248,318,348] and chain length.[360] Also compare refs 316 and 318. These changes occur because metachromatic compounds are unstable. Such compounds can be destroyed by heat, addition of salts, cetylpyridinium chloride,[346] a large excess of polyanion (including proteins), or the addition of dioxane, alcohol, or urea etc.[209,261,311,329,333,341,344-346,350]

It is clear, from the experimental evidence quoted, that the parameters which influence the spectral changes observed in the absence of a polyelectrolyte are in many cases also able to influence the spectral changes observed in the presence of a polyelectrolyte. Due to this complexity, it is frequently very difficult to unambiguously demonstrate, whether electrostatic dye–substrate interactions or hydrophobic (van der Waals) dye–dye interactions are responsible for the spectral changes observed in the presence of a polyelectrolyte.

Nevertheless, it is possible to gain a reasonable understanding of how the experimental parameters relate to the observed metachromasy by referring to Figure 8a. This diagram was adapted from ref 341 and shows the dye cations attached to adjacent anionic sites of the polyelectrolyte (also known as a chromotrope) by means of electrostatic bonds. Such dye ions may undergo effective polymerization, involving either hydrophobic bonds or other dye–dye bonds. These interactions depend upon the distance and angle between the groups involved (compare with the exciton

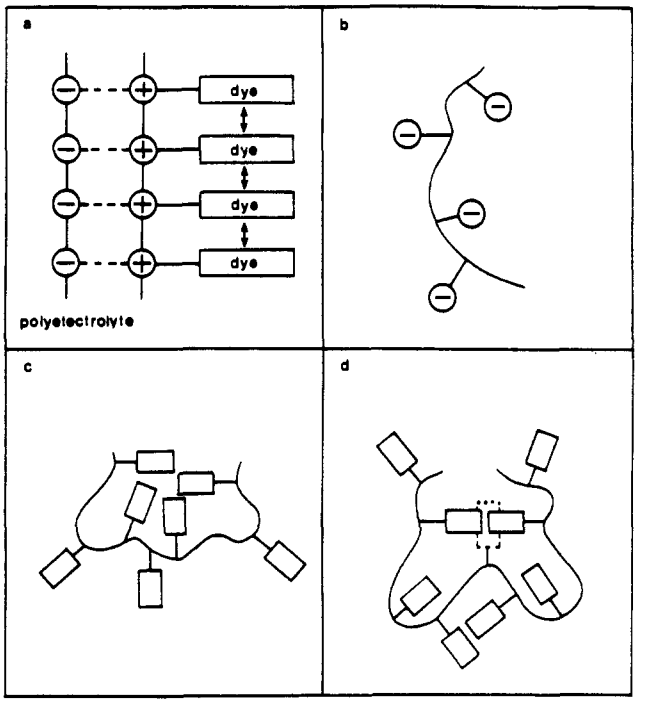


Figure 8. Dye binding to polymer substrates:[341] (- - -) denotes an electrostatic bond; (↔) denotes a hydrophobic bond or another type of dye–dye bond. (Reprinted from ref 341. Copyright 1958 Hüthig and Werf Verlag, Basel.)

theory mentioned previously) and are believed to be responsible for the observed metachromasy. This aspect explains why metachromasy is dependent upon the intersite spacing of the polymer (hence polymer configuration) and the dye concentration. Consequently, any reagent capable of destroying the dye–dye bonds will destroy metachromasy, irrespective of whether or not the dye is removed from the chromotrope. Ethanol, dioxane, and urea[345] are believed to effect metachromasy in this way. On the other hand reagents or elevated temperatures that are capable of breaking or inhibiting the electrostatic bond between the dye cations and the chromotrope will disturb the polymerization by removing the dye ions from the chromotrope. Electrolytes are believed to destroy metachromasy in this way because they displace dye ions from the anionic sites in the polyelectrolyte. Similarly cetylpyridinium chloride displaces basic violet 3 stoichiometrically from chondroitin sulfate and heparin. This process is not reversible and cetylpyridinium chloride tends to form hydrogen bonds with itself when attached to the polyanion. On the basis of the above discussion it is evident why conductivity measurements have been used to estimate the extent of interaction between the dye and the polyelectrolyte.[350]

Addition of excess polyelectrolyte affects metachromasy by binding the dyes at remote anionic sites on the chromotrope thereby inhibiting dye–dye interactions. The process involving desorption of the dye, however, necessarily involves breaking the dye–chromotrope electrostatic bond. This process is also worthy of brief discussion since it illustrates why viscosity measurements have been employed to examine metachromasy.

At infinite dilution all the ionizable groups on the polyelectrolyte are dissociated. The repulsion between

similarly charged groups causes the polymer to take up a fully extended configuration associated with the maximum possible separation of the charged groups and the solution has maximum viscosity (Figure 8b). As dye cations are added, the charged groups on the polymer are neutralized (Figure 8a). This enables the dye–polymer complex to coil up and will be reflected by a decrease in the viscosity of the solution (Figure 8c). Similarly, in the absence of dye, addition of a neutral salt to a polyelectrolyte solution will result in a lowering of viscosity. Coiling of the polymer in this way enables the dye to be effectively polymerized enhancing metachromasy. Steric restrictions prevent a situation like that depicted in Figure 8d from being achieved. These restrictions seem to promote desorption of the sterically hindered dye rather than uncoiling of the dye–polyelectrolyte complex and consequent rise in viscosity.

Other studies have attempted to extract the pure spectrum of the bound dye from the experimentally observed dye spectrum.[191,316,318,319,334,362] The techniques used have included the equilibrium dialysis method,[209] centrifuging or an adsorption technique combined with a graphical method,[342,343] a combination of absorption and binding measurements (including ultrafiltration)[191] and the extended principal-component analysis method[316,318,319,362,363] and other computer/spectral resolution techniques.[352] Some of these studies have also shown that the absorbance spectra of bound dye can also be affected by the pH,[191,319] dye to polyelectrolyte residue ratio,[362] the polyelectrolyte conformation,[318,319,362] and the reactive group(s) of the polyelectrolyte.[318] Despite this it has been noted, by Takatsuki and Yamaoka (compare refs 316 and 318) that spectral changes in the observed dye spectrum do not always reflect changes in the pure spectrum of the bound dye. They showed that the relative intensity of the metachromatic bands in the observed dye spectrum of basic violet 3 was effected by changing the chain length of sodium polyphosphate (compare refs 316 and 318), and yet when they examined the spectrum of the bound dye, they found that the latter was independent of the chain length of polyelectrolyte. Therefore, in order to obtain a clear and quantitative interpretation of metachromasy, it seems desirable to examine both the observed dye spectrum and the "extracted" bound-dye spectra (should there be more than one dye–polyelectrolyte complex). In a later paper,[362] Takatsuki showed that such considerations can yield the number of chemical species bound to a polyion and elucidate the nature of the interaction between the dye and polyelectrolyte and its dependence upon the experimental conditions. For example, this study[362] revealed that for a high (42.6–788) sodium polyphosphate to dye ratio, the amount of free basic violet 3 is small. Instead basic violet 3 binds to the polyelectrolyte, in the form of monomers, dimers, and tetramers. The fraction of the latter species decreases with increasing polyelectrolyte to dye concentration, whereas the fraction of the monomer increases. The fraction of bound dimer peaks at a polyelectrolyte to dye ratio of about 200. Furthermore, this study revealed that monomer dye bound to the polyelectrolyte produced a slight bathochromic shift relative to the free dye and that both the bound dye dimer and tetramer show metachromatic bands in

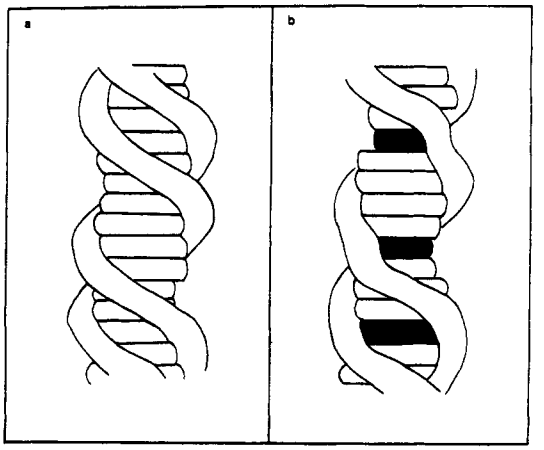


Figure 9. Intercalation of proflavine into DNA:[368] (a) the secondary structure of normal DNA; (b) DNA containing intercalated proflavine molecules. For both, the helix is drawn as viewed from a remote point, so that the base pairs and the intercalated proflavine appear only in edgewise projection, and the phosphate deoxyribose backbone appears as a smooth coil. A similar situation can be envoked for triphenylmethane dyes. (Reprinted from ref 368. Copyright 1964 Chapman and Hall Ltd.)

wavelength ranges both shorter and longer than the peak wavelength of free basic violet 3. On the other hand, it appeared that the bound-dye tetramer and free dye are present when the polyelectrolyte to dye ratio is low (0–1.21). On the basis of the above-mentioned studies, it has been proposed[362] that the dye orients itself to form a sandwich-type dimer when bound to sodium polyphosphate via hydrophobic and electrostatic type interactions.

e. The Interaction of Triphenylmethane Dyes with Proteins. From the above mentioned studies it is evident that triphenylmethane dyes interact with both synthetic and natural polyelectrolytes, and here it is worth emphazing the well-known fact that triphenylmethane dyes bind to protein substrates. While the use of this class of dye to color protein fibers diminishes in the textile industry, the biological sciences are taking advantage of the spectral changes accompanying dye–protein binding to assay proteins. A popular protein assay developed by Bradford[73] utilizes such spectral changes for the triphenylmethane dye acid blue 90. (Acid blue 83 has also been used successfully.[77]) A recent assessment of this technique[75] reveals that under assay conditions the dye anion binds with the protein provided it has a macromolecular form and certain reactive amino acid residues. In particular, interactions occur mainly with arginine, and the other basic amino acid residues (His and Lys) and aromatic residues (Try, Tyr, and Phe) give a slight response. Lysine, alanine, glycine, asparagine, and aspartamine residues do not interact significantly with the dye. Binding behavior was attributed to van der Waals forces and hydrophobic interactions.

Triphenylmethane dyes are also being utilized as probes of changes in the electrostatic potential on macromolecules such as proteins and ionic micelles[364] and are studied for their suitability as pH indicators for pH changes in mitochondria (see ref 365 and references therein) and chromatophores from *Rhodospirillum rubrum* (see ref 366 and references therein).

Investigations involving the interactions between basic dye cations and native DNA (while studied earlier)

gained momentum in the early 1960s. The interest was predominantly stimulated by the work of Lerman[367,368] who proposed that various types of aromatic dye cations have a tendency to intercalate between successive base pairs inside the double helix of DNA. This arrangement is depicted in Figure 9b for proflavine. Intercalation of a dye into a helix of DNA may occur via a local untwisting of the sugar–phosphate backbone and an elongation of the macromolecule (compare Figure 9, parts a and b). This process causes an increase in the viscosity of DNA[367] and the layer-line spacings in an X-ray diffraction pattern.[339] Planar molecules intercalate more readily into DNA than nonplanar molecules. The intercalation theory seems well accepted for planar acridine dyes,[67] and it has been suggested that this process is responsible for the remarkable mutagenicity exhibited by these dyes, which interfere with DNA replication by causing deletions or insertions of base pairs (see ref 369 and references therein).

Triphenylmethane dyes have also been found to inhibit DNA synthesis,[370] and they have been used to examine the binding of various drugs to DNA (see refs 371 and 372 and references therein). However, there has been considerable debate about whether or not the nonplanar triphenylmethane dyes bind to DNA by intercalation and this situation was not resolved until the late 1970s.

Both monovalent[117,209,324,325,333,336,337,373,374] and divalent triphenylmethane dyes[117,351,371-379] have been observed to interact with DNA. The possibility that triphenylmethane dyes intercalate into DNA received favor by many researchers, although the exact position of the dye inside the helix and the number of phenyl rings inserted between the base pairs of DNA remained in question.[67,209,336,368,374,379]

Other workers, however, seemed less certain of the exact nature of the interaction,[339,351] and during the 1970s, evidence mounted which disproved the theory that triphenylmethane dyes bind to DNA by intercalation.[117,371,373,377] The strongest evidence arose from the work of Nórden et al.[117,377] They showed that dyes such as basic violet 3 and basic red 9 formed a single complex with the B form of DNA where the plane of the dye formed an angle of about 55° to the local DNA helix axis. The proposed structure indicates that the charged amino group points toward the negative phosphate and that the main surface of the dye lies against the hydrophobic base-pair stack in the major groove of the DNA helix. A similar structure is proposed for basic blue 20 and basic green 4. In the former case it has been shown that the x and y axes [as defined in Figure 1 with $R_1 = R_2 = N(CH_3)_2$ and $R_3 = N(CH_3)_3$] are oriented at 48° and 90°, respectively to the local axis (Figure 10).[117,377] At low ionic strength, basic blue 20 appears to form a second complex. This results in exciton splitting in the linear dichroism and circular dichroism spectra. Such behavior is attributable to dye–dye interaction which causes exciton coupling of the transition dipoles approximately parallel to the helical strands (compare with the effect of dye aggregation). The situation is depicted in Figure 10.

Müller and Gautier[373] have shown that the above triphenylmethane dyes (except basic red 9) bind with high preference to two adjacent adenine–thymine base pairs in DNA.

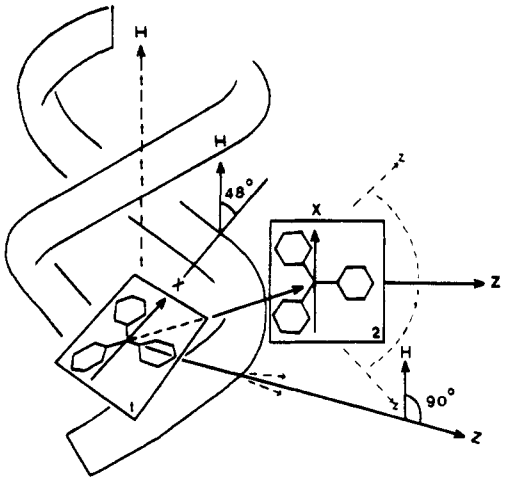


Figure 10. The suggested location of acid blue 20 in the major DNA groove (first complex) and on the peripheral site (second complex): (1) the suggested location for the first complex of acid blue 20 in DNA; (2) the suggested location for the second complex of acid blue 20 in DNA. (Adapted from refs 117 and 377. Copyright 1978 and 1977, respectively, Elsevier Science Publishers.)

f. The Interaction of Triphenylmethane Dyes with Surfactants and Micelles. The interaction between surfactants and triphenylmethane dyes in aqueous solution can also induce spectral changes,[40,41,44f,45,194b,202,203,224,238,335,380-404] and this has been the subject of several reviews.[40,401]

Triphenylmethane dyes can exist in protonated (D_A^+) and unprotonated (D_B^-) forms[5b] related to each other via the equilibrium

$$D_A^+ + OH^- \rightleftharpoons D_B^- \qquad (2)$$

It is evident that the predominant form will be determined by the pH of the solution. Similarly, pH may affect the ionization of the detergent, consequently, the solution pH determines the amount of the appropriate forms of the surfactant and dye available to interact with each other.[390] The interaction of the ionic surfactant with the dye disturbs the protolytic equilibrium depicted in eq 2.[405] This results in a spectral change, since D_A^+ and D_B^- absorb light of different wavelengths.[41,45,191,194b,202,224,381,393,396,404,406-410]

One of the earliest observations of this phenomenon was by Hartley[411] in 1934. Hartley devised a "sign rule" in order to predict or account for the effect of some micelles on certain indicator dye equilibria. This "sign rule" is based on the valence change of the indicator and subsequent electrostatic interactions with the micelle. In its simplest form it states that anionic and cationic micelles are not expected to affect the equilibria where charge changes are of the type ($- \rightleftharpoons - -$) and ($+ \rightleftharpoons ++$), respectively, whereas micelles of the opposite charge will have an effect. Surfactant effects are also expected on equilibria involving valence charges of the types: ($- \rightleftharpoons \pm$), ($0 \rightleftharpoons +$), and ($0 \rightleftharpoons -$). In general, the equilibrium of a neutral indicator will be displaced to the basic side by a cationic micellar system, but to the acid side by an anionic micellar system. The "sign rule" thus indicates that the micelle preferentially adsorbs the form of the dye with charge most unlike its own. Such interactions are responsible for the well-known "colloid or indicator error" and the "protein error"

documented in early works.[411,412] These errors are a consequence of micellization or aggregation and the resulting effect on equilibrium 2.[413b] The change in dye spectra is seen not only in aqueous systems but those utilizing organic reagents where the surfactant will form aggregates which may solubilize water and indicator dye in the polar interior.[223,224]

Electrostatic interactions alone, however, are unable to explain all the observed spectral changes. Furthermore, the "sign rule" does not take into account hydrophobic and microsolvent interactions, nor is it applicable for predicting the effects of nonionic surfactants.[389] It is, therefore, of limited value when used to predict micellar effects. Nevertheless, it is evident that spectral changes are particularly noticable when the charge on the surfactant is opposite in sign to that on the dissociated dye molecule.[40,238,335,381,385,411,414,415] On the basis of the work discussed earlier, there appears to be several possible reasons why such changes could occur. The surfactant could (1) induce a change in the pH of the solution thereby causing an intramolecular rearrangement of the dye, or it could (2) disturb a dye monomer–polymer equilibrium. Alternatively, the dye could bind to the surfactant. Current thought on this problem favors the latter and suggests that once the electrostatic interactions have brought the dye and surfactant together, other nonelectrostatic factors become important in determining the microenvironment of the dye and the consequent response of its chromophoric groups.

The dye–surfactant system is very complex and dynamic and in order to understand the interactions which may occur between the two species it is worthwhile to briefly examine each in terms of their associative properties.

Surfactant molecules are amphiphilic since they possess both polar and nonpolar moieties. At dilute concentrations they exist predominantly as monomers. As the concentration is increased it is found that there is a narrow range, in which the surfactant monomers form aggregates known as micelles. Micelles exist in dynamic equilibrium with the surfactant monomers from which they are formed. The critical micelle concentration (cmc) lies within this range. It is usually defined as the surfactant concentration corresponding to the point of intersection of two lines representing the rate of micelle formation at high and low surfactant concentrations. The exact size and structure of micelles is not certain but current opinion advocates that in aqueous solution they adopt an approximately spherical configuration with the polar head groups forming a peripheral charged layer known as the Stern (or palisade) layer. The counterions form a second outer layer surrounding the Stern layer. This is called the Gouy–Chapman layer and it neutralizes approximately 60–70% of the charge in the Stern layer.[416] The inner micellar core consists mainly of the nonpolar chains, but it is still being debated whether water is rigorously excluded from this hydrophobic interior. In one study it was shown that this region is virtually devoid of water, but there is significant contact with water at the hydrocarbon core interface.[417] Consequently, on the basis of current evidence it would seem that when dye is incorporated within a micelle it is probably exposed to water. At even higher surfactant concentrations, the spherical micelles may rearrange to form cylindrical or lamellar structures. The above micellar behavior is discussed in more detail in a number of sources.[40,45,413a,418]

Dyes are also amphiphilic, in the sense that they contain large organic moieties to which water-solubilizing ionic groups such as SO_3^- etc. are attached. Compared with surfactants, however, they lack long-chain alkyl groups and show very weak surface activity. Consequently, they do not form micelles in water, but they can (as was discussed previously) undergo aggregation, forming dimers, trimers, and higher aggregates, successively, with increasing dye concentration.

In view of the above, it is not surprising that the spectral changes, observed upon addition of surfactant to aqueous triphenylmethane dye solution, are dependent upon both the dye concentration[202,406] and the surfactant concentration.[41,202,335,385,399,404,406,407,414,419] At submicellar concentrations the dye will usually react with surfactant monomers,[224,381,383,398,420] and this may result in the formation of water-insoluble dye–surfactant salts or colloidal dye–surfactant submicellar aggregates.[401,406,407,409,421,422] The colloidal dye–surfactant aggregates are also known as mixed micelles, and as may be anticipated, they form when surfactant (at submicellar concentration) interacts with a dye solution containing dye aggregates. The solutions containing either mixed micelles or water-insoluble dye–surfactant salts are usually opalescent, turbid, or contain precipitate[381,384,396,407,423] although this is not a completely general phenomenon.[381] While the actual species formed depends mainly on the dye, dye–surfactant salts are most commonly encountered, when the dye and surfactant are oppositely charged.[40,381,424–426] These ionic associates are electrically neutral and often show poor solubility in water; however, they may be readily extracted into low-polarity solvents, such as chloroform, etc.[383,406,407,410,426] This is not always the case, however, as it has been observed[424] at high cetyltrimethylammonium cation concentrations ($>10^{-3}$ M), that chromazurol s (3″-sulfo-2″,6″-dichloro-3,3′-dimethyl-4-hydroxyfuchsone-5,5′-dicarboxylic acid) interacts with the surfactant to produce a blue precipitate (with a component ratio of 1:1) in chloroform, but this complex dissociates into ions in alcoholic solvents. The ratio of anionic dye to cationic surfactant, in ionic associates, is usually 1:1, 1:2, 1:3, or 1:4,[381,383,406,426,427] and for cationic dye to anionic surfactant, ratios of 1:1 and 1:3 have been reported[420] in these species.

At concentrations close to or greater than the critical micelle concentration, the dyes interact with the surfactant micelles,[392,398,409,420] and so the solubilizing ability of the micelle becomes important.[406,407,410,420] Turbidity, opalescence, or precipitation usually disappears,[41,423] and the solubility of the ionic associates increases[406,407] and in some cases their yield decreases slightly.[410] Solubilization may occur either when the ion associate is solubilized into the micellar phase and/or the dye is incorporated into the micelles (homomicelles). Most research on triphenylmethane dyes is in favor of the ionic associates being incorporated into the micelles.[396,406,407,410,427,428] Chernova and Savvin et al.[410,427] claim that the same ion associates which exist at submicellar concentrations may exist at tenside concentrations equal to or greater than the critical micelle concentration, because micelles are dynamic

structures coexisting with surface-active molecules from which they are formed.

The onset of micellization is accompanied by spectral changes and these have been used to estimate the critical micelle concentration of various surfactants.[45,237,393,414,420,429,430] The average aggregation number of association of polyoxyethylene(6)nonylphenol has also been determined by a similar method.[224] Despite the convenience of such a technique, it is advisable to exercise caution when interpreting the results obtained[194a,421,429] because the effect of the added dye, on the cmc value is often uncertain. It has been noted,[40,398,431] that such spectral changes may reflect the formation of mixed micelles or dye–surfactant salts rather than homomicelles. Mixed micelles have been observed to form at lower concentrations than the surfactant homomicelles.[399,414,420,431] Consequently, it is said that triphenylmethane dyes tend to induce micellization or aggregation at concentrations lower than would normally be observed in the absence of dye.[224,226,399] The spectral changes have also been used to probe the changes in electrostatic potential on ionic micelles.[191]

In general, the observed spectral changes are significantly effected by the chemical structure of the surfactant[41,194a,393,399,404,406] and the dye.[406] In particular, the substituents attached to the basic triphenylmethyl ion of the dye have a large influence on the interactions between the two species, which lead to the observation of such optical effects. These substituents allow triphenylmethane dyes to be classified into several subclasses. First, there are the diamino and triamino classes, which have been introduced, and are shown in Figure 1 such as basic green 4 and basic violet 3, respectively. In addition, the phthaleins, and sulfonephthaleins (including the phenol carboxylic acid derivatives) also exist[5a,5c] and these have found popularity as indicators in trace-metal analysis[21,42,44f,45,194a,b,202,203,381,383,386-388,399,400,404,406-408,415,419,422-424,427,432-440] where researchers have utilized the number, type, and steric arrangement of the substituents to enhance selectivity, specificity and sensitivity in metal-ion determinations.

For negatively charged water-soluble triphenylmethane dyes interacting with cationic surfactants, ion associates are formed via the negatively charged substituents (of a particular acid–base form) of the dye. In the case of triphenylmethane dyes, these groups are usually SO_3^-, COO^-, and O^-.[41,42,381,396,398,399,401,406,409,427,428] The sulfonic acid groups are generally attached to the triphenylmethyl ion to enhance the dye solubility in water. They dissociate prior to the hydroxyl and carboxyl groups[381,383,396,406,427] upon decreasing acidity. However, the electrostatic interaction, alone, between the two species does not appear to explain the observed spectral changes.[385] This is borne out by the evidence that tetramethylammonium, tetraethylammonium, tetrabutylammonium, ethylpyridinium and butylpyridinium, which are short chain cations that do not form micelles, do not change the observed spectra upon the formation of dye–surfactant ionic associates.[399,410]

In order to observe spectral changes, the dye chromophore has to be perturbed and this can be brought about by changing the microenvironment of the dye.[410] It is evident that hydrophobic interactions play a part in solubilizing the dye,[405,441] and during this process the dye will be transferred from a hydrophilic environment to a more hydrophobic one.[238] In the study by Savvin et al.,[410] it was observed that the cationic surfactants studied required a chain length of at least 11 carbons in order to observe spectral changes. This chain length corresponded to the onset of surface-active behavior in the surfactant. Furthermore, they concluded that the hydrocarbon chain length and hence hydrophobic interactions are far more important than the cationic head groups in determining the appearance of new peaks and/or band shifts in the spectra. The hydrophobic interactions appear to modify the structure of the solvent near the dye, the solvation process, the dielectric constant and the prototropic properties of the medium.[410]

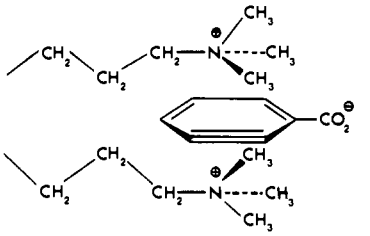


Figure 11. The possible spatial arrangement of sodium benzoate in micelles formed from quaternary ammonium ions. (Adapted from ref 442. Copyright 1974 American Chemical Society.)

The location of the dye in the proximity of the surfactant has received some attention, but the relative spatial orientation and arrangement of the two components seems vaguely defined for triphenylmethane dye–surfactant systems. Often it is simply stated that the hydrophilic groups are exposed at the surface and the hydrophobic groups are buried.[225] One study suggests that anionic triphenylmethane dyes are solubilized on or near the cationic micellar surface by virtue of electrostatic and hydrophobic interactions and protolytic dissociation occurs because of a favorable positive charge-dipole interaction (see ref 45 and references therein).

It has been suggested that the dye molecules may be perpendicularly oriented to the micelle surface.[406] Furthermore, it has been claimed that the negatively charged groups of (a particular acid–base form of) the dye associate with the positively charged surface of the micelle,[396,406,427] perhaps, as some have suggested,[410] acting as a counterion in the water-rich Stern layer. Such an interaction would allow hydration of the negatively charged dye substituents.

With the above-mentioned studies in mind, it is interesting to consider an alternative spatial arrangement based on the results of studies by Bunton et al.,[442,443] which examined the incorporation of aromatic sulfonate and carboxylate ions (e.g. benzenesulfonate and sodium benzoate etc.) into cationic micelles. These studies employed NMR spectroscopy and electrochemical and viscosity measurements to examine the relative location of the aromatic anion to the cationic surfactant molecules. In particular, the NMR studies indicated that the *N*-methyl proton signals of the cationic surfactant (cetyltrimethylammonium bromide) are shifted upfield (from water) due to the ring current of the incorporated aromatic group. These results were interpreted to indicate that the aromatic ions are located near the micelle surface. More specifically, the time-

average location of the dynamic system, is believed to be such that the electron-rich aromatic ring is located near the positively charged polar surfactant head group, with the anion substituents protruding into the Stern layer where they are solvated by water. This is shown in Figure 11 from which it can be seen that the arrangement allows van der Waals interaction between the adjacent surfactant chains. This would help stabilize the growing micelle. The acid forms of the aromatic compounds studied penetrate deeper into the hydrophobic micellar core. It has been suggested[40,442] that these results are applicable to dye–surfactant systems. In such a case, the dye may be incorporated into the Stern layer in a sandwich arrangement, allowing solvation of both the hydrophobic and hydrophilic portions of the dye. While this is reasonable, it should be noted that triphenylmethane dyes are much bulkier and are nonplanar[107,110,114,117,126,130,138] (also see Figure 2) unlike the aromatic anions tested by Bunton et al.[442,443] Furthermore, they often bear negative substituents on two or more phenyl rings (e.g. pyrocatechol violet (3,3′,4′-trihydroxyfuchsone-2″-sulfonic acid) at pH = 7.5.[410] In this way triphenylmethane dyes differ from the compounds studied in refs 442 and 443, and so it may not be surprising to find variations from the situation depicted in Figure 11.

The negative charge on the SO_3^- group is more isolated from the aromatic π-electron system of the dye than the COO^- group.[40] Since the charge is more delocalized, the COO^- group will be accommodated deeper within the micelle Stern layer than the sulfonic acid group and this will mean that its electrostatic interaction with a cationic surfactant will be weaker than for the SO_3^- group. Thus, in the proximity of micelles the dye clearly experiences a different microenvironment than in the bulk solution.

There appears to be some confusion in the literature regarding the extent of interaction of the SO_3^- group with the aromatic π-electron system of the dye. Many authors claim that the sulfonic acid groups are isolated from the π-electron system of the chromophore and hence the formation of an ionic associate via this group will not produce a color change.[42,381,398,406,427,428] However, this assessment seems unlikely since it has been shown for naphthalene monosulfonic acids that the SO_3^- is not isolated from the aromatic π-electron system.[444] In this study, it was shown that the three oxygen atoms in the sulfonate anion are not equivalent to one another. Protonation of the sulfonate anion (SO_3^-) was not reflected as a change in the absorbance spectrum but protonation of the neutral sulfonic acid group (SO_3H) was. Yakatan and Schulman[444] explained this by suggesting that the oxygen atom (at the site of protonation) in the sulfonate group is essentially uncoupled electronically to the aromatic system but the oxygen atom which becomes protonated in the sulfonic acid group (to form $SO_3H_2^+$) is strongly coupled to the π-electron system. On the basis of this, it is not unreasonable to expect that the electrons of the sulfonic acid substituent are coupled to the aromatic π-electron system of the dye. Interaction of the SO_3^- group with cationic surfactant will reduce the charge on the sulfonate group. While this interaction in itself will not cause a change in the absorbance spectrum, it will promote electron withdrawal from the aromatic π-electron system of the dye and aid the dissociation of ionizable hydroxyl groups on the dye.[432] It becomes understandable why the presence of cationic micelles enhance the dissociation of hydroxyl groups[42] and why the observed spectral changes may be correlated to the degree of dissociation of protons of the OH groups from the DH^- dye anions (where H represents a dissociable proton and D the remainder of the dye structure) observed by certain researchers.[396] The observed spectral changes depend upon the resulting electronic structure produced by changes in the microenvironment as a result of the dye surfactant interaction as described previously.[399,410] If deprotonation of the OH group occurs and enhances the delocalization of the π-electrons along a single conjugation plane, a bathochromic shift of the long wavelength absorption band will usually result.[381,398,427]

Similarly, it is clear that, when other atoms of dye substituents forming an integral part of the π-electron system of the dye interact with the surfactant, spectral changes can be anticipated, and this is consonant with experimental results.[381,406,427] However, it must be kept in mind that the resulting spectral shifts are not always bathochromic, but are determined by the particular dissociation form of the dye present, and in some cases hypsochromic shifts may be anticipated.[193,424] Moreover, the addition of an ionic detergent to an oppositely charged dye does not always result in such spectral changes.[383,398,439]

Most triphenylmethane dyes that have been studied are negatively charged, and hence, as may be expected from Hartley's "sign rule",[411] there are very few reports of anionic surfactants affecting the acid–base equilibria. Groups that have examined such interactions are cited in refs 393, 406, and 410. In keeping with this, Savvin et al.[410] noted that the reactions observed when anionic triphenylmethane dyes react with cationic surfactants are eliminated when the polar head group of the surfactant is changed to a negatively charged one, without altering the length of the hydrocarbon chain. It is possible, however, that the negative sites on a negatively charged dye will interact with cations in the Stern layer of the anionic micelle. (60–70% of the charges are usually balanced by the counterions in the micelles.[416]) A similar idea was proposed in order to explain the interaction between sodium dodecyl sulfate, beryllium, and chromazurol s.[194a] In this study, it was found that sodium dodecyl sulfate barely effected the free dye absorbance at 429 nm in comparison to several cationic surfactants. In ref 430, it is seen that the interaction between sodium dodecyl sulfate or sodium deoxycholate and acid blue 90 resulted in an increase in dye absorbance without changing the absorption spectrum. In contrast, the anionic surfactant micelles of sodium dodecyl sulfate reduced the intensity of the long wavelength band of bromothymol blue (α,α-bis-(6-bromo-5-hydroxycarvacryl)-α-hydroxy-o-toluenesulfonic acid γ-sultone) and increased the absorbance at 430 nm, at pH = 7 in water.[393]

Interestingly, it has been observed that nonionic detergents (such as Triton and Brij 35) can induce concentration-dependent changes in the absorption spectra of triphenylmethane dyes (e.g. acid blue 90[430] and chromazurol s).[406]

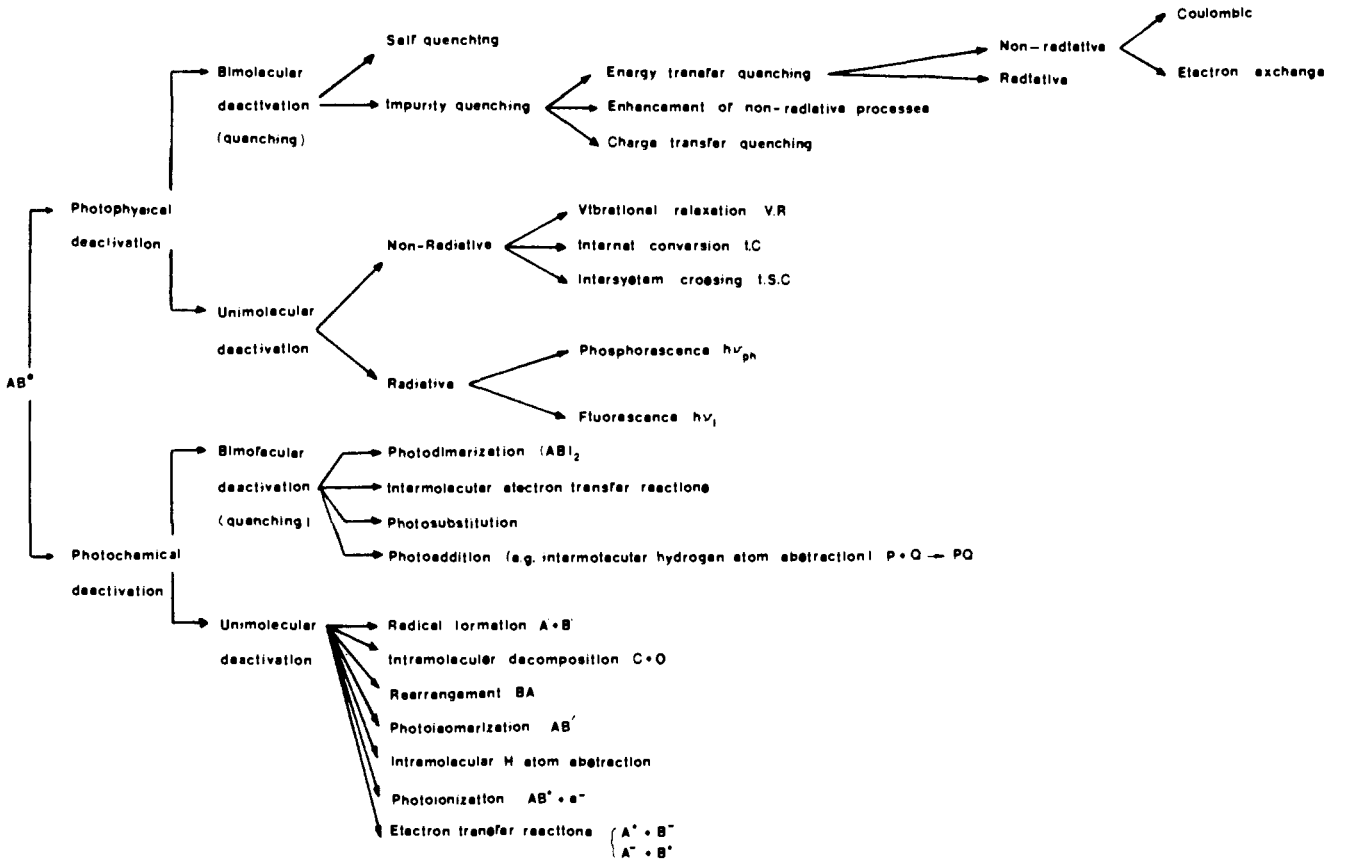


Figure 12. A classification of deactivation processes for excited-state molecules.

In contrast to ionic surfactants, nonionic surfactants do not dissociate into ions in aqueous solutions. Instead, their solubility in water is attributable to the presence of a large number of hydroxyl or ether groups in the molecule. They appear to effect the protolytic equilibrium of the dyes when present in the micellar form[42,401,430] although individual surfactant molecules may also be able to influence the protolytic properties of the dyes.[397] Usually, changes in the absorption spectra are evident when the surfactant reaches a concentration greater than or equal to its critical micelle concentration.[430] Hydrogen bonding is also believed to participate in the observed color changes.[224,395,406,445]

In the case of chromazurol s, such interaction involves hydrogen bonding between the hydrogen atom of the carboxyl groups of the indicator and the ether oxygens of the surfactant.[397] The resulting color change is essentially the same as that which occurs upon changing the solution pH.[395,401,446] In addition, the change in the nature of solvation of the dye when passing from bulk solution to the interior of the micellar phase will alter the spectra.[397] The dyes are usually believed to exist within the polyoxyethylated interior of the micelles.[430,446] More specifically, work on chromazurol s suggests that the nonpolar portions of the dye are localized in the hydrocarbon nucleus of the micelle while the polar portions of the dye reside in the poly(oxyethylene) layer.[397] Many of the spectral changes observed for dyes in the presence of nonionic surfactants can be explained in terms of lipophilicity rather than electrostatic interactions.[40]

It may be anticipated from the previous discussion that dye–surfactant interactions, like dye–polyelectrolyte interactions, may be dramatically effected by solution additives and/or changes in solvent. Such disturbances of a system would be expected to be reflected by changes in the absorbance spectrum, particularly if the additives or solvent alter the cmc of the surfactant, or the extent of dissociation of the dye.

It has been reported, in many cases, that the addition of strong electrolytes reduces the cmc of ionic surfactants[40,41,389] but only slightly alters that of nonionic surfactants.[40,389] Salts may also alter the dimensions, aggregation number, charge density, counterlayer composition, and potential difference across the double layer of the micelles.[40,194a,226,237] They have also been reported to decrease deprotonation of the dye.[396] Clearly, addition of a strong electrolyte to a dye–surfactant system will alter the interaction between the dye and the surfactant. It is not surprising then, that addition of strong electrolytes to a dye–surfactant system has been observed to effect the absorbance spectra.[202,396,399,404,406,425] For several triphenylmethane dyes in the presence of cationic surfactants the effect on the absorbance spectra depends mainly on the nature of the inorganic anion.[202,399,404,425] Nitrates exhibit a stronger effect than chlorides and sulfates,[202,399,404,425] but the effect of the cations of the salts is small.[202,399,404] Both the nature and concentration of the electrolytes seem to be important.[226,425] The order $F^- < Cl^- < Br^- < N_3^- < NO_3^-$ reflects the relative abilities of the anions to lower the cmc and increase the aggregation number of cationic surfactants.[226] The nature of the dye is also important in determining the salt effect.[41]

Apart from the effect of strong electrolytes, the absorbance spectra of a dye–surfactant system may also be effected by changes in the solvent employed or added to the system.[408] This is to be expected considering

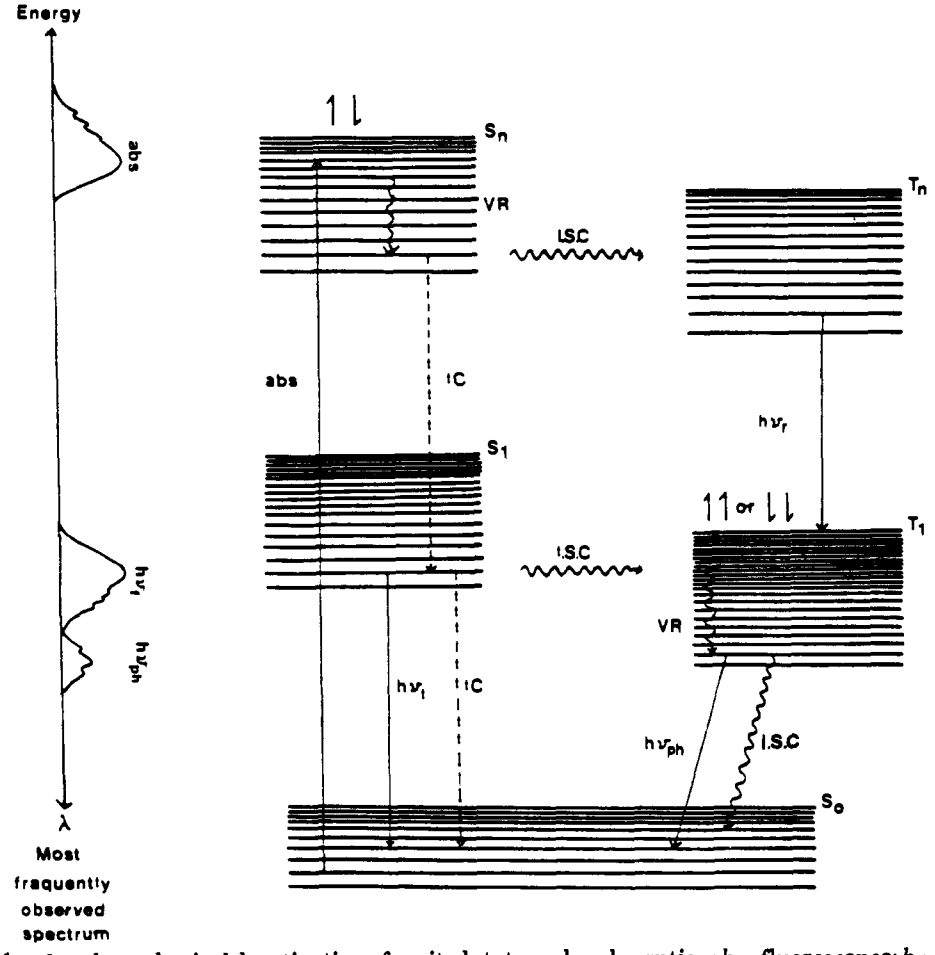


Figure 13. Unimolecular photophysical deactivation of excited states: abs, absorption; $h\nu_f$, fluorescence; $h\nu_{ph}$, phosphorescence; IC, internal conversion; ISC, intersystem crossing; VR, vibrational relaxation.

solvents such as alcohol etc. can markedly change the properties of micelles.[40]

B. Photophysical Deactivation of the Excited States of Triphenylmethane Dyes

Once in an excited vibronic (vibrational and electronic) state a molecule is not in equilibrium with its surroundings, and so it tries to dissipate its excess energy by producing stable ground-state species. This can be done in a number of ways which may be broadly classified as photophysical and photochemical deactivation processes. These may occur unimolecularly or via interaction with another molecule. Since photophysical and photochemical deactivation processes are in competition with each other, the most efficient process will determine the most favorable pathway of molecular photodegradation. A general classification of possible deactivation processes for excited state molecules is shown in Figure 12, and in particular the photochemical deactivation processes of triphenylmethane dyes are discussed in section IV.B.

Photophysical deactivation of an excited state occurs by converting the excited vibronic state to an alternate vibronic state without resulting in a chemical change. Photophysical deactivation may occur via the emission processes, fluorescence and phosphorescence, and via nonradiative processes such as internal conversion, intersystem crossing, and vibrational relaxation as depicted in Figure 13. In general, typical lifetime ranges for molecular fluorescence and phosphorescence are 10^{-9}–10^{-6} and 10^{-3}–10 s, respectively. For triphenylmethane dyes, in low viscosity solvents, fluorescence lifetimes of the order of picoseconds have been reported. For example, the fluorescence decay time of basic green 4 in water was found to be 2 ± 1 ps.[447] There have been very few reports of phosphorescence lifetimes for triphenylmethane dyes. Pant et al.,[259] however, reported an approximate phosphorescence lifetime for basic violet 14 in a glycerine–water solution (liquid–air temperature) at 680 nm of 0.4 s. Lewis et al.[135] reported phosphorescence decay times of 10^{-1} and 10^{-2} s for the green and red emissions from basic violet 3 in glycerol at 178 K.

Interestingly, anomolous $S_2 \rightarrow S_0$ fluorescence and $T_2 \rightarrow S_0$ phosphorescence has been observed for several derivatives of the classic triphenylmethane dyes.[448] Lifetimes in the range 1.7–6.5 ns were measured for the $S_2 \rightarrow S_0$ process and 95–1540 ms for the $T_2 \rightarrow S_0$ process at 77 K. Fluorescence from the S_1 states gave lifetimes in the range 1–5.7 ns at 77 K.[448]

Perhaps one reason for the small number of phosphorescence studies on triphenylmethane dyes is that an efficient radiationless internal conversion process is available to compete with both the luminescent processes and the other radiationless relaxation pathways.[102,103] The internal conversion is believed to occur via a synchronous rotation of the phenyl rings in the dye.[102,449,450] Such efficient internal conversion causes the intersystem crossing process to the triplet state to be small.[449] Windsor[103] has estimated from picosecond

studies on basic violet 3, basic violet 4, and basic red 9 that less than 3% of the molecules populate the triplet state. Cremers and Windsor[449] report that when the solvent viscosity is greater than 180 P, 10% of the initially excited basic violet 3 exists in the triplet state 4.8 ns after excitation. They found no evidence for the triplet state at the lower viscosity of 0.86 P. Clearly, the population of the triplet state is dependent upon solvent viscosity.

In the simplest cases, photophysical deactivation generally follows the scheme depicted in Figure 13. Where molecular conformational changes may take place, such as the rotation of the phenyl groups of triphenylmethane dyes, it is possible that an additional intermediate state participates in the deactivation process. This would make the photophysical deactivation scheme more complicated than that shown in Figure 13.

Over the past 20 years, researchers have tried to elucidate the actual photophysical deactivation scheme of triphenylmethane dyes (see later in this section).

The main issues studied have included (1) the existence and nature of a possible intermediate electronic state, S_x, (2) the number of excited electronic states reached immediately after absorption of visible light, and (3) the magnitude of a possible potential energy barrier encountered by the initially prepared excited state when trying to relax to the proposed intermediate state, S_x.

Such studies, have usually been performed in the picosecond regime. However, with the attainment of shorter laser pulses and improved optical techniques, the initial relaxation of several photoexcited triphenylmethane dyes has been observed on the femtosecond time scale.[60c,451,452] The decay curves obtained exhibited oscillatory behavior which was tentatively ascribed to quantum beating between two molecular eigenstates of an isolated large dye molecule. More recently, several workers have confirmed this work.[453-456] As a result, it is apparent that the phenomenon reported by Rosker and co-workers[60c,451,452] does indeed correspond to quantum beats. Furthermore, the observed damped oscillations, with a period close to 150 fs, correspond to a previously reported vibrational breathing mode at around 225 cm^{-1} for basic green 4.[112,138,454,456] This skeletal vibrational mode appears to be a characteristic common to both triaminotriphenylmethane dyes and diaminotriphenylmethane dyes.[112] Subsequently, Fragnito et al.[457] utilized femtosecond techniques to observe periodic deformations in the absorption spectrum of basic green 4, in ethylene glycol, due to nuclear motion brought about by coherent excitation of the manifold of vibrational levels. This study, also examined a high-frequency oscillation, with a period of around 20 fs, in the stimulated emission at 701 nm. Fourier transform analysis of the data revealed that several vibrational modes with energies in the 1200–1600-cm^{-1} range were excited. These were attributed to double bond carbon–carbon vibrations and are consistent with results obtained using femtosecond photon echo techniques[458] which have recently been the subject of theoretical discussions.[459]

The photophysical radiationless relaxation of triphenylmethane dyes, in the picosecond regime, shows interesting viscosity and temperature dependences which have been correlated with the internal conversion process. These properties have been investigated in both experimental and theoretical studies, which will be discussed in more detail in the forthcoming text. However, it is worthwhile noting here, some significant predictions of several representative theories, namely those of Kramer[460] and Förster and Hoffman,[461] which have been employed in an attempt to explain the observed viscosity and temperature dependence of the relaxation rate of several triphenylmethane dyes. These theories were, until recently, the most frequently cited and respectively describe diffusive barrier crossing and barrierless behavior.

In 1940 Kramer[460] modeled a general chemical reaction as the passage of an effective particle over a parabolic barrier (of height E_a, where $E_a > kT$, and k is Boltzmann's constant and T is the absolute temperature), where the particle was exposed to Brownian frictional forces. Kramer determined that the rate of barrier crossing increased linearly with viscosity in the low viscosity (inertial) region and then reached a maximum and began to decrease with increasing viscosity (intermediate region). In the high viscosity region (also known as the Smoluchowski limit region) the rate was found to decrease linearly with increasing viscosity. Accordingly, Kramer derived two useful equations, one for the low viscosity region and another for the intermediate and high viscosity limit, but no useful expression was determined for the turnover region. This theory is to be contrasted with that of Förster and Hoffman[461] which is based on molecular conformational changes.

In Förster and Hoffman's model the phenyl rings in the excited-state molecule, produced immediately upon light absorption, have the same equilibrium position as in the ground-state molecule θ_0. The rings then synchronously rotate toward a new equilibrium position, θ, with a rate assumed to be viscosity dependent. Ring rotation is driven by steric repulsion between the ortho hydrogen atoms on the phenyl rings. In this model the nonradiative deactivation rate was assumed to be quadratically proportional to the angle $[(\theta - \theta_0)^2]$ of rotation of the phenyl ring, whereas the radiative rate was assumed to be independent of θ. Förster and Hoffman used this model to explain the relationship $Q \propto \eta^{2/3} \propto \tau_f$ (where Q is the quantum yield of fluorescence, τ_f is the excited singlet state lifetime, and η is the macroscopic solvent viscosity) observed in the viscosity range of 0.006–250 P.

In higher viscosities, the quantum yield of fluorescence was observed to approach a constant limiting value (0.35). To account for this, Förster and Hoffman incorporated a nonradiative deactivation process, which was both independent of angle and viscosity, into their theory.

Not only do these two theories predict different solvent viscosity behavior they also predict different temperature-dependent properties. For example, in situations where Kramer's theory is applicable, an Arrenhius plot[462] will yield an activation energy greater than zero (and $> kT$). In contrast, if Förster and Hoffman's barrierless diffusion model is applicable an Arrenhius plot will yield an activation energy of zero.

The following paragraphs will indicate that many of these predictions have not been borne out by experi-

ment. It has, in fact, become apparent that the photodynamics of triphenylmethane dyes are both interesting and more complex than originally anticipated. This behavior will now be discussed in the following paragraphs beginning with a discussion of fluorescence.

The changes in the absorption spectrum which occur when a triphenylmethane dye aggregates, complexes with another dye, or binds to a substrate, are often accompanied by a corresponding change in the intensity and wavelength position (which usually moves to longer wavelengths) of the fluorescence spectrum.[306,315,327]

Numerous fluorescence studies have indicated that the fluorescence exhibited by triphenylmethane dyes in solvents of low viscosity is very weak, and that the lifetimes of the fluorescing states are of the order of picoseconds.[447,461,463-466,467a,468-476] However, stronger fluorescence is observed in highly viscous media (or at low temperatures)[135,144,246,259,448,449,461,463-465,469,470,472,476,477,478-486] upon dye binding to a substrate or polyelectrolyte[309,315,327,348,478,482] or adsorption onto a solid.[65,263] Furthermore, it has been noted that the related xanthane dyes (in which the two phenyl rings are joined by a bridge) fluoresce more strongly than substituted triphenylmethane dyes.[144,145,294,315,487] These findings suggest that molecular rigidity is a necessary requirement for fluorescence.

It has been observed that when molecular rigidity is enhanced by binding the dye to a polymer, the emission behavior can be related to the polymer conformation[327] and the ratio of polymer residue to dye.[327,348] Jones and Goswami[327] found that at high poly(acrylic acid) residue to dye ratios (e.g. 1000) and pH = 3.2, when the polymer existed in its uncoiled (globular) form, basic violet 3 exhibited fluorescence indicative of the monomeric dye. On the other hand, at pH = 6 with a polymer residue to dye ratio of 10, fluorescence from the dimer was observed. Interestingly, basic violet 4 exhibited similar behavior, whereas basic red 9 did not.

Dimer emission was also observed when basic violet 3 was adsorbed onto the surface of cadmium sulfate at 77 K.[263]

The weak fluorescence emission from triphenylmethane dyes has aided workers examining the energy-transfer process occurring between a xanthene (donor) dye and a triphenylmethane (acceptor) dye.[60b,61-65,293,488-490] Such studies have been performed utilizing a variety of media, including solid inorganic substrates such as Vycor glass,[65] silica gels,[61-64] and controlled-pore glasses[61-63] or in viscous media such as glycerol[488] or dihexadecyl phosphate vesicles.[60b] Most frequently, the process is investigated by examining the fluorescence decay function of the donor molecule. It has been analyzed in terms of Förster singlet–singlet energy transfer,[486,489b] and in some cases fractal analysis has been applied.[60b,61-63,65] Although it should be noted that in the case of the work presented by Even et al.,[65] it has been suggested that the apparent "fractal dimension" determined, may result from an excluded volume effect and not due to a real fractal structure, existing in the Vycor glass.[66]

Maeda has reported that lasing can be observed from glycerin solutions of triphenylmethane dyes when excited with a ruby laser.[491a,b]

Oster et al.[246,478] examined the fluorescence from numerous triphenylmethane dyes in glucose glasses. All dyes tested from the triaminotriphenylmethane and diaminotriphenylmethane classes exhibited red fluorescence when illuminated with white light. Basic violet 3 was among those dyes tested and this has also been studied by Lewis and co-workers,[135] who attributed all fluorescence to the A isomer. Furthermore, excitation of the green colored diaminotriphenylmethane dyes (e.g. basic green 4) with near ultraviolet (365 nm) light results in green fluorescence,[246] whereas irradiation with blue light (435 nm) gives both green and red fluorescence.[478] These two colored emissions have been attributed to the existence of two excitation systems, probably corresponding to the two dichroic axes of the dye molecule.

Since the x and y absorption bands correspond to two mutually perpendicular polarized transitions, it could be expected that in viscous media, where a molecule has little chance of rotating during the lifetime of the fluorescing state, the observed fluorescence will exhibit the same polarization as the exciting light. This idea led Lewis and Bigeleisen[113] to examine the direction of polarization of fluorescence from basic green 4, and subsequently Adam and Simpson[107] have studied 4,4′-bis(dimethylamino)fuchsone and methoxy basic green 4 (Figure 1). In both studies, excitation into the x band produced fluorescence of the same polarization; however, excitation into the y band produced fluorescence polarized in the same sense as that emerging from excitation into the x band. Both research groups explained this apparently anomalous result by assuming that before the excited state has time to reemit its normal fluorescence it suffers partial quenching to reach the first excited state. As a result of this process the y oscillations change to x oscillations. Other workers have studied the polarization of the luminescence spectra from symmetric triphenylmethane dyes.[111,119] In particular, the work of Martin et al.[119,492-494] confirms the existence of two overlapping electronic transitions for basic violet 4 and that the lower electronic state is indeed the fluorescent state.

Apart from luminescence emanating from the S_1 state, anomalous $S_2 \rightarrow S_0$ fluorescence has been observed in di- and tricarboxylic acid derivatives of triphenylmethane dyes.[448] It is interesting to note that these compounds form complexes with rare earth ions which have been shown to reduce the $S_1 \rightarrow S_0$ fluorescence lifetimes of most of the dye derivatives studied.

Over the past 20 years there has been an increasing interest in the viscosity- and temperature-dependent relaxation processes available for triphenylmethane dyes.[102,103,105,124,125,127,129,134,136,144,145,273,384,447,449-452,461,463,465,467a-d,468-476,480,483,486,489b,495-502,503a,504-523] This process is very efficient, and so in contrast to the structurally related xanthene dyes, triphenylmethane dyes show very weak fluorescence.

In order to elucidate the mechanism of viscosity- and temperature-dependent electronic relaxation, on the picosecond time scale, researchers have examined several regions of the triphenylmethane dye absorbance and emission spectra. These are the absorption region for the $S_0 \rightarrow S_1$ transition, the absorption region for the $S_0 \rightarrow S_n$ (where $n > 1$) transitions, and the fluorescence region for the $S_1 \rightarrow S_0$ transition, and they have been

Table II. Some Results from Studies on the Dependence of the Ground-State Recovery Time (τ_{gsr}), Excited-State Absorption Time (τ_{esa}), Fluorescence Lifetime (τ_f), and Quantum Yield of Fluorescence (Q_f) on Solvent Viscosity (η)

parameter	dye[a]	viscosity (P)	γ	component	ref(s)
τ_{gsr}[b]	MG	1–10000	1/2	long	507
τ_{gsr}	MG	1–1000	2/3	fast	507
τ_{gsr}	MG	0.006–14	1/2	long	105
τ_{gsr}	MG	100–1000	2/3	fast	105
τ_{gsr}	MG	<0.05	2/3		514
τ_{gsr}	CV	0.01–120	1/3		102
τ_{gsr}	CV	0.1–103	1/3		102
τ_{gsr}	CV	0.01–120	1/3		103
τ_{gsr}	CV	0.005–0.05	0.98		465
τ_{gsr}	CV	<0.5	2/3		514
τ_{gsr}	EV	0.01–0.1	0.4–1.9		467b
τ_{gsr}	EV	0.13–10	0.33–0.54		467b
τ_{gsr}	EV	<0.5	2/3		514
τ_{esa}[b]	CV	0.005–0.05	0.97		465
τ_f[b]	MG	5–100	1/3	long	469
τ_f	MG	5–100	1/3	fast	469
τ_f	MG	0.8–50	1/3	long	470
τ_f	MG	0.8–50	1/3	fast	470
τ_f	MG	1–60	2/3		472
τ_f	MG	60–1000	1/2		472
τ_f	MG	>1000	constant		472
τ_f	MG	1–60	2/3		476
τ_f	CV	0.55–0.15	0.82	long	467a, 468
τ_f	CV	0.55–0.15	0.3	fast	467a, 468
τ_f	CV	<200	2/3		461
τ_f	CV	0.8–50	2/3	long	470
τ_f	CV	0.8–50	2/3	fast	470
τ_f	CV	10–120	2/3		477
Q_f[b]	MG	7–70	2/3		469
Q_f	CV	0.006–250	2/3		461
Q_f	CV	1–250	0.82		144
Q_f	CV	0.01–1000	2/3		464
Q_f	CV	15.4–131.7	2/3		480

[a] MG = basic green 4; CV = basic violet 3; EV = basic violet 4. [b] Note: In general it has been found that τ_{gsr}, τ_{esa}, τ_f, and Q_f are all proportional to η^γ (see text).

examined by probing the ground-state repopulation,[102,103,105,127,129,134,136,273,449,465,467b,471,473,489a,501,502,503a,504,507,515,517,524] excited-state absorption,[103,127,449,465,471] and spontaneous and stimulated emission[144,273,447,461,464,465,467a,469–473,475,467,480,483,486,512] phenomena, respectively. The emission from the S_n (where $n > 1$) state has also been examined using a two photon fluorescence technique which enables the lifetime of the S_1 state to be determined.[473,474] The main techniques employed include various picosecond time-resolved techniques (such as absorption recovery[102,103,127,129,134,136,273,449,465,467b,471,473,489a,502,503a,504,507,517,524] and kinetic fluorescence measurements[144,447,450,465,467a,468–476,483,486]) along with fluorescence quantum yield,[144,461,464,469] frequency domain,[514–516,518] and theoretical studies.[103,129,144,461,499,500,508,521,525,526] From such investigations it is found that the fluorescence, ground-state recovery, and excited-state absorption kinetics can be fitted to functions with one, two, or more exponential terms depending upon the subclass of triphenylmethane dye and solvent viscosity.

It is also evident that the ground-state recovery time (τ_{gsr}), excited-state absorption time (τ_{esa}), fluorescence lifetime (τ_f), and quantum yield of fluorescence (Q_f) are all dependent on solvent viscosity (η). Each quantity increases with solvent viscosity and is usually fitted to an equation, such that it is proportional to viscosity i.e. $\tau_{gsr} \propto \eta^\gamma$,[102,103,105,465,467b,507,514] $\tau_{esa} \propto \eta^\gamma$,[465] $\tau_f \propto \eta^\gamma$,[467a,469,470,472,476] or $Q_f \propto \eta^\gamma$.[144,461,469] It is worthwhile noting that, these relationships imply that high viscosities hinder repopulation of the ground state. In these equations γ is usually quoted as being a fixed value less than one (Table II). There is, however, evidence that the actual value of γ observed experimentally will depend upon the viscosity regime employed for the measurements. For example, recent measurements of τ_{gsr} for basic violet 3 in normal alcohol solutions suggest that γ changes from one to less than one as the viscosity goes from low to high (>5 cP) values.[465] Similarly, Sundström and Gillbro[467b] and Pellegrino et al.[472] also observed a larger value of γ at smaller viscosities in their ground-state recovery and fluorescence lifetime work respectively (Table II). As mentioned in the introduction to this section a linear viscosity dependence is to be expected for Kramer's barrier crossing model in the Smoluchowski limit.[460] It is also predicted by the barrierless models of Oster and Nishijima,[527] described later in this review, and for the average nonradiative rates predicted by the Gaussian and Lorentzian sink models (for $\eta > 1$ P) and the pinhole sink model of Bagchi et al.[499] In contrast, sublinear viscosity behavior is predicted by the barrierless model of Förster and Hoffman.[528]

Studies which independently varied the analyzing and exciting wavelengths have revealed that τ_{gsr} for the triaminotriphenylmethane dyes are dependent upon the wavelength at which they are monitored (λ_{an}), but not the wavelength used to excite the sample (λ_{ex})[129,134,497] as previously suggested.[524] Sundström et al., in studies using $\lambda_{an} = \lambda_{ex}$,[136,467b,503a,504] observed that the ground-state recovery kinetics could be divided into three different regions. At one particular wavelength (λ_{iso}), when $\lambda_{an} = \lambda_{iso}$, the kinetics were single exponential, whereas for $\lambda_{an} > \lambda_{iso}$ or $\lambda_{an} < \lambda_{iso}$ double exponential functions fit the observed kinetics. As the solvent viscosity is increased, λ_{iso} is red-shifted.[136] The τ_{gsr} values measured in the region $\lambda_{an} > \lambda_{iso}$ were found to be approximately half the τ_{gsr} values measured with $\lambda_{an} < \lambda_{iso}$. This suggests that the ground-state recovery is longer in the blue end of the spectrum than in the red. On the contrary, other workers, using tunable laser excitation and a continuum probe pulse found that the bleaching of the ground state of basic violet 3 in methanol measured around 550 nm decayed faster than that measured around 590 nm.[127] This apparent contradiction, is rationalized in view of the studies by Ben-Amotz and Harris who independently varied λ_{ex} and λ_{an}.[465,497] These works reveal that τ_{gsr}, for the same solute–solvent system appears to go through a maximum near 589 nm (the peak of the absorbance spectrum) where the ground-state recovery process is slower than at 530 and 605 nm. A similar increase in the τ_{gsr} has been observed for basic violet 3 in higher viscosity solvents (glycerol) when measuring at the blue end (550 nm) of the absorption band as opposed to the red end (595 nm).[134]

In contrast to the triaminotriphenylmethane dyes, τ_{gsr} for the diaminotriphenylmethane dyes are usually found to be constant over the entire wavelength region studied.[136,467b,504] As implied, this is not always the case, since Migus et al.[471] found τ_{gsr} for basic green 4 in water to be dependent upon the wavelength of the probe pulse

when excited with 620-nm radiation.

Both diamino and triamino subclasses of triphenylmethane dye, in high-viscosity solvents, exhibit fluorescence lifetime and emission spectra which are independent of both the excitation and detection wavelengths.[102,136,467b,486,470] Furthermore, the fluorescence decay exhibits dual exponential behavior.[467b,469,470,483,513] Doust[467a,488] observed similar behavior for basic violet 3 in low viscosity solvents (e.g. alcohol). The lifetime of the long-lived component was independent of the analyzing wavelength, but it could not be determined for certain whether the lifetime of the short-lived component was independent of the analyzing wavelength. Single exponential fluorescence decays were previously observed in the same viscosity regime[473] but this difference is probably due to the resolution of the techniques employed.

Interestingly, Ben-Amotz and Harris[497] observed stimulated emission from basic violet 3 in *n*-octanol at probe wavelengths of 660, 720, and 900 nm. The peak amplitude of the signals, decay shapes, and times were found to vary with probe wavelength; however, it was not possible to determine whether these changes were due to wavelength dependent changes in the excited-state absorption or in the emission cross section of the emitting state.

Comparisons between the fluorescence data and ground-state recovery data have been made in order to elucidate the kinetic mechanism. In several cases it has been possible to determine which electronic states responsible for particular ground-state recovery lifetimes give rise to fluorescence.

Several researchers observed a double exponential fluorescence decay, from basic violet 3 in alcohol, at 660[465] and 646 nm[467a,488] after excitation at around 589 nm. The slower fluorescence component seems to arise from the same excited state responsible for the fast ground-state recovery decay component observed by Sundström et al.,[136,467b,504] in their $\lambda_{ex} = \lambda_{an}$ experiments, when analyzing with wavelengths greater than λ_{iso}. The slower ground-state recovery component did not appear to give rise to fluorescence.[136,465,467b,488,504] Similarly, Beddard et al.[470] observed a double exponential fluorescence decay at 649.6 nm by using a fluorescence upconversion technique on basic violet 3 in glycerol–water mixtures, excited with 595-nm radiation. The fluorescence lifetimes extracted in this case agreed with the ground-state recovery lifetimes extracted by Sundström et al.[136] when probing at wavelengths greater than λ_{iso}.

The fluorescence and ground-state recovery data have also been compared for basic green 4 in glycerol or glycerol–water mixtures.

Several investigations by Hirsch and Mahr[469] and by Beddard et al.[470] observed double exponential fluorescence decay. The faster component observed in these works (60 ps at 10 P, inferred from Figure 2 of ref 469, and 58 ps at 11.5 P measured by Beddard et al.[470]) agrees with the fluorescence decay measured by Yu et al.[476] (90 ps in glycerol at 28 °C) and Pellegrino et al.[472] (90 ps in glycerol at room temperature i.e. 6.29 P) and the slow ground-state recovery component (50 ps at 10 P, inferred from Figure 4 of ref 507 observed by Ippen et al.).[105,507] The slow ground-state recovery component measured by Sundström et al.[136] (130 ps at 8.2 P) is comparable to the slow fluorescence component measured by Beddard et al.[470] (153 ps at 11.5 P). Ippen et al.[105,507] compared their fast ground-state recovery rate (20 ps at 10 P, inferred from Figure 4 of ref 507) to the fluorescence lifetime inferred from the work of Förster and Hoffman[461] and found this to be in reasonable agreement. The fast ground-state recovery component measured by Sundström et al.[136] was found to be 30 ps at 8.2 P.

In lower viscosity solvents, agreement has been found between the fluorescence decay time of basic green 4 in water (2 ± 1 ps)[447] or in ethanol (5 ± 3 ps)[473] and the ground-state recovery times measured in methanol (2.1 ps[105,489a,507] or 2.8 ± 0.14 ps[136]) and water reported by Engh et al. (1.29 ± 0.33 ps),[502] Song et al. (1.2 ± 0.1 ps),[515] and Trebino and Siegman (1.2 ± 0.3 ps).[518] A lower ground-state recovery time is reported by Saikan and Sei (0.7 ps)[516] for basic green 4 in water.

Subsequent work reports that the ground-state recovery is best described by at least two time constants.[471,518] Trebino and Siegman's work[518] yielded results consistent with either two time constants (0.78 ± 0.1 and 7.4 ± 3 ps) or a uniform range of time constants ranging from 0.34 ± 0.04 to 7.2 ± 3 ps. Migus et al.[471] considered that their data resulted in the two time constants 0.65 ± 0.05 and 3.5 ± 0.1 ps.

In a recent study by Kemnitz and Yoshihara,[450] triexponential fluorescence decays were observed for basic green 4 in the mixed solvent, EPA (diethyl ether, isopentane, ethanol, 5:5:2), for temperatures between 298–130 K, whereas biexponential behavior was observed at 120 K and single exponential behavior was observed between 60 and 4 K. However, without a knowledge of the viscosity dependence of this solvent with temperature, it is not possible to compare these results with the previously obtained ground-state recovery results. Nevertheless, it can be said that all lifetimes extracted from the observed fluorescence decays were seen to increase with decreasing temperature and, hence, increasing viscosity, which is in accordance with the works discussed above. In contrast, when a tenth of a monolayer of basic green 4 was adsorbed onto quartz, the lifetime of the dominant fast component (46 ± 5 ps) was seen to be independent of temperature, in the range 298–4 K.[450] Such behavior, has enabled basic green 4 to be considered as a sensitive probe of free volume in a variety of solid media.[450]

Other points of importance include (a) τ_{gsr} and the relaxation times measured using polarization spectroscopy increase with increasing size of the phenyl ring group (R in Figure 1),[103,449,504,514,516] (b) τ_{esa} and τ_{gsr} decrease with increasing temperature,[103] (c) stimulated emission signals (which are equivalent to time-resolved fluorescence) have been found to decay faster than excited-state absorption for both diaminotriphenylmethane and triaminotriphenylmethane dyes in low viscosity solvents,[465,471] and (d) the decay of the excited-state absorption does not obey a simple exponential function.[103]

In order to account for the observed photophysics, various kinetic schemes have been proposed. The most notable being those proposed by Cremers and Windsor,[449] Sundström et al.,[136] Menzel,[127] and Ben-Amotz et al.[463,465,497,498] Each has succeeded to varying extents.

Cremers and Windsor concentrated on explaining the observed multiexponential decay functions.[449] They proposed that because the ground-state potential surface is shallow with respect to a synchronous variation between the phenyl rings, there is a wide distribution of ground-state conformers. When each is excited, a wide distribution of conformers is formed in the excited state. The decay of these is highly dependent upon the S_0–S_1 energy gap and this is determined by the phenyl ring angle (and hence also the viscosity of the medium). At high viscosities, conformational change is slow and each conformer decays with its characteristic decay time. This results in a multiexponential decay function. At lower viscosities, conformational changes are able to occur during the relaxation time, and the multiexponential decay function reduces to a few terms. This model suggests that the fluorescence decay time, of each conformer, is uniquely related to the S_0–S_1 energy gap for that particular conformer. The model therefore predicts that the fluorescence decay time should vary with the analyzing wavelength. Beddard et al.[470] were, however, unable to detect such a variation over the wavelength range of 650–800 nm, in their fluorescence upconversion experiment on basic violet 3 in a glycerol–water solution (11 P at 21.5 °C). Furthermore, since each excited-state conformer will possess its own unique emission properties (fluorescence decay time and spectrum), the observed fluorescence spectrum should be time dependent. This, however, was not seen by Hirsch and Mahr[469] when examining basic green 4 in glycerol (18 P at 15 °C).

The model proposed by Sundström et al.[136] is based upon the proposal by Lewis et al.[135] that the absorbance spectra of triaminotriphenylmethane dyes may be interpreted in terms of two overlapping absorption bands α and β (Figure 5), which can be attributed to two ground-state conformers (A and B respectively, Figure 2) in equilibrium with each other.

As suggested by Lewis et al.,[135] the A isomer absorbs in the long wavelength region of the visible absorption peak of the dye. Conversely, the B isomer absorbs preferentially in the short wavelength region of this peak. The diaminotriphenylmethane dyes do not possess the conformer absorbing in the short wavelength region. When excited to its first excited singlet state, S_1, each conformer was suggested to relax back to the ground state, S_0, through a consecutive process involving a twisted electronic state S_x. Time-resolved emission spectroscopy on triaminotriphenylmethane dyes in alcohol indicated that this is associated with a ground state.[136] The relaxation schemes for a single conformer in low viscosity (alcohol) and high viscosity (glycerol) solvents are depicted in Figure 14. The consecutive relaxation processes of each conformer, in either solvent, causes double exponential absorption recovery kinetics. In this model, the existence of two ground-state conformers is said to cause the absorption recovery decay lifetimes for the triaminotriphenylmethane dyes in alcohol (unlike those for diaminotriphenylmethane dyes) to show wavelength dependence. For the same reason the fluorescence of the triaminotriphenylmethane dyes in alcohol is double exponential whereas the diaminotriphenylmethane dyes exhibit single exponential behavior. In glycerol, both the fluorescence

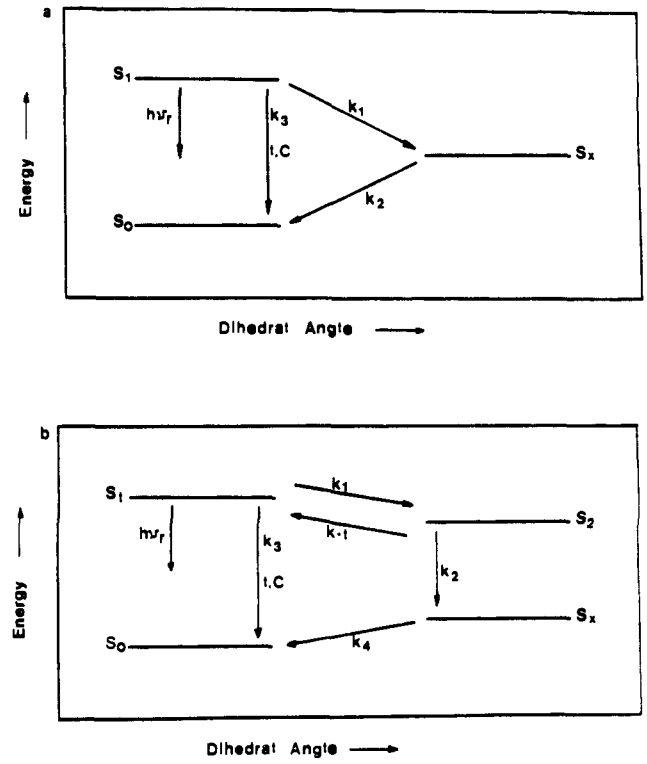


Figure 14. The relaxation mechanisms of triphenylmethane dyes in alcohol and glycerol: (a) in alcoholic solvents; (b) in glycerol. For both parts the symbols are as follows: S_0, the ground state; S_1, the first excited singlet state; S_x, a twisted electronic ground state; S_2, a twisted excited electronic state; k_{-1} and k_1 to k_4, the relaxation rates; IC, internal conversion. (Adapted from refs 136, 503a, and 504. Copyright 1982, 1982, and 1984, respectively, Kluwer Academic Publishers, Elsevier Science Publishers, and Springer-Verlag New York Inc.)

and absorption recovery kinetics of both types of triphenylmethane dye exhibit double exponential behavior. The fluorescence lifetimes are independent of the excitation and detection wavelengths and appear to arise from the conformer absorbing in the long wavelength region of the absorption spectrum. To account for this lack of wavelength dependence, Sundström et al.[136,467b] proposed that the initially excited state, S_1, existed in rapid equilibrium with a twisted excited state, S_2. This mechanism is analogous to that for p-type fluorescence.[529a,b] In general, it is apparent that there is a very low rotational energy barrier separating these two separate energy levels.[145,504] Some authors claim that the rotational motion is largely controlled by diffusion with slip or subslip boundary conditions.[504] In addition, this theory accounts for the wavelength-dependent relaxation rates observed for the triaminotriphenylmethane dyes in both solvents since it proposes that the relaxation rates (k_1 to k_4) are different for both conformers (the relaxation of the B isomer being slower). A subsequent study by Doust[486] showed that some of the kinetic features of the fluorescence decay of triphenylmethane dyes, observed at short times, could not be accounted for by the model proposed by Sundström et al.[136,467b,503a,504]

In contrast to Lewis et al.,[135] other researchers have interpreted the absorbance spectra of triaminotriphenylmethane dyes as arising from two electronic transitions, from a single ground-state conformer into two neighboring electronic transitions.[107,124,125,140] Menzel et al.[127] based their kinetic model, for basic violet

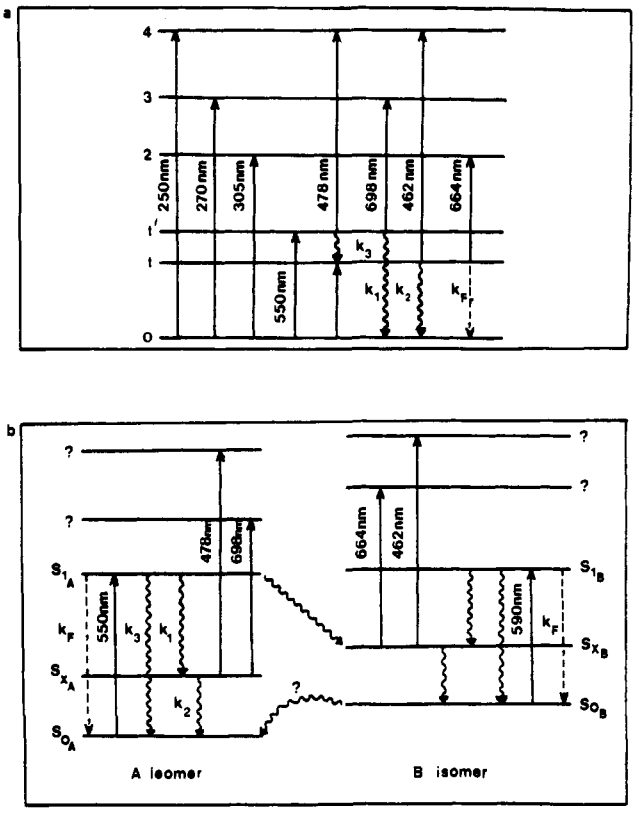


Figure 15. A comparison of the relaxation mechanisms of basic violet 3 in methanol proposed by (a) Menzel et al.[127] and (b) Sundström et al.[136,503a,504] (Adapted from refs 127, 136, 503a, and 504. Copyright 1985, 1982, 1982, and 1984, respectively, Kluwer Academic Publishers, Elsevier Science Publishers, Springer-Verlag New York Inc.)

3 in methanol, upon this concept. Their proposed kinetic scheme is depicted in Figure 15. It can be seen from this that both the ground- and excited-state absorptions occur in pairs. The dual exponential absorption recovery kinetics are explained by attributing the fast component to the $(k_1 + k_3)$ process and the slow component to k_2. In addition, the delay in fluorescence detected by Doust,[488] at short decay times, can be attributed to the k_3 process which populates level 1 from which fluorescence occurs.

The previously discussed works attribute the faster relaxation rate for basic violet 3 in *n*-alcohol, found when probing the red side of the visible absorption peak, to either the presence of the two ground-state conformers (A and B)[129,134,136,467b,503a,504] or to two neighboring excited electronic states.[125,127] Ben-Amotz et al.,[465,497] like several other workers[127,134] and unlike Sundström et al.,[136,467b,503a,504] collected their data using an analyzing wavelength different from that of the excitation wavelength. From such studies, these workers obtained results that suggest that this faster decay process occurs because part of the ground-state recovery signal may be attributed to stimulated emission. Consequently, they suggest that most of the observed photophysical processes may be explained by invoking only one ground state and one excited electronic state in the kinetic scheme. This kinetic scheme is only able to partially explain the dependence of the ground-state recovery kinetics on the probe wavelength. It does not address the question of why there is a decrease in the absorption recovery lifetime measured at the blue end of the visible absorption peak. In this respect Ben-Amotz et al.[465] were unable to distinguish between the kinetic schemes proposed by Sundström et al.[136,467b,503a,504] and Menzel et al.,[127] discussed above.

It has been suggested that the major mode of radiationless relaxation is due to rotation of the phenyl ring about the bond between the central and ring carbon atoms. Such motion is believed to reduce the energy gap between the ground and excited states and produce an excited-state molecular conformation from which efficient internal conversion occurs to repopulate S_0.[102,103,449,461,472-474,476,489] In support of this, it has been observed[102,507] that the ground-state recovery process is both fast and complete, causing the intersystem crossing process to be small.[449] In fact, it is believed that less than 3% of the molecules populate the triplet state upon picosecond excitation.[103] These observations have not been taken into account in several of the photochemical degradation studies[530-534] discussed in section IV.C of this manuscript. Accordingly, the reader will notice, in section IV.C, that some workers have claimed that dye photodegradation, in low-viscosity solvents, predominantly proceeds via the excited triplet state dye. Such an interpretation for dye fading, in low viscosity solvents, must however, be questioned, since the evidence presented in this section indicates that the excited singlet state of the dye should play a more important role in dye fading. The rate of the radiationless relaxation process is believed to be governed predominantly by the rate of change of molecular conformation (in vibronic levels above the lowest vibrational level of S_0). For basic violet 3 in alcohol, the rate of torsional twisting is believed to be faster in the ground state than in the excited state.[465] In view of the above, it is not surprising that a great deal of research has been devoted to examining several factors which will influence the rate of rotational motion. These include (a) the nature of the intramolecular potential surface in the excited[103,129,144,145,465,483,488,504,517] and ground[103,144,145,364,449,465,488] states, (b) the kind of frictional forces between the solvent and solute,[129,504,517,521] which is dependent on (c) the solvent viscosity,[102,129,136,273,465,467a,b,468-470,472,480,486,499,500,502-504,507,517,521] which can be altered by varying the solvent composition[102,136,465,467a,469,470,486,502,503a,504,507] the temperature[103,129,136,144,469,472,486,497,503a,504] and pressure[463,480] of the solution, (d) the molecular volume of the solvent,[129,504,517] and (e) the volume, shape, and flexibility of the rotating portion of the dye responsible for electronic relaxation.[103,129,136,144,449,470,483,488,503a,504,535]

Finally, the driving force behind such rotational motion has been considered.[103,144,145,461,483,488,513] It has been suggested that the force which causes the phenyl rings in the excited molecule to undergo torsional motion arises due to steric hindrance between the hydrogen atoms ortho to the central carbon atom in the dye structure.[461] Little attention has been paid to the effect that stretching of the central carbon bonds would have in relieving steric hindrance.[103,364,497,498,511] However, the concept of relieving steric hindrance does not explain why systems like triphenylamine do not undergo rapid relaxation like triphenylmethane dyes.[294] Nor does it explain why the dimethylmethano-bridged derivative of basic green 4[144] relaxes more slowly than the same carbon-bridged derivative of basic violet 3. It seems, that electronic effects may also be important as

suggested in several works.[144,145,483,486,513,536] From such considerations Vogel and Rettig proposed that the S_1 excited state is in equilibrium with a twisted intramolecular charge-transfer state (TICT)[144,145,483] or biradicaloid charge-transfer state (BCT).[486] They proposed a TICT, like that suggested by Grabowski,[537] or a BCT state that can be formed by rotation of one phenyl ring or two phenyl rings simultaneously. Strong acceptor groups in the dye molecule were found to accelerate the rate of formation of the TICT state. This had the effect of shortening the fluorescence decay and lowering the fluorescence quantum yield of S_1, since for triphenylmethane dyes the TICT state is nonemissive. Consequently, population of this state favors radiationless relaxation to the ground state. This effect is also seen in bridged derivatives of triphenylmethane dyes.[506] Vogel and Rettig[144,145,483,513,538] found that the energy difference between the S_1 and TICT state could provide the driving force for rotational relaxation of triphenylmethane dyes. Korppi-Tommola et al.[124] have also suggested that some degree of intramolecular charge transfer may take place.

Recently, Rettig[513] and Lippert et al.[536] have reviewed TICT compounds and discussed the factors affecting their formation and their relevance to triphenylmethane dyes.

The majority of the research discussed above assumes that solvent viscosity is the predominant factor influencing the radiationless relaxation mechanism of triphenylmethane dyes. If this were the only factor, then the ground-state recovery time, or decay of the excited-state absorption, for any solution of a particular viscosity, should be the same irrespective of whether the viscosity was produced by changing the pressure, temperature, or solvent composition. Several researchers[129,463,497,504] have not found this to be the case. It has been suggested that another solvent property, apart from viscosity, may influence the radiationless decay of triphenylmethane dyes.[129,497] In particular, solvent properties such as solvent polarity, dielectric constant, dielectric friction, and molecular size of the solvent have been mentioned.[473,497] It has been reported[463] that some such solvent properties may change with temperature and pressure in a correlated way with changes in viscosity. Ben-Amotz et al.[463,497] have made detailed studies of the effect of changing temperature, pressure, and solvent composition on the relaxation behavior of triphenylmethane dyes. They have tentatively ascribed such variations between the temperature, pressure, and solvent composition-dependent relaxation behavior, at low viscosity, to temperature- and pressure-induced conformational changes in the ground state of the dye.

The excited-state lifetime of basic violet 3 shows a linear dependence on viscosity (at constant temperature) in the viscosity range, 0.5 cP $< \eta <$ 10 cP, but is nonlinear at higher viscosities.[497] Linear viscosity dependence, in the low viscosity regime, is the outcome of Oster and Nishijima's theory.[527] Kramers theory,[480] on the other hand, predicts that the decay time will decrease with increasing viscosity, in the low-viscosity regime, but predicts linear behavior in the Smoluchowski limit. The more complex pinhole sink and nonlocal sink (for $\eta >$ 1 P) models of Bagchi et al.[499] also predict a linear viscosity dependence. Linear viscosity dependence is, therefore, seen to be a property of both barrierless and barrier diffusive theories. Ben-Amotz and Harris[497] considered that the behavior in the low viscosity regime together with the short decay times of triphenylmethane dyes, in most solvents, implies that the excited-state relaxation coordinate is barrierless.

When the excited-state decay rate[497] or ground-state recovery time,[129] for basic violet 3 in various n-alcohols ($n \leq 6$,[129] $n \leq 8$,[497]) at fixed viscosity, is plotted against temperature, in the Arrhenius form (log k versus $1/T$), the isoviscosity lines show positive slopes[129,497] for all viscosities in the range 0.6–8 cP[497] and at 10 cP[129] in the respective temperature ranges 275–310[497] and 210–275 K.[129] At higher temperatures, in longer chain alcohols, the slope of each isoviscosity plot changed to a negative value.[129,497] This unusual behavior, appears to be correlated with the curvature observed in isothermal plots of τ_{gsr}[129] (or excited-state decay time[497]) versus viscosity for n-alcohols. Sundström and Gillbro[129] have attributed this behavior to be the result of solvent-dependent potential changes, which create a small barrier in the relaxation coordinate of the dyes in long-chain alcohols.[129] Accordingly, Sundström and Gillbro[129] suggested that the turnover behavior of the relaxation of triphenylmethane dyes in long-chain alcohols corresponds to passing from the low friction region to the intermediate friction regime in a Kramer's type barrier crossing theory.[480] Ben-Amotz and Harris,[497] however, claim that this would correspond to an unrealistically high viscosity of about 10 cP. On this basis, they alternatively suggested that the turnover effect is due to saturation of the microscopic friction in long chain alcohols.[497] In such an event the macroscopic friction is not proportional to the microscopic friction.[497] The importance of microviscosity has been subsequently examined.[486]

The relaxation behavior of basic violet 3 in alkyl halide solvents is markedly different from that observed in the normal alcohols.[497,498] In this case, the possibility that the reaction coordinate varies with the solvent cannot be excluded.

The actual nature of both the ground- and excited-state surfaces has long been a matter for debate.[129,144,145,384,463,465,483,486,497-500,521] Over the years several principal theories have emerged. The first considers a model in which the excited-state potential surface is flat and barrierless with respect to free rotational diffusion of the phenyl rings. In this theory the initially prepared excited-state population, may diffuse in either direction along the potential surface, by a one-dimensional random walk (or Brownian motion), until it reaches one of two regions (or "sinks" equally distanced from it) from which radiationless relaxation to the ground state may occur. Oster and Nishijima[527] applied this idea to the phenyl ring rotation of diphenylmethane dyes. Subsequently, the idea that triphenylmethane dyes may encounter a relatively flat, barrierless excited-state potential surface with respect to ring rotation has been invoked to describe the radiationless process of triphenylmethane dyes in solvents of low viscosity.[129,465] A modified version of Oster and Nishijima's idea,[527] which allows for arbitrary placement of the initially excited state between the two sinks, has been able to explain much of the observed

dynamics of basic violet 3 in various solvents.[498]

The second theory was studied by Förster and Hoffman[461] and was previously mentioned in the introduction to this section. They assumed a harmonic well potential for S_1 and S_0 and that the energy minima of the ground and excited states are greatly displaced. Consequently, the molecule in the photoexcited state is driven "downhill", toward a new equilibrium position during the relaxation process. The nonradiative decay rate is assumed to vary continuously with the synchronous rotation of the phenyl rings. The new equilibrium position is characterized by a high rate of radiationless relaxation. Although the theory predicts the relationship, $Q_f \propto \eta^{2/3}$, between the quantum yield of fluorescence (Q_f) and the solvent viscosity (η), observed by some workers,[144,461,464,469] (and by Mastrangelo and Offen[460] when the proportionality constant is assumed to be a pressure-dependent variable), the predicted time dependence of the excited-state relaxation has not been observed.[472,476,521] Such a model also predicts that the fluorescence spectrum would shift to the red as the S_1–S_0 energy gap decreases with increasing time. Furthermore, molecular orbital calculations predict that the difference in the potential surface minima is only a few degrees, in contrast to the large displacement suggested by the model.[496] Ben-Amotz et al.[498] and Bagchi[495] have also found that the model of Förster and Hoffman[461] is not suitable for describing the excited-state decays of triphenylmethane dyes.

Bagchi et al.[495,499,500] have also considered the electronic relaxation of triphenylmethane dyes in the absence of a barrier on a harmonic excited state potential surface. The relaxation process of an excited molecule on the potential surface is modeled by a position dependent sink. Three different types were considered. These were (a) a pinhole sink located at the minimum of the excited-state well, (b) a Gaussian sink with maximum probability of decay at the same location and (c) a Lorentzian sink with maximum decay also at the minimum of the potential surface. Subsequent work by Ben-Amotz and Harris[498] has shown that the pinhole sink model of Bagchi et al.[499] is able to describe the excited-state decay of basic violet 3 in n-alcohol solutions reasonably well.

Various barrier-diffusive theories have been considered for describing photophysical relaxation processes. One of the most notable is that in which the excited-state potential surface of S_1 takes the form of a double minimum. Initially, the molecule is excited into one side of the double well. As the excited-state relaxation of the molecule proceeds, it encounters a barrier of height E_0, which it must surmount before it is transferred into the second well. The excited-state population continues to diffuse along the potential surface until it reaches a final position from which maximum internal conversion may occur. For such an excited-state potential surface, theories for an activated barrier crossing process, like that proposed by Kramer[460] can be used to describe the relaxation process of the molecule, if $E_0 \gg kT$. Sundström et al.[129] have suggested that a Kramer's type theory can explain the relaxation of triphenylmethane dyes in long chain n-alcohols (C_8–C_{18}). They believe, in contrast to Ben-Amotz et al.,[60a,497] that the development of an excited-state barrier when passing from short-chain n-alcohols (C_7 and lower) to long chain n-alcohols causes the relaxation rate of triaminotriphenylmethane dyes to depend nonlinearly on viscosity.

Several outstanding issues remained in debate in the 1987 literature on the photophysical relaxation of triphenylmethane dyes. These were (1) the existence of an intermediate electronic state in the deactivation pathway, (2) the nature of the proposed intermediate electronic state, (3) the height of the small potential energy barrier encountered by the initially prepared excited dye molecule when trying to reach the new molecular configuration of the proposed intermediate state, and (4) the number of ground or excited electronic states responsible for the visible light absorbance spectrum.

Since 1987, there has been considerable activity in both the theoretical and experimental picosecond and femtosecond studies on triphenylmethane dyes. These have led to significant advancements in this field. So that this review will be of maximum benefit to the reader the most important recent advances and references are briefly noted below. This discussion will then be followed by an examination of the phosphorescent behavior of triphenylmethane dyes.

First, it is noted that recent photophysical hole-burning experiments on basic violet 3 in methanol and 2-propanol[539] have determined that the lifetime of the S_1 state in 2-propanol is 12.5 ± 2 ps, in agreement with previous kinetic experiments.[136]

Martin et al.[119,492–494,540] used time-resolved spectroscopy to study the fast electronic relaxation of basic violet 4 in a variety of solvents of varying viscosity and dielectric constants. They maintain that the shapes of the measured transmission curves indicate that molecular relaxation involves the formation of an intermediate nonradiative state (S_x). Thus, contrary to Ben-Amotz and Harris[465,497] who favor a two level relaxation scheme involving S_0 and S_1, the model proposed by Martin and co-workers considers three electronic levels, S_0, S_1, and S_x. [The upper excited electronic states (S_n where $n > 1$) were assumed to relax so rapidly that they do not contribute to the observed kinetics.] The geometries of both the S_1 and S_x states are unknown. However, Martin et al.[492–494] have determined that the transient S_x state of basic violet 4 has a similar absorption spectrum to S_1, except that it is blue-shifted. The absorption spectrum of S_x for basic violet 4 in ethanol peaks at around 410 and 610 nm whereas the S_1 state absorption is observed maximally at 440 and 640 nm. On the basis of these spectral observations and the fact that deactivation rates were not influenced by the solvent dielectric constant, Martin et al.[119,493,494] suggest that S_x is a distorted form of S_1 possibly with a charge-transfer nature. Unlike the particular case of basic green 4 examined by Robl and Seilmeier,[541] the work on basic violet 4 in ethanol does not appear to suggest that S_x is a hot vibrational level of S_0. Furthermore, these workers observed that the excited-state decay rate is independent of the excitation wavelength[492] and suggest[493] that the dependence of the absorbance decay upon probe wavelength can be explained by the superposition of the absorbance and gain spectra of the S_0, S_1, and S_x states involved in the photophysical process. Their polarization studies confirm two overlapping electronic transitions ($S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$) in

the visible ground-state absorption for basic violet 4. The lower S_1 state being fluorescent. This is in accord with the studies discussed in section IV.A.1 of this review and also with the band-shape analysis study by Menzel and Kessler[128] and the polarization study performed by Mokhtari et al.[120] The latter workers also found, from their polarization study, that while the dyes basic green 4 and basic violet 3, in water, had molecular symmetries approximating C_2 and D_3, respectively, they were better described as a thermal population of twisted states distributed around the initial symmetry (as discussed in section IV.A.1 of this review), when analyzing the photodynamical behavior of triphenylmethane dyes.

As mentioned above, the time- and frequency-resolved investigations performed on basic green 4 in benzyl alcohol by Robl and Seilmeier[541] suggest that the intermediate state S_x corresponds to a vibrationally excited state of the ground electronic state, with an internal temperature of 600 K. Analysis of their kinetic data also suggests that a three level scheme is appropriate in describing the ground-state recovery of basic green 4 in low-viscosity solvents. Their results provide evidence for the transfer of excess energy from S_1 to the vibrational manifold of S_0 via internal conversion with a time constant of 3 ps. The excess energy of S_x is then dissipated to the surrounding solvent with a time constant of 10 ps. These workers were unable to comment on the details of the internal conversion process due to the time resolution of their experiments (2 ps). However, Mokhtari, Fini, and Chesnoy[120] could resolve the behavior of basic green 4 and basic violet 3 in water (η = 1 cp) and dimethyl sulfoxide (η = 2 cp) on a femtosecond time scale. In their pump–probe-induced photoabsorption recovery experiments, they observed a biexponential relaxation component in the short time (<0.5 ps) dynamics of both dye/solvent systems. One component was attributed to torsional equilibration in the S_1 state and had a torsional relaxation time of $T_\psi \approx 0.5$ ps for both dyes in both solvents. The other faster component, which decayed in less than 100 fs for both dyes in water was attributed to vibrational relaxation of the S_1 low-frequency modes. Ultrafast vibrational redistribution was also observed to occur in less than 100 fs, in their subsequent subpicosecond fluorescence studies.[364] The lifetimes of both components exhibited solvent dependence. Additionally, they reported a 0.63-ps component which was associated with the relaxation of S_1 (Figure 16a).[120] The subsequent study by Mokhtari et al.[364] reported a biphasic fluorescence decay for basic green 4 in water. In addition to the 0.6-ps component seen in both studies,[120,364] a previously unobserved fluorescence decay of 150 fs was observed in the early time dynamics (<0.5 ps) of this biphasic decay. However, due to the different experimental configurations employed, these researchers were not able to compare this result with those obtained in their previous pump–probe experiment.[120] They did, however, speculate that the 150-fs decay may be associated with the internal conversion process that preferentially occurs from a given torsional configuration. Figure 16 shows the three recently proposed kinetic relaxation schemes. Notice that the 3-ps decay is attributed to the relaxation of S_x by Mokhtari et al.[120] (Figure 16a), but, in contrast, it is attributed to the relaxation of S_1 by Robl and Seilmeier[541] (Figure 16b).

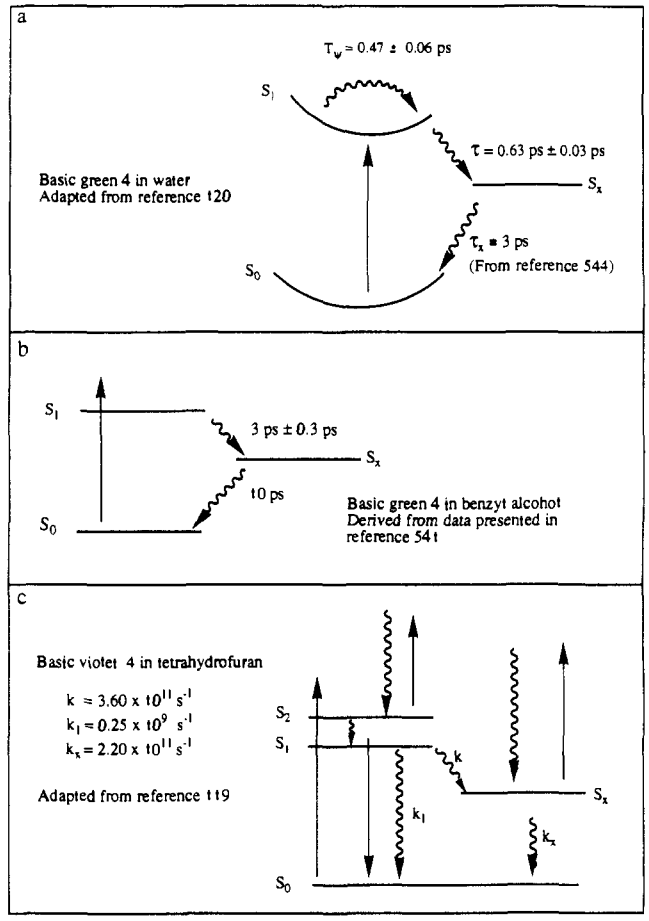


Figure 16. Three recently proposed kinetic relaxation schemes for several triphenylmethane dyes. (Adapted from refs 119, 120, and 541. Copyright 1989, 1987, and 1988, respectively, Elsevier Science Publishers and the American Institute of Physics.)

Recently, determination of Raman to fluorescence intensity ratios have been used to estimate the fluorescence lifetimes for basic violet 3 and basic green 4 in water.[542] The estimated values of 1.2 and 0.8 ps for aqueous solutions of basic violet 3 and basic green 4 agree well with the reported literature values of 1.1 ps,[514] for the violet dye and 0.7,[514] 0.93,[501] and 1.2 ps[515] for basic green 4, obtained from ground-state recovery measurements.

The sensitivity of the photodynamical behavior of triphenylmethane dyes to their environment has lead to another recent study which concludes that basic green 4 can be used as a sensitive probe of free volume in a variety of solid media.[450] The details of this study were discussed more fully previously in this section.

Apart from the above mentioned experimental studies, new theoretical studies have also considered the electronic relaxation of triphenylmethane dyes. In addition to considering the effect of including an arbitrary initial excited state population in the pinhole sink, Gaussian sink,[495,499,500] and the Oster–Nishijima model[527] previously discussed in this section, Bagchi[543] has introduced another zero-barrier model, which may be more appropriate in describing the electronic relaxation of triphenylmethane dyes. This new model is referred to as the staircase model. In this model an

arbitrary Gaussian excited-state population is prepared on the flat excited-state potential surface. As a diffusing molecule moves along this surface it encounters an elastic barrier on one side and a sink on the other. Decay is achieved only when the diffusion molecule reaches the sink. Describing the excited-state population as a Gaussian rather than a δ function as in the previous studies[495,499,500,527] leads to a faster decay in the short-time region. When a Gaussian function is used to describe the initial excited-state population in both the Oster–Nishijima model[527] and the staircase model[543] it is found that the long time decay predicted by the former model is four times faster than that predicted by the latter model. This is to be expected since the staircase model has one sink from which a molecule may decay whereas in the other situation there are two sinks.

In summary, the recent studies, discussed above, have confirmed that the electronic singlet states of triphenylmethane dyes are strongly dependent upon the twist angles between the central sp^2 carbon and the benzenic plane of the dyes. While the molecular symmetry is close to D_3 for basic violet 3 and close to C_2 for basic green 4, the situation is better described as a thermal population of twisted states distributed around the initial symmetry,[120] when analyzing the photodynamics of this class of dye.

Absorption polarization studies[107,119] have confirmed the existence of two electronic transitions in the visible ground-state absorption of the triaminotriphenylmethane dyes basic violet 3 and basic violet 4. Similarly, band-shape analysis of the absorption bands of basic violet 3 and basic green 4 in methanol and glycerol also support this conclusion.[128] The polarizations of the transitions for D_3 symmetry for basic violet 3 are shown in Figure 3 along with those for a C_2 symmetry for basic green 4.[120] Again, it is noted that, such simplified schemes are best used as a first approximation when analyzing the photodynamics of triphenylmethane dyes.

The relaxation dynamics of triphenylmethane dyes seems to be best described by at least a three-level system. On the subpicosecond time scale the relaxation dynamics of the diaminotriphenylmethane subclass of dyes appears to involve two processes. The first was attributed by Mokhtari et al.[120] to the conformational relaxation of torsional modes. The second, and faster, process is believed to arise from solvent limited vibrational relaxation.[120] This assignment is supported by the studies of Rosker et al.[451] who observed quantum beating in the lowest frequency breathing mode of 220 cm^{-1} for basic green 4 in water.

On the picosecond time scale the relatively long time dynamics of the relaxation of S_x to S_0 has been observed by numerous workers, such as Migus et al.[544] and others (see text). This is the rate-determining step in the relaxation process down to S_0. In some systems, it has been said to represent intermolecular energy dissipation to the solvent,[541] while in others[119,492–494] such an interpretation has not been deemed necessary.

Both the nature of the intermediate state S_x as well as the height of the possible energy barrier between S_1 and S_x are still a matter for debate. However, it is clear that the possible energy barrier must be small.[497] For basic green 4 in water S_x appears to be a hot ground state with torsion-induced charge transfer character.[364] Thus, S_x is nonfluorescent and no red-shift is expected or observed in the S_1 fluorescence spectrum.[364] For the triaminotriphenylmethane subclass, the situation is less clear, as weak infrared stimulated emission has been reported.[497] This emission may be due to either the tail end of fluorescence from S_1 or alternatively to a TICT state corresponding to S_x. Other workers[119,492–494] studying triaminotriphenylmethane dyes, however, do not invoke the idea of a TICT state (as defined by Grabowski[545]). Instead S_x is simply suggested to be a distorted form of S_1, possibly with charge-transfer character. This characterization is based on the observation that the absorption spectrum of S_x was found to be similar to that for S_1, but shifted to higher energies, and the observation that deactivation of S_x is independent of the dielectric constant of the solvent. With these concepts in mind, it is now pertinent to pursue a discussion of the phosphorescence behavior of triphenylmethane dyes.

When internal conversion from the first excited singlet state to the ground state is suppressed by increasing molecular rigidity, the number of transitions to the triplet state should increase. Several studies have verified this[135,246,259,478,546,547a,b] and noted that phosphorescence is more easily observed when the criterion of molecular rigidity is fulfilled. Suppression of molecular mobility may be achieved by binding a dye to a polymer or incorporating it into a rigid medium such as a glass or solid polymer matrix. In both instances population of the triplet state will be favored by the reduction in (a) collisional deactivation and (b) accessibility of oxygen (a triplet-state quencher)[548] to the dye.

Many researchers have utilized this property. For example, Nouchi and Silvie[549] have measured the triplet–triplet absorption of basic violet 1, basic violet 3, and basic violet 4 in solid (and liquid) media. Antonucci and Tolley incorporated basic violet 3 into an ethanol–methanol (4:1) glass at 77 K[550] to measure the triplet ESR signal of the dye photolyzed with a mercury lamp.

Lewis et al.[135] examined the phosphorescence of basic violet 3 in glycerol at 178 K. When excited with visible light two emissions were observed, one in the red and the other in the infrared. From the temperature dependence of this phosphorescence, the red phosphorescence was found to be α-type phosphorescence (or delayed fluorescence) while the infrared phosphorescence was β-type phosphorescence. When excited with ultraviolet light at 90 K (and down to 20 K), a second phosphorescent state was formed which gave rise to green β-type emission. Green phosphorescence has been reported in several others works.[546,551] Lewis and co-workers[135] attributed all phosphorescence to the A isomer. Oster et al.[246,478] observed similar results for several triaminotriphenylmethane dyes in glucose glasses. They observed that the red α-phosphorescence could be correlated with the ability of the dyes to undergo photoreduction (section IV.C.2). More recently, Janowski and Rzeszotarska[448] observed anomalous $T_2 \rightarrow S_0$ phosphorescence in tri- and dicarboxylic acid derivatives of triphenylmethane dyes and attributed this to a large $S_2 \rightarrow S_1$ energy gap which enhanced $S_2 \rightsquigarrow T_2$ intersystem crossing.

In addition to suppressing internal conversion, dye aggregation can enhance the quantum yield of phos-

phorescence, at the expense of fluorescence. Mc Rae and Kasha[552] first drew attention to this fact in 1958. Aggregation is favored by high dye concentrations[553,554] and adsorption onto solid surfaces (including polymers).[245,553-555] Dye aggregation causes the excited singlet levels of the aggregate to split relative to those of the monomer[302a,552] (Figure 6). The splitting of the triplet levels is very slight and the lowest excited singlet state levels for both types of dimerization (shown in Figure 6) have similar energy to the first excited triplet state. Moreover, phosphorescence will be enhanced when the lifetime of the S_1 state of the dimer is larger than the lifetime of the S_1 state of the monomer. This will occur predominantly in the case of sandwich-type dimerization because the transition dipole moments for each monomeric component of the dimer are opposed (Figures 6 and 7) and thus the lifetime of the S_1 state is increased because the $S_1 \rightarrow S_0$ transition is forbidden. In the case of head-to-tail dimerization the enhancement of phosphorescence is not as large, since the component dipole moments reinforce each other (Figures 6 and 7) making the $S_1 \rightarrow S_0$ transition allowed. It is worthwhile noting here that similar considerations of the transition dipole moments and reference to Figures 6 and 7 reveal why the fluorescence of a head-to-tail dimer and the fluorescence of a sandwich-type dimer are red-shifted relative to the monomer transitions.[303,259]

C. Photochemical Reactions of Triphenylmethane Dyes

Considerable evidence exists to suggest that the photodegradation mechanisms of triphenylmethane dyes may be broadly classified as either photooxidation or photoreduction. Several electrochemical studies have shown that oxidation[556-558] or reduction[556-562] of these dyes is possible under certain experimental conditions. It has also been observed that several triphenylmethane dyes, within a given structural series, often rank in the same order when faded by light or when oxidized or reduced chemically.[563]

From such studies a general rule was formulated; that fading usually entails oxidation of dyes on nonprotein substrates and reduction on protein substrates. For dyes that obey this rule, the order of the degree of photodegradation would be expected to be reversed for dyes on a protein substrate compared to a nonprotein substrate. This trend was observed by the author when comparing the fading of acid blue 1, acid green 9, acid blue 15, and acid violet 17 on wool to that on methyl cellulose.[183]

Product analysis of stable photoproducts and intermediates has revealed several important modes of photodecomposition, namely (1) electron ejection from the dye, (2) reaction with ground-state or excited singlet state oxygen, (3) cleavage of the central carbon–phenyl ring bonds to form amino substituted benzophenones, (4) direct reaction of the carbinol form of the dye to form amino-substituted benzophenones, (5) reduction to form the colorless leuco dye, and (6) electron or hydrogen atom abstraction to form radical intermediates.

These modes of photodecomposition will be discussed in more detail under the broader headings of photooxidation and photoreduction of triphenylmethane dyes, since product analysis suggests that several modes may occur under the same experimental conditions. However, the experimental conditions will determine the relative degree to which each mode will occur.

The lightfastness of triphenylmethane dyes has been discussed in the work by Gordon and Gregory[2c] and in the reviews by Sinclair,[564] Evans[302c] and Leaver.[302d]

1. Photooxidation of Triphenylmethane Dyes

Photooxidation has been observed when dye is in powdered form,[565,566] when the dye is dissolved in solution[531-534,565,567-571] and when it is incorporated into solid substrates such as wool,[572] cellulose,[531] modified cellulose,[532] and various polymer media.[570,573] It is usually favored however, under aerobic conditions[566,567,569,571,573,574,575] and when the medium (solid or liquid) containing the dye is more easily reduced than the dye itself. Thus, photooxidation is observed more frequently on nonprotein substrates than on protein substrates,[563] and in solids and liquids of poor electron[570] or hydrogen atom donating ability.[570,576]

Several workers have suggested that the initial process in photooxidation is the ejection of an electron from the dye cation $^3D^+$ (presumably in the triplet state).[531,565,567] The proposed importance of the triplet state of the dye must, however, be questioned for studies in low-viscosity solvents, since the evidence presented in section IV.B of this paper suggests that the excited singlet state of the dye should play a more important role in dye fading. In particular, the reader should bear this in mind when reading the following text and discussions regarding the studies presented in refs 531–534.

Bangert et al.,[531] who studied the photodegradation of basic green 4 and basic violet 3 in modified cellulose and aqueous solutions, suggested that the photooxidation process produced a radical dication $D^{\bullet 2+}$ and a solvated electron e^- (solvated)

$$D^+ \xrightarrow{h\nu} {}^1D^+ \rightarrow {}^3D^+ \quad (3)$$

$$^3D^+ + \text{solvent} \rightarrow D^{\bullet 2+} + e^- \text{(solvated)} \quad (4)$$

The radical dication may recombine with the solvated electron to regenerate the dye. Alternatively, dye fading may occur via reaction of the radical dication with oxygen to form a dye peroxide which decomposes to the observed products

$$D^{\bullet 2+} + O_2 \rightarrow \text{(peroxide)?} \rightarrow \text{products} \quad (5)$$

and/or via the reaction

$$D^+ + e^- \text{(solvated)} \rightarrow D^\bullet + \text{solvent} \quad (6)$$

$$2D^\bullet + H_2O \rightarrow DH + D^+ + OH^- \quad (7)$$

$$e^- \text{(solvated)} + O_2 \rightarrow O_2^{\bullet-} + \text{solvent} \quad (8)$$

$$O_2^{\bullet-} + H_2O \rightarrow HO_2^\bullet + OH^- \quad (9)$$

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \quad (10)$$

$$HO_2^\bullet + e^- \text{(solvated)} \rightarrow HO_2^- + \text{solvent} \quad (11)$$

$$HO_2^- + H_2O \rightarrow H_2O_2 + OH^- \quad (12)$$

Another possibility suggested by these workers was that photooxidation involves the attack by O_2 on the dye triplet

$$^3D^+ + O_2 \rightarrow \text{(peroxide)?} \rightarrow \text{products} \quad (13)$$

In support of reactions 7, 10, and 12, both hydrogen peroxide and the leuco dye DH were detected as reaction products. The fully reduced leuco dyes, leuco basic violet 3 (I) and leuco basic green 4 (II) (Figure 17) have been detected among the photoproducts in other studies,[565,566,568,571] in addition to a number of other photoproducts. The above mechanism may well represent dye fading in modified cellulose but may not appropriately describe dye fading in aqueous solution, since the excited triplet state of the dye has erroneously been proposed to play a major role in dye degradation.

Iwamoto[566] exposed powdered basic green 4 (oxalate) and basic violet 3 (oxalate) to sunlight and air and isolated the respective decomposition products, 4-(dimethylamino)benzophenone (III), and 4,4′-bis(dimethylamino)benzophenone (Michler's ketone) (IV) (Figure 17). Similarly, other workers[531-533,565,568,569,571,572,575] have identified amino-substituted benzophenones as end products of photooxidation of certain triphenylmethane dyes and during ozonization of basic green 4 in the absence of light.[92]

Porter and Spears[532,533] studied the photodecomposition of basic green 4 in aqueous solution and isolated the 4-(dimethylamino)phenol (XI) in addition to 4-(methylamino)benzophenone (XII) and 4-(dimethylamino)benzophenone (III) (Figure 18). To account for these findings, they proposed that photodecomposition commences with the absorption of light by the leuco carbinol (VIII) dye. The excited carbinol dye (possibly the triplet state, see previous section) is then converted to the decomposition products by two possible pathways (a) fragmentation into radicals (IX and X) which react with water and oxygen to form the end product XI and (b) a concerted reaction with oxygen and water to give the end products III and XII directly (Figure 18). Oxygen seemed to be necessary for the formation of the products III, XI, and XII and this is in agreement with the results of Iwamoto[566] for the formation of III. Evidence to suggest that the dye fades via the carbinol form VIII, rather than the cation VII, include the findings that (a) the rate of photodecomposition of several triphenylmethane dyes in aqueous solution

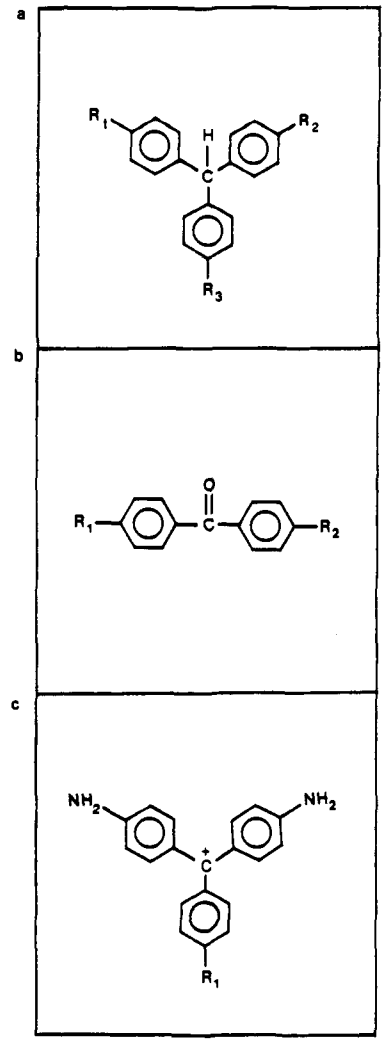


Figure 17. Some triphenylmethane dye photoproducts: (a) where $R_1 = R_2 = R_3 = N(CH_3)_2$ for leuco basic violet 3 (I) and $R_1 = R_2 = N(CH_3)_2$, $R_3 = H$ for leuco basic green 4 (II); (b) where $R_1 = H$ and $R_2 = N(CH_3)_2$ for 4-(dimethylamino)benzophenone (III) and $R_1 = R_2 = N(CH_3)_2$ for 4,4′-bis(dimethylamino)benzophenone (Michler's ketone) (IV); (c) where $R_1 = H$ for 4,4′-diaminotriphenylmethyl cation (Doebner's violet) (V) and $R_1 = NH_2$ for fuchsine (*p*-rosaniline) (VI).

increases with increasing pH[531,577,578] and (b) removal of light of wavelengths absorbed by the carbinol base, either by filtering the incident light[579] or by introducing ultraviolet absorbing compounds such as phloroacetophenone,[577] 2,2′-dihydroxy-4,4′-dimethoxybenzophenone[579,580] or 2,2′-dihydroxy-4-methoxybenzophenone[580] into a dyed system, frequently inhibits fading. Porter and Spears[532] also obtained evidence for the formation of the ketones III and XII in chemically modified cellulose and regarded this as evidence that the fading mechanism which occurs in solution is applicable for the dyed solid substrates. Accordingly, the slower fading of basic green 4 observed on sulfoethylated cellulose compared to carboxylated cellulose was explained by proposing that the concentration of the carbinol form of the dye was smaller on the former substrate.

Bangert et al.[531] proposed similar reaction schemes to account for the photoproducts of basic green 4 and basic violet 3 in cellulose fibers and aqueous solutions

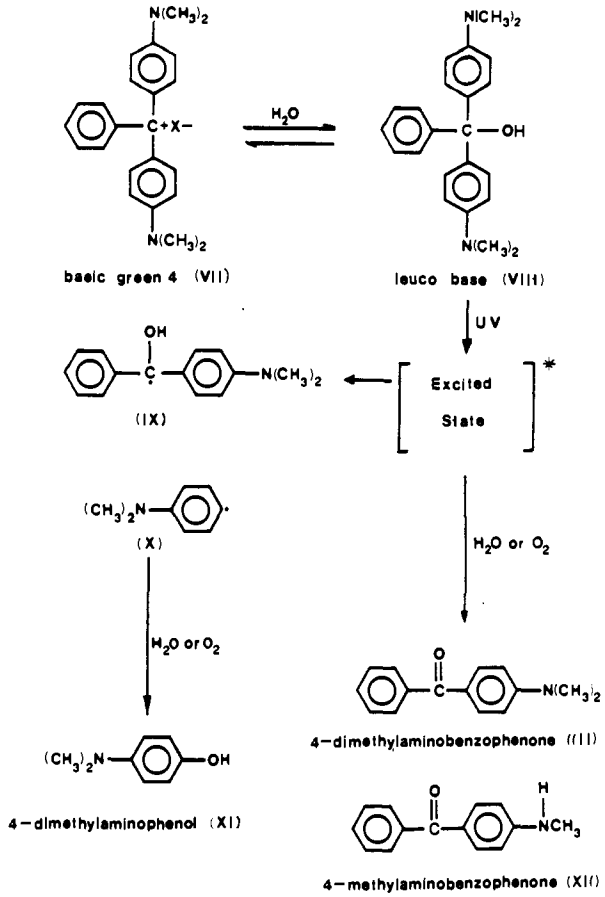


Figure 18. The decomposition mechanism for basic green 4 proposed by Porter and Spears. (Adapted from refs 532 and 533. Copyright 1970 and 1973, respectively, American Association of Textile Chemists and Colorists and the Textile Research Institute.)

(Figure 19). Briefly, these reactions include the following:

(1) N-Dealkylation of the dyes via *N*-oxide precursors (XXVI–XXX) of the demethylated products (XIX–XXIII). All of which were positively identified, in the case of basic violet 3 using thin-layer chromatography. The *N*-oxides of basic green 4 (XXVII and XXIX), however, were too unstable to be detected. In contrast to findings of other workers,[569,575,576,578] it appears that only one methyl group can be removed from each dimethylamino substituent and that *N*,*N*′,*N*″-trimethyl-*p*-rosaniline (XXIII) is the end product of the demethylation process of basic violet 3.

(2) Oxidation of the dyes to the amino-substituted benzophenones. These being IV, XXIV, and XXV for basic violet 3 and III and XII for basic green 4. As shown in Figure 19, these benzophenone derivatives may be formed by a number of pathways.

(3) Reduction to form leuco basic violet 3 (I) and leuco basic green 4 (11), and the additional demethylated leuco products XIII, XV, and XVII for basic violet 3 and XIV and XVI for basic green 4. All leuco compounds, especially the demethylated products were formed in very small amounts. It is interesting to note here that during the course of this investigation, demethylation products, *N*-oxides, ketones, and surprisingly, the leuco dyes and their partially demethylated derivatives were produced by chemical reaction of triphenylmethane dyes with hydrogen peroxide. The

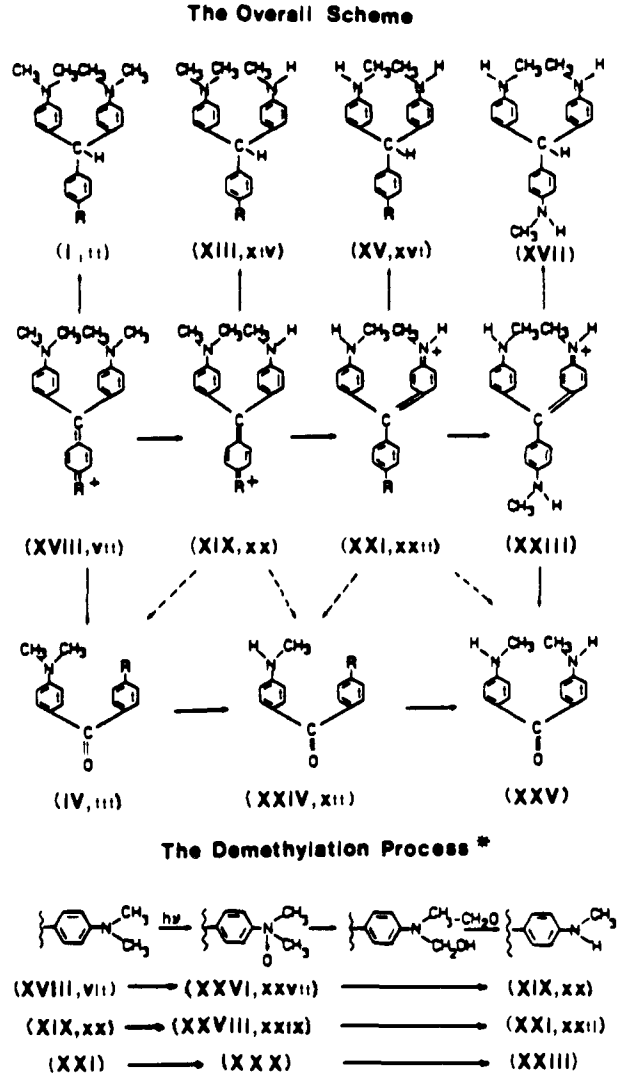


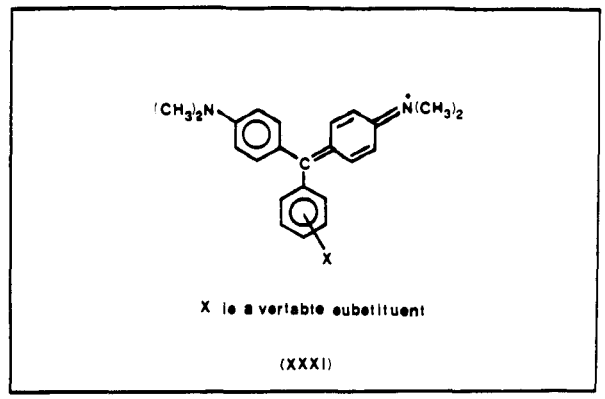
Figure 19. The photodegradation of basic violet 3 and basic green 4. Basic violet 3 and its photoproducts are denoted by the larger sized Roman numerals. The smaller sized Roman numerals refer to basic green 4 and its photoproducts. R = $N(CH_3)_2$ for basic violet 3 and R = H for basic green 4. * It has been suggested that compounds III and IV undergo a similar demethylation process. (Adapted from refs 302d and 531. Copyright 1980 and 1977, respectively, Melliand Textiberichte and Elsevier Applied Science Publishers.)

production of leuco dyes by hydrogen peroxide has been noted by Desai and Vaidya,[565,588] and it has been suggested that the hydrogen peroxide produced in the reaction scheme of eqs 3–13 can react with the dye to give oxidation products[567] e.g.

$$D^+ + H_2O_2 \rightarrow \text{oxidation products} \qquad (14)$$

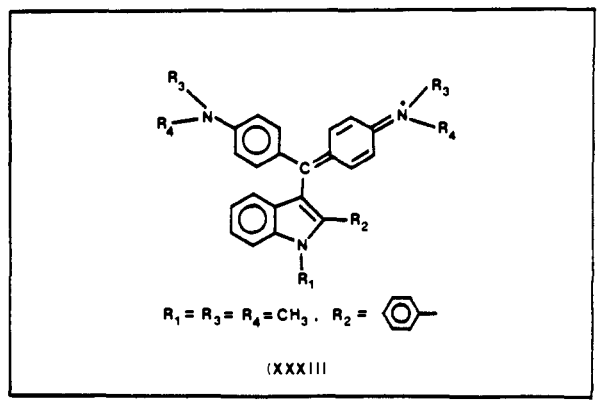
In the mechanism proposed by Bangert et al.,[531] dealkylation was established as a main photodegradative pathway for basic green 4 (VII) and basic violet 3 (XVIII). Dealkylation was first proposed by Henriquez[578] to account for the color changes observed when aqueous solutions of basic green 4 and basic violet 3 were exposed to ultraviolet light. Analysis of these solutions revealed that the fading products of these dyes were 4,4′-diaminotriphenylmethyl cation (Doebner's Violet) (V), and fuchsine (VI), respectively (Figure 17). Dealkylation products have since been detected in a number of other studies.[532,533,565,569,575,576,581] In the

a



(XXXI)

b



(XXXII)

Figure 20. Structural analogues of basic green 4 and acid blue 123 studied by Evans and Stapleton:[582] (a) basic green 4; (b) acid blue 123. (Reprinted from ref 582. Copyright 1973 Society of Dyers and Colourists.)

recent study by Nakamura and Hida,[576] leuco basic green 4 and basic green 4 were identified as photoproducts of basic violet 3, (in 2-propanol and acetonitrile solutions), using high-pressure liquid chromatography and absorbance spectroscopy. These photoproducts have not been reported previously for basic violet 3, and this assignment may be questioned upon the basis of the work by Bangert et al.[531] Bangert and co-workers noted that the absorption spectra of the *N*-oxides, XXVI, XXVIII, and XXX (Figure 19) were very similar to basic green 4. This occurs because the nitrogen atom no longer has unpaired electrons available for conjugation with the π-electron ring. However, the *N*-oxides differ from basic green 4 by their running time on silica gel with the solvent benzene/methanol (90:10). In contrast, Nakamura and Hida[576] used the slightly different solvent benzene/ethanol (7:3), which may not have been adequate to differentiate between the *N*-oxides and basic green 4. Their suggestion that leuco basic green 4 is formed as a photoproduct raises the question whether the leuco compounds XIII, XV, and XVII (Figure 19) may be formed by successive demethylation of I involving analogous *N*-oxide intermediates.

In addition to product analysis, further evidence to support dealkylation has been sought by examining the lightfastness of a number of structural analogues of basic green 4 (XXXI) and acid blue 123 (XXXII) on wool[582] (Figure 20). Evans and Stapleton[582] observed that the replacement of the *N*-methyl groups of XXXII by *N*-aryl groups raised the lightfastness by 1 to 2 points on a 1 to 8 point scale. Similar observations were made for the basic green 4 series of dyes (XXXI). In addition, it was found that varying the X substituent in the phenyl ring of basic green 4 (XXXI) had little effect on the lightfastness. They acknowledged that there are two possible explanations for these results. One is based on the suggestion made by Wegmann[583] that methylation of the amino groups or introduction of further amino groups into the dye increases the basicity of the dye. This manifests itself by reducing the lightfastness of triphenylmethane dyes on poly(acrylonitrile) by increasing the ionic nature of the dye–fiber bond. Similar correlations have been made between dye structure and lightfastness for a number of triphenylmethane dyes on polyester and poly(acrylonitrile) by Johnson and co-workers.[584-586] Although they also point out that the triphenylmethane dyes studied by Wegmann are acids, not bases, and therefore it is more realistic to attribute the decrease in lightfastness with increasing amino substituents to the increased positive charge delocalization in the dye. Thus, contrary to Wegmann's hypothesis, the more ionic the dye–fiber bond, the higher the lightfastness of the dye. As an alternative to Wegmann's proposal, Evans and Stapleton suggested that their results may indicate that dealkylation occurs on wool. Furthermore, in subsequent work (see p 261 of ref 4e), they noted that the correlation between the number of methylated or unmethylated amino groups in the dye and lightfastness is not always observed on wool and this suggests that different fading mechanisms may be operating on the wool and synthetic substrates.

The reaction of singlet oxygen ($^1\Delta_g O_2$) with triphenylmethane dyes has received increasing attention over the last 17 years. Zweig and Henderson[587] showed that triphenylmethane dyes, like most other classes of dye, produce singlet oxygen upon photolysis with visible light in cellulose acetate. However, from their results they were unable to find a simple relationship between singlet oxygen production and dye degradation. Stevens and Kaplan[534] studied basic green 4 in air-saturated 95% ethanol. In contrast to Zweig and Henderson[587] they found that basic green 4 neither produced singlet oxygen nor showed any reactivity toward it. Similarly, other workers have claimed that basic violet 3 is unable to generate singlet oxygen,[588] since methionine is stable when irradiated in the presence of this dye.[589,590] To account for the fact that dye fluorescence was not quenched by oxygen and that dye photodegradation did not occur in the absence of oxygen, Stevens and Kaplan[534] proposed that the triplet state of the dye reacts with a ground-state molecule of oxygen to produce photooxidation products. The importance of a triplet state dye molecule in promoting photooxidation as a major decomposition pathway, in low viscosity solvents, must however be questioned on the basis of the photophysical studies presented in section IV.B. It is apparent from these studies that the excited singlet dye molecule will have a greater concentration than the excited triplet state species in solvents of low viscosity. As noted previously, this comment is also applicable to the solution studies performed by Bangert[531] and Porter and Spears.[532,533]

More recently, Kuramoto and Kitao[569,575] photolyzed basic green 4 and basic violet 3, in various solvents, using light of wavelengths greater than 300 nm and

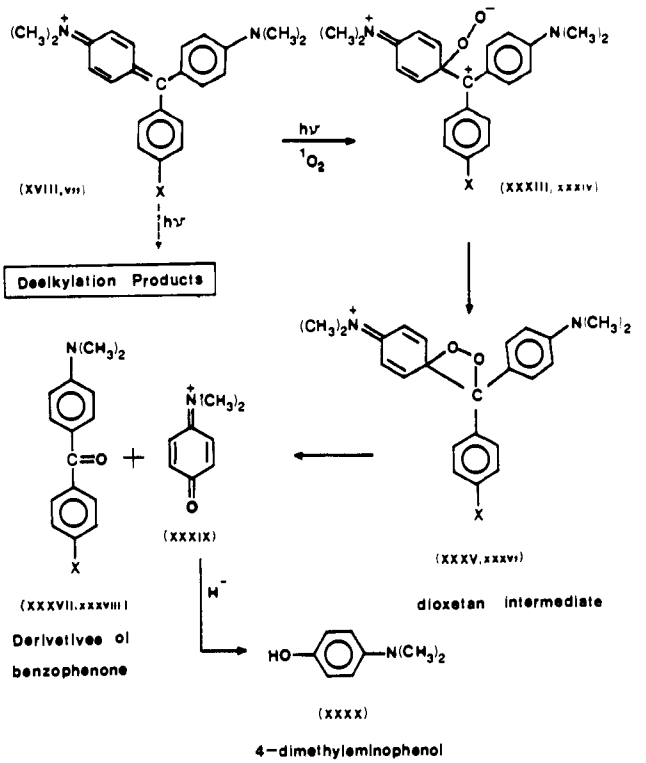


Figure 21. The photodecomposition of basic violet 3 and basic green 4 involving singlet ($^1\Delta_g O_2$).[575,569] Compounds XXXIX and XXXX are formed during the photodecomposition of both dyes. Compounds XXXIII, XXXV, and XXXVII are photoproducts of basic violet 3 (XVIII) [where X = $N(CH_3)_2$]. The photoproducts of basic green 4 (vii) (where X = H) are xxxiv, xxxvi, and xxxviii. (Adapted from refs 575 and 569. Copyright 1982 and 1982, respectively, Elsevier Applied Science Publishers and the Society of Dyers and Colourists.)

aerobic conditions. The photodegradation of basic violet 3 in dichloromethane, was accelerated by basic blue 9 (a singlet oxygen sensitizer) and retarded by singlet oxygen quenchers such as β-carotene and nickel dimethyl dithiocarbamate. On the other hand, fading was only slightly altered by addition of 2,6-di-*tert*-butyl-*p*-cresol, a good free-radical scavenger. Basic green 4 showed similar behavior to basic violet 3.

4,4′-Bis(dimethylamino)benzophenone, *p*-(dimethylamino)phenol, and small amounts of basic red 9 were identified as the photodegradation products of basic violet 3 photolyzed in dichloromethane, by comparison with authentic samples. Since the amount of basic red 9 formed was small, dealkylation was considered to be less important than singlet oxygen oxidation. Accordingly, Kuramoto and Kitao[569,575] proposed that dye fading occurred by attack of singlet oxygen to form an unstable dioxetan intermediate XXXV, which decomposes to give 4,4′-bis(dimethylamino)benzophenone XXXVII and *p*-(dimethylamino)phenol XXXX (Figure 21), and suggested that basic green 4 behaved similarly.

In the absence of additives, the fading of the dyes was found to be dependent on the solvent. Fading occurred to the greatest extent in dichloromethane and this was followed by acetone and finally methanol where, in comparison, fading was barely noticeable. The rate of reaction was attributed to the dependence of the lifetime of singlet oxygen upon the solvent. In view of these results, the apparent lack of reactivity of basic green 4, toward singlet oxygen, as observed by Stevens and Kaplan[534] becomes understandable, since singlet oxygen has a very short lifetime in alcohol[591,592] being about 8 μs in methanol and 11 μs in ethanol.

Recently however, the importance of singlet oxygen in the fading mechanism has been questioned. Allen et al.[567] noted that the experiment of Kuramoto and Kitao,[569] using nickel dimethyl dithiocarbamate, may be reinterpreted since such nickel complexes are known to destroy hydroperoxides in the absence of light.[593] Allen et al.[567] found that addition of tetracyanoethylene (an electron trap) or 1,4-diazabicyclo[2.2.2]octane (DABCO, a singlet oxygen) scavenger have little effect on the fading of basic violet 3 lactone color. In this study it was confirmed that oxygen does in fact accelerate dye fading, but the ability of the nickel complex to retard fading may imply that the action of hydrogen peroxide is more important than singlet oxygen attack.

The role of singlet oxygen in the fading of acid blue 1, acid green 9, acid blue 15, and acid violet 17 in methyl cellulose was examined by the author.[183] In this study, sodium azide, a known singlet oxygen quencher[594] was found to enhance dye fading. The azide ion, N_3^-, however, is known to be a typical electron donor.[595] This suggests that electron transfer reactions are more important in triphenylmethane dye photodegradation in solid substrate than singlet oxygen attack.

In addition Nakamura and Hida[576] have recently tentatively suggested that the fading of basic violet 3 in acetonitrile may involve the participation of singlet oxygen. However, further investigations were considered necessary to test the validity of this proposal. It is worthwhile noting here that acetonitrile is a model for poly(acrylonitrile), and subsequent studies by Nakamura and Hida[570] revealed that the fading of basic violet 3 proceeds via a photooxidative mechanism on this substrate. Presumably, this occurs because poly(acrylonitrile) is both a poor hydrogen atom and electron donor and therefore does not readily support photoreduction (section IV.C.2). It was also suggested that the fading of basic violet 3 on poly(acrylonitrile) was governed by the state of aggregation of the dye (section V.B) and noticed that demethylation and didemethylation reactions contribute to dye degradation.

In studies concerned with the treatment of industrial waste, several triphenylmethane dyes have been decomposed by ozone, and the process was found to be accelerated by ultraviolet radiation. However, the mechanism of the reaction was not investigated.[91]

2. Photoreduction of Triphenylmethane Dyes

Triphenylmethane dyes have been reported to act as oxidizing agents in the excited state and hence will themselves be reduced.[4c,596]

Photoreduction competes with photooxidation (and N-dealkylation) to provide the most favorable pathway by which the dyes degrade. It may involve either an electron or hydrogen atom abstraction process, and these are also in competition with each other.[597] Thus, it may be generalized that dye photoreduction is favored under anaerobic conditions and in the presence of compounds which are oxidized more readily than the dye. Consequently, the fading of triphenylmethane dyes on protein substrates is usually associated with a photoreductive mechanism.[563]

Several workers have found evidence to suggest that the excited triplet state of the dye is the photoactive species responsible for photoreduction.[246,315,478,530,598-630] While this assessment may be appropriate for dye fading in situations where rotation of the phenyl rings is impeded, the photophysical studies discussed in section IV.B clearly indicate that rapid internal conversion in low-viscosity solutions ensures that the triplet state population is very low. This indicates that caution must be exercised when using liquid media to model the photochemistry in solids. Furthermore, some of the solution studies discussed in the following text may require further investigations. Allen et al.[530] observed that the presence of the triplet sensitizer, benzophenone, markedly accelerated photoreduction of basic green 4 in poly(acrylonitrile) and poly(vinyl alcohol). Several other dyes were studied in addition to basic green 4.[530,598,604] It was proposed[598] that, in all cases, following light absorption, the excited singlet state dye underwent intersystem crossing to the excited triplet state which ejected an electron. Subsequently, the ejected electron reduced a ground-state dye molecule to form a triphenylmethyl radical. Radical products of this type have been previously identified by Leaver[605] for the one-electron reduction of basic violet 3 (namely, the tris[4-(dimethylamino)phenyl] methyl radical). Furthermore by using flash photolysis, Allen et al.[530] observed that the formation of such triphenylmethyl radicals, produced during dye photoreduction in anaerobic solutions of 2-propanol, could be inhibited by admitting oxygen to the system. The reduced concentration of the radicals was attributed to the efficient quenching of the excited triplet state dye by oxygen. It could also be attributed to the ability of oxygen to scavenge radicals.[606,607] Naguib et al.[608] point out that the studies by Allen et al.[530,598,604] are not consistent with the photophysical studies on triphenylmethane dyes (section IV.B). Furthermore, they ask why electron ejection should occur more readily from a low-energy triplet state than from a singlet state.

Mason et al.[600,601] and Duxbury[183] observed that several triphenylmethane dyes were able to abstract an electron from solid poly(vinyl alcohol), methyl cellulose, and gelatin films (cast from aqueous solution). This process was inhibited when either the excited triplet state quencher Mn^{2+}, or the electron scavenger $CdSO_4$ were incorporated into the systems.

Reduction of dye fading in the presence of paramagnetic metal ions may be expected to be a general phenomenon when fading proceeds via an excited triplet state, since these ions are able to promote triplet deactivation by spin-orbit coupling.[609] In solution however, where the population of the excited triplet state is small (section IV.B), it has been shown by Marczenko et al.[610,611] that the reduction of basic violet 3 and basic green 4 is enhanced by the nonparamagnetic ion Sn(11) in the presence of light.

Oster and co-workers[246,315,599] found a strong correlation between dye phosphorescence and photoreduction. Of the triphenylmethane dyes examined in glucose glasses, notably the symmetric dyes basic violet 3, basic red 9, and acid violet 19, which exhibit α-phosphorescence at room temperature, were susceptible to photoreduction induced by white light.[246] In support of this, Leaver[155] noted that the triplet electron spin resonance signals of basic violet 3 and basic red 9, in an ethylene glycol–water mixture (1:1) at 90 K which were excited by wavelengths greater than 500 nm, were noticably larger and easier to detect than the signal for the asymmetrically substituted dye, basic green 4.

As discussed in section IV.B, an increase in molecular rigidity facilitates population of the excited triplet state of the dye. In accordance with this Oster and coworkers,[246,315,322,599,602] observed that both dye phosphorescence and photoreduction are enhanced when the dyes are incorporated into viscous glasses such as glucose or when bound to high molecular weight polymers such as poly(methacrylic acid). For example, they observed that in the unbound state, basic violet 3, basic violet 4, and basic green 4 were not reduced by the mild reducing agent, ascorbic acid.[315] However, when poly(methacrylic acid) was added to the system, the dyes were irreversibly photoreduced to colorless products. Furthermore, Oster et al. observed that ascorbic acid quenched the phosphorescence but the fluorescence remained unchanged. In support of these findings, a flash photolysis experiment[478] revealed that a metastable state (presumably the triplet state) was detected only in the presence of a high molecular weight polymer. In agreement with these studies, Oster and Bellin[315] proposed the following reaction scheme for the fading of triphenylmethane dyes in the bound state in the presence of a reductant, R:

$$D \xrightarrow{h\nu} {}^1D^* \tag{15}$$

$${}^1D^* \rightarrow D + \text{heat (and/or fluorescence)} \tag{16}$$

$${}^1D^* \rightarrow {}^3D^* \tag{17}$$

$${}^1D^* + D \rightarrow {}^3D^* + D \tag{18}$$

$${}^3D^* \rightarrow D + \text{phosphorescence} \tag{19}$$

$${}^3D^* + R \rightarrow D + R \tag{20}$$

$${}^3D^* + R \rightarrow [\text{complex}] \tag{21}$$

$$[\text{complex}] \rightarrow \text{colourless products} \tag{22}$$

Step 18 was included to account for the self-quenching of fluorescence, inappreciable self-quenching of phosphorescence, and enhanced photoreduction, which were observed when the concentration of bound dye was increased. This step, however, is not in agreement with the Wigner spin conservation laws.[612]

It is worth noting here that Lenka et al.[613] suggested that in the initial stages of basic violet 3 sensitized methyl methacrylate photopolymerization, an excited state of the dye reacted with a complex formed between ascorbic acid and Na_2HPO_4, to produce the colorless leuco dye DH and other species, some of which initiated polymerization.

The work of Oster and co-workers[246] has also revealed that the rate of photoreduction may be a complicated function of temperature. In glucose glass the rate of photoreduction of acid violet 19 was observed to increase up to a temperature of 60 °C and then decrease for higher temperatures. To rationalize this in keeping with their kinetic and spectral data, they suggested that three factors need to be considered, (1) suppression of internal conversion from the first excited singlet state to the ground state by increasing the solvent viscosity, (2) transition from the triplet state to the ground state, and (3) reaction between the triplet state dye and the glucose glass.

The first process is favored by lowering the temperature, whereas processes two and three are not. These factors serve to illustrate how the probability of a bimolecular reaction occurring between the dye and the reductant (if this is not the medium containing the dye) will be decreased as the conditions favoring molecular rigidity are increased. Consequently, it is understandable how dye fading in solution may proceed by a different mechanism than in a solid substrate.

The amount of evidence supporting the formation of a triphenylmethyl radical during photoreduction is increasing. It has been detected in a variety of systems including poly(vinyl alcohol),[597,605] poly(methyl methacrylate),[603] nylon,[570,597] cellophane,[570] and pressed dye powder films,[559] and solutions[289] particularly when deoxygenated.[528,530,604,605,608,614,615] Radicals have also been detected in triphenylmethane-dyed methyl cellulose and gelatin films after exposure to ultraviolet radiation.[183]

In a study of basic violet 3 by Leaver,[605] the semiquinone radical was only detected when the samples were photolyzed with light of wavelengths greater than 500 nm. This was attributed to the instability of the radical to light in the vicinity of its absorbance (408 nm), and this property has also been observed by other workers.[530,570] Interestingly, Böttcher et al.[614] claim to have generated the D• radical (absorbance 400 nm) by exciting D^+ of basic violet 3 at 347 nm in the presence of dimethylaniline. The luminescence of similar triphenylmethyl radicals has also been studied by many workers.[616-618] This radical was also identified by Hinzmann et al.[619] Leaver was able to identify the radical as the semireduced tris[*p*-(dimethylamino)phenyl]methyl radical by comparing its electron spin resonance spectrum in pure and dilute solutions of dimethylformamide with those of the electrolytically generated radical previously reported by Miller and co-workers[560] and Kemula.[620] Further evidence to support this assignment, included the similarity between the fluorescence excitation and emission spectra of the semiquinone radical of basic violet 3 in dimethylformamide and those of a number of para-substituted triphenylmethyl radicals previously reported.[621] Evidence was also found for the radical derived in a similar manner from the related dye basic green 4.

Leaver[605] suggested that the semiquinone radical is the most likely precursor to the formation of the leuco dye which has been detected as a major decomposition product by many workers.[570,576,597,603,622,623-625] However, it is interesting to note that Favaro and Mazzucato[607] have reported that triphenylmethyl radicals trapped in solution at 77 K react with oxygen when warmed to room temperature and are converted to benzophenone.

During their electrochemical ESR study on triphenylacetic acid in moist acetonitrile, Compton et al.[626] noted that triphenylmethyl radicals could react with oxygen to form triphenylmethyl hydroperoxide [$(C_6H_5)_3COOH$]. This undergoes further reaction to form benzophenone [$(C_6H_5)_2C{=}O$] and phenol [C_6H_5OH].

Pak and Shigorin and co-workers[627-631] studied the leuco compounds of basic violet 3, D–X, and maintained that free radicals, D•,[627-629] cation radicals, $D^{\bullet+}$,[628-631] or cations, D^+ [628-631] can be produced from the excited triphenylmethane molecule, with the radical being formed in one of the following ways:

$$D\text{–}X + e^- \rightarrow D^\bullet + X^- \quad (23)$$

$$D^+ + e^- \rightarrow D^\bullet \quad (24)$$

where X = H, OH, or CN, and that the formation of the cation depends on the surrounding medium and conditions.[631]

Since the work discussed in this review is concerned with the behavior of triphenylmethane dyes, no further discussion regarding the leuco compounds will be entered into except to note that they have also been studied by several groups,[228,503b,535,606,614,616-619,632-645] with the triphenylmethyl-type radical being frequently observed in many of these studies. For a recent review on the photodecomposition of these compounds refer to ref 646 (and references therein).

As mentioned above, photoreduction of a triphenylmethane dye to form the corresponding dye radical species may involve either an electron abstraction or hydrogen atom abstraction process. In particular, several workers have proposed that the substrate is able to donate the hydrogen atom[563,570,573,576,597] or the electron[570,586,598,600] to the dye or that the counterion of the dye salt is the electron donor.[250,289,584,597,603,605] These proposals will now be considered.

Feichtmayr and Schlag[250] proposed that dye fading proceeded via a one-step electron transfer from the counterion X^- to the excited dye cation $*D^+$ as follows:

$$*D^+ + X^- \rightarrow *D^\bullet + X^\bullet \quad (25)$$

Electron-spin resonance studies indicated the presence of free radicals in photolyzed samples of triphenylmethane-dyed polymers; however, the identity of the radical was not established. They observed that the lightfastness of basic violet 3 and basic blue 7, in liquids which promoted the formation of contact ion pairs (where the dye cation and counterion are in close proximity), increased with decreasing ability of the counterion to donate an electron. Accordingly, lightfastness was generally observed to be in the order ClO_4^- > *p*-$CH_3C_6H_4SO_3^-$ > Cl^- > Br^- > I^- > $C_2O_4^{2-}$. A similar trend was observed in polystyrene films; however, sometimes other factors, such as the solvent content remaining in the film after solidification, masked the effect of the counterion. In support of their hypothesis Feichtmayr and Schlag noted that in polar solvents,

where the dye salt is dissociated, the effect of the counterion was not very distinct.

Jones and Goswami[289] have also examined this effect. They observed that addition of NaBr to 2-propanol solutions of basic violet 3 did not appreciably alter the rate of fading whereas addition of NaI inhibited it.

Owen and Allen[603] studied the fading of basic violet 3 and basic green 4 in films of poly(methyl methacrylate). In agreement with the findings of Feichtmayr and Schlag,[250] they observed that the extent of dye fading was dependent on the counterion. Furthermore, they suggested that the rate of formation of the triplet state dye would depend upon the heavy atom quenching effect if the counterion was a halide ion.

More recently, Nakamura and Hida[597] have made a detailed study of the effect of the counterion on the photoreduction of basic violet 3 in anaerobic solutions of 2-propanol and acetonitrile and poly(vinyl alcohol) films. The effect of the counterion was only observed in deoxygenated acetonitrile which supports the formation of contact ion pairs. Similarly, the lack of effect of the counterion in degassed 2-propanol was thought to be caused by the fact that the dye salt was dissociated and that the dye had a higher reactivity toward hydrogen atom abstraction from the solvent than electron abstraction from the counterion. Jones and Goswami[289] have suggested that at low counterion concentrations (10 μM) ion pairing is unimportant and the dye cation D^+ exists in equilibrium with the leuco ether $DOCH(CH_3)_2$. In this case the observation that the photolysis is independent of the halide ion was ascribed to the greater importance of the cleavage of the leuco ether (Scheme II, reaction 65).

The fading of basic violet 3 induced by visible light was also examined in nylon films.[570,597] In this case the dye appeared to abstract an electron from both the carboxylate anion of the substrate[570]

$$^1D^* + RCO_2^- \rightarrow D^\cdot + RCO_2^\cdot \quad (26)$$

$$RCO_2^\cdot \rightarrow R^\cdot + CO_2 \quad (27)$$

and from OH^- arising from residual water in the film.[597] In all cases, fading was observed to increase with increasing ability of the anion (whether this was the dye counterion or was derived from the substrate) to donate electrons. In contrast to other workers (see above), Nakamura and Hida[570] proposed that the photoactive species abstracting electrons is the first excited singlet state of the dye. This is in keeping with the photophysical studies discussed in section IV.B, which indicate that as molecular mobility is restricted the lifetime of the excited singlet state dye will increase. However, it should be noted here that such an effect will also enhance intersystem crossing to the corresponding excited triplet state.

In order to ascertain the importance of hydrogen atom donation during photoreduction, Owen and Allen[603] incorporated benzhydrol into poly(methyl methacrylate) films containing a fixed amount of triphenylmethane dye. This additive enhanced the rate of dye fading and therefore the following mechanism was proposed to account for dye fading in the presence of a hydrogen atom donor:

$$DX \xrightarrow{h\nu} {}^1DX^* \quad (28)$$

$$^1DX^* \rightarrow DX + \text{fluorescence/heat} \quad (29)$$

$$^1DX^* \rightarrow {}^3DX^* \quad (30)$$

$$^3DX^* + BH_2 \rightarrow \text{products} \quad (31)$$

$$^3DX^* \rightarrow DX + \text{phosphorescence/heat} \quad (32)$$

$$^1DX^* + DX \rightarrow {}^3DX^* + DX \quad (33)$$

$$^3DX^* \rightarrow D^\cdot + X^\cdot \quad (34)$$

$$X^\cdot + RH \rightarrow XH + R^\cdot \quad (35)$$

$$D^\cdot + RH \rightarrow DH + R^\cdot \quad (36)$$

where R = p-$C_6H_4N(CH_3)_2$, DX is the dye salt, and BH_2 is the hydrogen atom donor. Reaction 33 was included to account for the fact that the quantum yield of triplet formation was observed to be dependent on the dye concentration, suggesting that more than one dye molecule is involved in the process leading to triplet formation. This step is similar to reaction 18 proposed by Oster and Bellin,[315] and similarly it too does not obey the Wigner spin conservation laws. The proposed mechanism, however, accounts for the observed formation of the leuco dye.

Allen et al.[530] have employed benzhydrol as a H donor in several of their studies on triphenylmethane dyes, and recently the role of benzhydrol as a sensitizer in the fading of basic violet 3 has been examined more closely by Naguib et al.[608] These researchers found that basic violet 3 was stable to photolysis in acetonitrile, even in the presence of hydrogen donors such as benzhydrol and 2-propanol when wavelengths greater than or equal to 366 nm were used. For wavelengths less than 366 nm the quantum yield of dye fading was larger, particularly in the presence of benzhydrol. The sensitization observed could not be attributed to the hydrogen-donating ability of benzhydrol alone, since 2-propanol barely sensitized dye fading in acetonitrile at irradiation wavelengths less than or equal to 366 nm. Instead, it was attributed to the presence of benzophenone as an impurity in benzhydrol. Accordingly, sensitized dye fading for irradiation wavelengths less than or equal to 366 nm was proposed to occur via the following mechanism:

$$(C_6H_5)_2CO \xrightarrow{h\nu} {}^3[(C_6H_5)_2CO]^* \quad (37)$$

$${}^3[(C_6H_5)_2CO]^* \rightarrow (C_6H_5)_2CO \quad (38)$$

$${}^3[(C_6H_5)_2CO]^* + D^+ \rightarrow \text{quenching and/or reaction} \quad (39)$$

$${}^3[(C_6H_5)_2CO]^* + (C_6H_5)_2CHOH \rightarrow 2(C_6H_5)_2C^{\bullet}OH \quad (40)$$

$$2(C_6H_5)_2C^{\bullet}OH \rightarrow ((C_6H_5)_2COH)_2 \quad (41)$$

$$(C_6H_5)_2C^{\bullet}OH + D^+ \rightarrow (C_6H_5)_2CO + H^+ + D^{\bullet} \quad (42)$$

$$(C_6H_5)_2C^{\bullet}OH + D^{\bullet} \rightarrow (C_6H_5)_2CO + DH \quad (43)$$

If 2-propanol is used in place of benzhydrol as the hydrogen donor then reactions 40 and 42 would be replaced by reactions 44 and 45, respectively.

$${}^3[(C_6H_5)_2CO]^* + (CH_3)_2CHOH \rightarrow (C_6H_5)_2C^{\bullet}OH + (CH_3)_2C^{\bullet}(OH) \quad (44)$$

$$(CH_3)_2C^{\bullet}(OH) + D^+ \rightarrow D^{\bullet} + H^+ + CH_3COCH_3 \quad (45)$$

Reaction 46 would also play a role

$$(C_6H_5)_2CO + (CH_3)_2C^{\bullet}(OH) \rightarrow (C_6H_5)_2C^{\bullet}OH + CH_3COCH_3 \quad (46)$$

Furthermore, Naguib et al.[606] note that the termination reaction 43 could alternatively be replaced by reactions 47 and 48.

$$D^{\bullet} + D^{\bullet} \rightarrow D^+ + D^- \quad (47)$$

$$D^- + H^+ \rightarrow DH \quad (48)$$

This study has shown that electron abstraction and hydrogen donation play an important role in dye degradation, as does reaction of the dye with benzophenone. This latter observation is particularly interesting as it suggests that the amino-substituted benzophenone photoproducts observed during dye photooxidation (discussed in section IV.C.1) may further sensitize dye fading.

Nakamura and Hida[576] have also observed the importance of the hydrogen atom donating ability of the medium-containing dye. In degassed solutions of 2-propanol, ethanol, and acetonitrile, the reactivity of basic violet 3 increased with the ability of the solvent to donate a hydrogen atom, when ultraviolet light was used to excite the dye. The main photoproducts included leuco, demethylation, and didemethylation compounds. Since acetonitrile is a poor hydrogen atom donor, residual water in the solvent was considered to contribute to dye photoreduction. During this study, the mechanisms of dye photooxidation and photoreduction were established to be in competition with each other. In the presence of oxygen, the reactions in alcohol were reduced compared to the degassed solution and were a mixture of photoreduction and photooxidation. This occurred because the leuco basic violet 3 formed during fading was photooxidized to regenerate the dye. In contrast, the presence of air barely changed the reactivity of the dye in acetonitrile. In this case photooxidation was considered to occur, although the photoproducts were not identified. Figure 8 of ref 576 clearly illustrates the interdependence of photooxidation and photoreduction in acetonitrile and 2-propanol. Unfortunately, however, permission could not be obtained to reproduce this figure here.

Jones and Goswami[289] have also studied the photoreduction of basic violet 3 in aqueous 2-propanol due to ultraviolet irradiation and have proposed two reaction schemes to account for their results. Scheme I is based upon the idea that at high counterion concentrations, photolysis of the dye ion (D^+)/counterion (X^-) ion pair is important.

Scheme I

$$D^+ + X^- \rightleftharpoons D^+\cdots X^- \quad (49)$$

$$D^+\cdots X^- \xrightarrow{h\nu} (D^+\cdots X^-)^* \quad (50)$$

$$(D^+\cdots X^-)^* \rightarrow D^{\bullet}\cdots X^{\bullet} \quad (51)$$

$$D^{\bullet}\cdots X^{\bullet} \rightarrow D^+\cdots X^- \quad (52)$$

$$D^{\bullet}\cdots X^{\bullet} \rightarrow D^{\bullet} + X^{\bullet} \quad (53)$$

$$D^{\bullet} + X^{\bullet} \rightarrow D^+ + X^- \quad (54)$$

$$X^{\bullet} + (CH_3)_2CHOH \rightarrow HX + (CH_3)_2C^{\bullet}OH \quad (55)$$

$$X^{\bullet} + X^- \rightarrow X_2^{\bullet -} \quad (56)$$

$$X_2^{\bullet -} + (CH_3)_2CHOH \rightarrow HX + (CH_3)_2C^{\bullet}OH + X^- \quad (57)$$

$$D^+ + (CH_3)_2C^{\bullet}OH \rightarrow D^{\bullet} + (CH_3)_2C^+OH \quad (58)$$

$$2D^{\bullet} \rightarrow D^{2\bullet -} + D^+ \quad (59)$$

$$D^{\bullet} + (CH_3)_2C^{\bullet}OH \rightarrow DH + CH_3COCH_3 \quad (60)$$

$$D^{2\bullet -} + (CH_3)_2CHOH \rightarrow DH + (CH_3)_2CHO^- \quad (61)$$

$$(CH_3)_2C^+OH + (CH_3)_2CHO^- \rightarrow CH_3COCH_3 + (CH_3)_2CHOH \quad (62)$$

The electron-transfer process in reaction 51 is believed to take place in an upper singlet excited state of D^+. In the case of $X^- = I^-$, a charge-transfer transition may be important.

At low (10 μM) concentrations of counterions, ion pairing is not significant. In this case photolysis is best described in terms of reaction Scheme II which shows the importance of $DOCH(CH_3)_2$, the leuco ether in equilibrium with D^+ in alcohol solutions.

Scheme II

$$D^+ + (CH_3)_2CHOH \rightleftharpoons DOCH(CH_3)_2 + H^+ \quad (63)$$

$$DOCH(CH_3)_2 \xrightarrow{h\nu} (DOCH(CH_3)_2)^* \quad (64)$$

$$(DOCH(CH_3)_2)^* \rightarrow D^\cdot + (CH_3)_2CHO^\cdot \quad (65)$$

$$(DOCH(CH_3)_2)^* \rightarrow D^+ + (CH_3)_2CHO^- \quad (66)$$

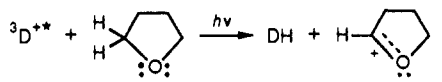
$$D^+ + (CH_3)_2CHO^- \rightarrow DOCH(CH_3)_2 \quad (67)$$

$$D^\cdot + (CH_3)_2C^\cdot OH \rightarrow DH + CH_3COCH_3 \quad (68)$$

$$(CH_3)_2CHO^\cdot + (CH_3)_2CHOH \rightleftharpoons (CH_3)_2CHOH + (CH_3)_2C^\cdot OH \quad (69)$$

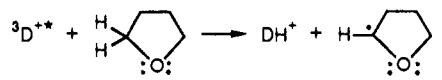
In support of these schemes, it was found that addition of counterion depleted the fluorescence of D^+ and $DOCH(CH_3)_2$ and that the products, DH, the leuco dye, acetone, and H^+, could be identified. Other species which were confirmed include $DOCH(CH_3)_2$ (by equilibrium studies), $D^\cdot$ and D^+ (both by laser flash photolysis studies). Furthermore, reaction 58 has been independently observed.[647]

None of the above-mentioned photoreactions were reported to be reversible in the absence of light. A reversible photobleaching reaction, however, has been reported for basic violet 3 in tetrahydrofuran solution.[623] This process was reported to involve hydride ion abstraction, from tetrahydrofuran, by the excited triplet state of the cation, to form the leuco dye, and the resonance stabilized cation depicted in reaction 70.



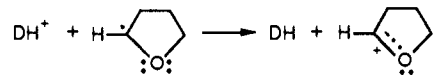
(70)

Furthermore, it was proposed that the overall reaction 70 may proceed in a minimum of two steps. The first step involving hydrogen atom abstraction from tetrahydrofuran



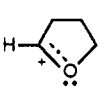
(71)

and the second reaction involving rapid electron transfer



(72)

The most likely reverse dark reactions are the transfer of a hydride ion from DH by



or the macro radical formed during photolysis according to the equation

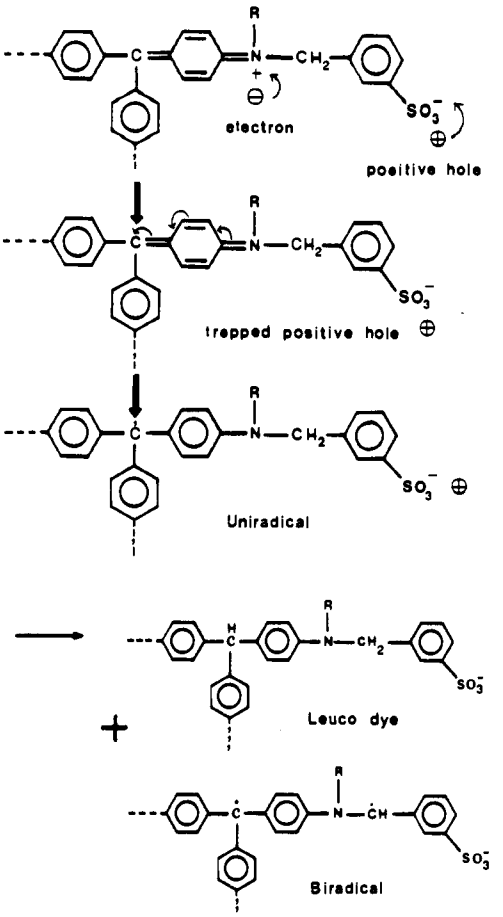
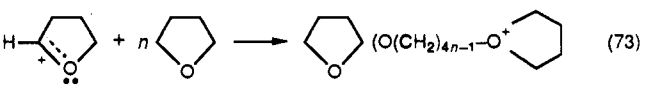


Figure 22. Uniradical and leuco dye formation as proposed by Patterson and co-workers. (Adapted from refs 622 and 624. Copyright 1967 and 1966, respectively, Oil and Colour Chemists' Association and the Royal Society of Chemists.)



(73)

As noted before, in solution the triplet state population will be much lower than that of the singlet state population (section IV.B).

Vartanyan and Sidorov[648] found that, in the absence of light, basic violet 3 is reduced by hydrazine (N_2H_4) and reoxidized to the original dye in the presence of air.

Owen and Al-Hassan[649] studied the photoinduced dark reaction of basic green 4 in cyclohexanone. They suggested that subsequent to photolysis the resonance-stabilized cyclohexanone radical (formed during photolysis of the solution) reduced the ground-state dye cation to produce a triphenylmethyl type radical. This species underwent further reaction with ground-state cyclohexanone to produce leuco basic green 4 and cationic cyclohexanone as overall products.

Patterson and co-workers[622,624,625] have employed photoconductivity measurements to elucidate the fading mechanisms of three triphenylmethane dyes (acid blue 104, acid blue 109, and acid blue 83) in anaerobic conditions. Their work has been discussed in ref 650 and briefly below. From their studies, Patterson and co-workers proposed a free radical mechanism in which the dye traps an exciton (which is an electron and

positive hole loosely held together by Coulombic forces of attraction and able to travel short distances through the crystal before disproportionation into an electron and a positive hole) to produce a monoradical (called a uniradical by the researchers) according to the reaction shown in Figure 22. Disproportionation between two such monoradicals leads to the formation of the observed photoproduct, the leuco dye. It is interesting to note, that the lightfastness of these dyes increased when the positive charge on the central carbon atom became more localized. This is in agreement with the proposal by Johnson and co-workers[584-586] and was attributed to the increase in extra energy (thermal activation energy) required to promote an electron from the photopopulated trapping sites in the crystal lattice into the conduction band, as the positive charge becomes more localized on the central carbon atom. Photoconductivity of triphenylmethane dyes has been examined by other workers[651] as has their photoelectrochemical behavior with respect to solar cells,[56] but this will not be entered into here.

The underlying motivation behind much of the above mentioned photochemical studies on triphenylmethane dyes is the question of why this class of dye exhibits higher lightfastness on synthetic substrates such as poly(acrylonitrile) than on natural fibers such as wool, cotton, and silk. In this context, several proposals, which directly relate the photochemical findings to the lightfastness of triphenylmethane dyes on both natural and synthetic substrates, are yet to be discussed.

Zollinger and co-workers[584,588] evoked the idea of the importance of the anion of the substrate in order to explain the higher lightfastness of triphenylmethane dyes on poly(acrylonitrile) compared to the lightfastness on cyanoethylated and tanned cotton. Upon irradiation in modified cotton, the excited state of the dye is able to abstract an electron quite readily from the carboxylate groups of the substrate, whereas, in acrylic fibers electron abstraction from the sulfonic groups in the substrate is more difficult. Thus, in the former case carbon dioxide is irreversibly formed and radical recombination is impossible, the dye radical formed then undergoes further decomposition. In acrylic fibers, however, the sulfate anions have little tendency to form radicals and so dye fading is slower. This idea has also been applied by Nakamura and Hida[570] to explain the faster fading of basic violet 3 on nylon films compared to poly(acrylonitrile) films.

Allen et al.,[530,604] using flash photolysis, observed a strong transient absorption in deoxygenated 2-propanol (a model for cotton) but not in deoxygenated acetonitrile [a model for poly(acrylonitrile)]. Transient formation was not observed in the presence of oxygen. The compounds, benzophenone and benzhydrol, initiated transient formation in acetonitrile,[530] and Allen et al. interpreted this as indicating the importance of the triplet state of the dye and hydrogen atom donation, respectively. However, on the basis of the discussion regarding the photophysical deactivation of triphenylmethane dyes in low viscosity solvents (section IV.B), it would seem that the triplet state dye would only be able to provide a minor photodecomposition channel. Furthermore, the studies by Naguib et al.[608] have shown that dye sensitization by benzhydrol is not purely attributable to the hydrogen-donating ability of the compound, but due to benzophenone which is present as an impurity. The details of their findings are expressed in reactions 37–48. The transient species was attributed, by Allen et al.,[530,604] to the triphenylmethane radical formed by electron transfer from the solvent to the dye, in accordance with the results of Leaver.[605] On the basis of these results, it was proposed that the transient was responsible for the low lightfastness of triphenylmethane dyes on cotton. Support for this proposal was obtained when strong correlations were found between the results obtained in liquid media and those obtained in solid polymer substrates. For instance, benzophenone and benzhydrol accelerated fading in poly(vinyl alcohol) and poly(acrylonitrile), benzophenone being the most effective. In a subsequent study,[598] they observed that the electron traps, tetracyanoethylene, acetone, and nitrous oxide, inhibited transient formation in 2-propanol more effectively than the radical traps, Topanol OC-2,6-di-*tert*-butyl-*p*-cresol and the 4-hydroxy-2,2,6,6-tetramethylpiperidine *N*-oxy radical. Similarly, fading on poly(vinyl alcohol) was inhibited by tetracyanoethylene, whereas the 4-hydroxy-2,2,6,6-tetramethylpiperidine *N*-oxy radical barely reduced the fading. These results further suggest that the electron-trapping ability of the cyano groups on poly(acrylonitrile) may be responsible for the higher lightfastness observed on this substrate.

Duxbury[183] also investigated the question why triphenylmethane dyes exhibit higher lightfastness on synthetic polymers than on protein substrates, and found that fading was photosensitized by components of the protein substrate. In particular, the guanidino group of arginine and the carboxylic groups of glutamic and aspartic acids. In contrast, neither lysine, histidine, nor excited singlet state oxygen appear to sensitize fading of the dyes in protein substrates. Both one-step transfer (of an electron and a hydrogen atom) and exciplex mechanisms were proposed for the sensitized photoreduction of the dye monomers. Subsequent electron-spin resonance measurements supported these proposals for dye fading in the presence of acetate groups, but not for dye fading in the presence of guanidino groups.

Shah and Jain[652] examined the lightfastness of basic violet 3 on brominated poly(propylene) fiber. They did not undertake mechanistic studies, but observed that an iodine after treatment improved the lightfastness rating of the dyed sample. Interestingly, exposure of the sample, dyed with basic violet 3, to radiation for 30–60 h resulted in improved mechanical properties of the fiber, but longer times resulted in fiber photodegradation.

V. Other Factors Influencing Dye Fading

The chemical structure of a dye is generally the prime factor which determines the various types of photochemical reactions a dye can undergo. For example, it has been found that dyes having a *p*-alkoxyphenyl group attached to the *p*-nitrogen group are faded less readily than when this group is absent[1b] and that certain pigments formed by the reaction of triphenylmethane dyes with either phosphotungstic or phosphomolybdotungstic acid are resistent to fading.[1b,83] In addition, several other factors, characteristic of the dye substrate system as a whole, the surrounding atmosphere and

the incident radiation, participate in determining which photodegradative pathway is favored and the rate at which fading proceeds. Sometimes these factors are of overiding importance, manifesting themselves by obscuring trends that would otherwise be observed (or expected) on the basis of chemical structure alone. These factors have been the subject of discussion in a number of review articles.[268,302,428,509,653-658]

A. Temperature, Humidity, Gaseous Reactants, and Water-Soluble, Nonvolatile Photodegradation Products

Various factors such as temperature, humidity, gaseous reactants (O_2, O_3, SO_2, and NO_2), and water soluble, nonvolatile photodegradation products have been shown to influence fading,[268,302,428,653-655,657,659] and from the investigations performed, it has emerged that they exhibit a certain amount of interdependence. It is partially due to this complex behavior that observations for the fading of a particular dyed substrate cannot be applied to dyes and substrates in general.

Under conditions of constant temperature it has been observed that an increase in the relative humidity of the atmosphere increases the fading of a dye for a variety of dye–substrate systems.[657,660-665] As the relative humidity of the atmosphere increases, a fiber will swell because the moisture content of the fiber (fiber regain) increases, and it has been suggested[574] that this aids diffusion of gaseous reactants through the substrate allowing them easier access to the dye. In a rigid structure, such as anodized aluminum an increase in humidity would not be expected to cause the substrate to swell. In accordance with this hypothesis, Giles et al.[666] observed that the fading of a range of dyes adsorbed on this substrate is independent of relative humidity. In this respect wool exhibits anomolous behavior since it undergoes significant swelling with increasing fiber regain; yet dye fading, in general, appears to be relatively insensitive to humidity[302,667] when compared to other systems such as dyed cotton. This property has resulted in wool being chosen in preference to other fibers as the substrate for the ISO lightfastness tests and appears to imply that the photochemical reaction between the substrate and the dye is more important than the interaction between the dye and moisture or gases.

In order to examine more closely the proposal that fading is enhanced under conditions that assist gaseous diffusion through a substrate, Giles and co-workers[574,666,668] have examined dye fading in sealed substrates and compared it with fading in unsealed substrates. In anodic aluminum films[668] and in nonprotein films,[574,668] sealing improved the lightfastness of a variety of dyes.

Several gases, particularly those in high concentrations in polluted environments (i.e. SO_2, NO_2 and O_3) have been observed to promote fading both in the presence and absence of light,[669] and an increase in humidity increases this effect. As a result of this work, it was postulated that the gas fading reactions are accelerated by the presence of light.

Oxygen is another important gaseous constituent of the atmosphere, and it has been found that in some cases it is not essential for fading, while in others, substantial loss in lightfastness is observed in its presence.[670-672] These differences are frequently interpreted in terms of the relative ease with which a dye undergoes oxidation or reduction in a particular dye–substrate–atmosphere system. This is particularly well illustrated in the study by Schwen and Schmidt,[672] who examined the effect of oxygen, nitrogen, and moisture on four cationic dyes on six different fibers, including both natural and synthetic substrates. From this study it became clear that the fading of the triphenylmethane, oxazine, and methin dyes studied was enhanced by moisture and oxygen. The two diazacyanine dyes tested behaved differently on most fibers, fading more rapidly in nitrogen than in oxygen. To account for this difference it was suggested that the diazacyanine dyes may have undergone reduction whereas the others may have experienced oxidation.

In several articles by Egerton,[654,655] it has been reported that dye oxidation, particularly in dry environments, may occur by the action of singlet oxygen. However, in the presence of water, it would seem that in many cases, the effective oxidizing species is hydrogen peroxide, which is formed by photochemical combination of water and oxygen (since the lifetime of singlet oxygen in water is very small).

When the relative humidity is maintained constant, it has been observed that an increase in the temperature increases the rate of dye fading.[660,663,667,673] In practice, however, where the atmospheric conditions are not controlled, a rise in temperature will reduce the moisture and gas content in the immediate environment surrounding a dyed substrate and, particularly in hydrophilic fibers,[268] will retard fading. In order to assess the effect of this phenomenon on the fading of dyes McLaren[665,674-676] developed the concept of effective humidity, which is the humidity of the air in contact with the surface of the sample. By using this parameter it became possible to explain why some dyed substrates faded more on dull humid days (high effective humidity) than on bright sunny days (low effective humidity).

Other studies[659] have shown that the removal of water-soluble, nonvolatile photodegradation products reduced the rate of fading of basic green 4 and basic violet 14 on wool, silk, and acrylic substrates. These products were not identified but it was noted that their removal was more successful in inhibiting fading when the substrate was protein.

B. Dye Concentration

An increase in dye concentration is generally believed to increase the lightfastness of a dye.[183,268,653] Eaton et al.[677] attributed this to dye aggregation within the fiber. It is believed that the dye molecules most susceptible to fading are those on the surface of the dye aggregate since these are exposed to air, light, and moisture. This effect is particularly important in substrates with large porosity where dye aggregates may retard the diffusion of water vapor and oxygen through the substrate. The size and form of these aggregates thus influences the kinetics of fading, and Giles and co-workers[268,302b,678,679] have classified the five most commonly observed fading curves according to the state of aggregation of the dye (Figure 23). Similarly, Grewal and Balakrishnaiah[659] who examined the fading of basic green 4 and basic violet 14 on wool, silk, and acrylic substrates, found that the kinetics of dye fading was determined by the size of the dye particles.

The absorption spectra of many dyes show two overlapping bands [α- and β-bands (section IV.A)] in the visible region of the absorbance spectrum. The long wavelength α-band corresponds to monomer absorption, while the short wavelength β-band corresponds to the dimer absorption. In accordance with the observation that aggregated particles fade slower than monomeric dye, it is frequently observed upon exposure to light that the absorbance of the α-band decreases more rapidly than that of the β-band. Some dyes from the azoic[268] and triphenylmethane[183,250,266,570] classes, however, have been reported to show opposite behavior. Giles and co-workers[268] attributed the more rapid disappearance of the β-band to the superimposition of the fading effect and an increase in the proportion of monomeric dye brought about by the breakdown of aggregates in the heat of the lamp. Nakamura and Hida[570] have, contrary to the generally accepted theory, proposed that in the case of basic violet 3, the dimer (D–D, whose structure was not elucidated) fades more rapidly than the monomer. The mechanism of fading of the dimer being given as

$$\text{D–D} \xrightarrow{h\nu} [\text{D–D}]^* \quad (74)$$

$$[\text{D–D}]^* \rightarrow \text{D}^{\bullet+} + \text{D}^{\bullet-} \quad (75)$$

$$\text{D}^{\bullet+} + \text{D}^{\bullet-} \rightarrow 2\text{D} \quad (76)$$

$$\text{D}^{\bullet+} \rightarrow \text{demethylation products} \quad (77)$$

$$\text{D}^{\bullet-} \rightarrow \text{reduction or oxidation products} \quad (78)$$

While the likelihood of this alternative proposal cannot be discounted, it is worthwhile making a closer examination of the interpretation of the evidence upon which it is based. Nakamura and Hida examined basic violet 3 in three substrates, nylon, cellophane, and poly(acrylonitrile), and the ratio of the absorbance of the α-band to that of the β-band was used as an indication of the degree of aggregation of the dye. The ratio for the dye in nylon was found to be 1.3, and since this was the same as that obtained in solution, they concluded that the dye existed in the monomeric form in this substrate. In contrast, it can be determined from the data in ref 302a that a 2×10^{-5}M solution of basic violet 3 gives an α/β ratio of 1.5. Since this is larger than 1.3, it suggests that a small amount of the dye within the film may be aggregated. It was claimed that both dimers and monomers exist in poly(acrylonitrile), but only dimers were considered to be present in cellophane. The spectrum presented for dyed cellophane reveals that the β-band does not have a higher intensity than the α-band, yet examination of the spectrum of a 2×10^{-3}M solution of basic violet 3 reveals that the β-band can be more intense than the α-band.[302a] This suggests that a higher degree of dye aggregation is possible within the film.

If we accept that it is very rare for a dye to exist in a fully aggregated or monomeric form in a solid substrate (Figure 23), the rapid disappearance of the β-band may alternatively be attributed to the superimposition of the fading of the dimer and the monomer with the dissociation of the aggregate brought about by the photolysis source. The dissociation process may be envisaged to produce the radicals $\text{D}^{\bullet+}$ and $\text{D}^{\bullet-}$ which recombine to form dye monomers as suggested by Nakamura and Hida[570] in reactions 74–78. An alternative pathway may be the weakening of van der Waals interactions which could hold the monomers together in the aggregate. In this case, dye monomers could be produced directly upon photolysis of the aggregate without the radical intermediates. Similarly, it may also be suggested, from the dimer fading mechanism proposed by Nakamura and Hida[570] (reactions 74–78), that the monomer appears to fade slower than the dimer because the radical recombination reaction 76 replenishes the monomer concentration. This type of fading would result in nonlinear fading curves (plots of log e of dye absorbance versus time of exposure to radiation) being observed. Nakamura and Hida[570] did not analyze their data in this manner; however, it is possible from the data they have presented in ref 570 to show that the fading curves of basic violet 3 in nylon and poly(acrylonitrile) exhibit curvature, when fading is monitored at the α- and β-bands. No such conclusion could be drawn by analyzing the data for cellophane, due to the errors involved in taking the data from the figures presented in ref 570.

The curvature observed in the fading curves obtained using the data of Nakamura and Hida[570] may also arise as a result of the formation of colored photoproducts. In the case of fading in nylon, the leuco form of basic violet 3 was detected, and this may be oxidized to form the dye. In poly(acrylonitrile), however, no evidence was obtained for the leuco dye and so it is likely that curvature arises because of the combined degradation

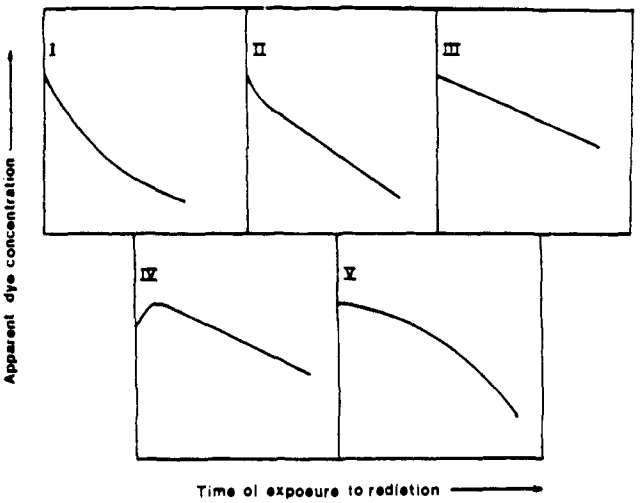


Figure 23. A classification of the kinetics of dye fading as determined by Giles and co-workers:[268,302b,678,679] (I) First- or second-order photodecomposition (rarely observed). Dye molecules are monomolecularly dispersed or in the form of small aggregates. (II) Initially as I, then followed by zero-order photodecomposition, III. The dye molecules exist partly in molecular dispersion and partly in the form of large aggregates. (III) Zero-order fading (constant rate). Dye is present in large aggregates or firmly enmeshed in substrate molecules. (IV) Initial negative fade (usually associated with the breakdown of aggregates in the heat of illumination) followed by type III fading. (V) Fading accelerates with time due to continued breakdown of aggregates. [Adapted from refs 268, 302b, 678, and 679. Copyright 1963, 1980, 1961, and 1968, respectively, Elsevier Applied Science Publishers and Textile Research Institute (the original source of publication).]

of the dimer and monomer. Similar behavior has been observed by the author, when examining the fading of several triphenylmethane dyes in poly(vinyl alcohol) and gelatin films.[183]

It is worthwhile pointing out that, in dilute solutions, the faster disappearance of a β-band compared to an α-band could be explained by the dye counterion attraction theory proposed by McKay and Hillson.[258] These authors have reported that the α- and β-bands correspond to two distinct species, namely the dissociated and associated dye salt, respectively. Since good electron-donating counterions have been reported to facilitate the fading of triphenylmethane dyes,[250,597,603] dye counterion attraction would be expected to promote fading. Thus, it may be expected that because the associated dye salt absorbs predominantly at the β-band, photodegradation measured at the β-band would be faster than that monitored at the α-band.

C. The Spectral Distribution of the Irradiating Light

The ability of a light source to cause photochemical change in a dye is dependent upon (a) the spectral distribution of the light source, in particular the proportion of radiation of wavelengths most effective in causing a change and (b) the quantum yield of dye degradation as a function of wavelength. Very little is known about the latter factor. Nevertheless, it has been found that not all wavelengths of light exhibit the same efficiency in initiating photochemical reactions. On the basis of photochemical principles it would be expected that light of higher energy (short wavelengths) would be more effective at causing fading than light of lower energy (long wavelengths). Several studies[680,681] have revealed that this is not always the case. McLaren[681] studied over 100 dyes of different classes and found that generally the most fugitive were faded more efficiently by visible light, while those of higher lightfastness were degraded mainly by ultraviolet light. This effect was particularly well illustrated during the sunlight exposure of the first six lightfastness standards (BS1006) on wool which belong to the triphenylmethane dye class. Furthermore, he found that while the fugitive dyes are faded by light of any wavelength, the lightfast dyes are faded by light only if it is below a critical wavelength. The existence of a critical wavelength for fading in certain dyes has also been observed by Luszczak and Zukriegel.[682]

In contrast to the findings of McLaren, numerous workers have found that other fugitive dyes, such as those from the triphenylmethane dye class, are faded more rapidly by ultraviolet light than visible light in solution,[289,532,533,568,571,576,578,608] and on solid substrates.[532,578,579]

Maerov and Kobsa[579] found that the wavelengths of sunlight between 350–425 nm are the most effective in promoting the fading of the triphenylmethane dyes, basic green 1, basic blue 7, and basic violet 14 on polyester fiber. Light of wavelengths lower than 350 nm is photochemically active but does not produce a large change since its abundance in sunlight is small. For these dyes, the quantum yield of dye fading is low for wavelengths greater than 425 nm.

Marczenko and Kalinowski[610] found that photoreduction of basic violet 3 and basic green 4 in the presence of Sn(II) was more efficient in sunlight than in artificial light.

Desai and Vaidya[566] have shown that photochemical reaction of certain triphenylmethane dyes in aqueous solution takes place for all wavelengths, but the extent of the reaction is dependent upon the light source. The diaminotriphenylmethane dye basic green 1 was studied in detail. The absorbance spectrum of this dye shows three bands around the wavelengths 600, 430, and 313 nm.[588] Excitation into these bands with a filtered mercury lamp reveals that the 313-nm band is nearly as active as the 430-nm band and the latter band is nearly one and a half times more active than the 600-nm band.

In a more recent study, Nakamura and Hida[576] have examined the quantum yield of fading of basic violet 3 as a function of wavelength in degassed and aerated solutions of 2-propanol and acetonitrile. This dye is of the triaminotriphenylmethane type and exhibits a different absorbance spectrum to basic green 1. The results of this study indicate that ultraviolet light is more effective in promoting fading than visible light. In degassed 2-propanol, the quantum yield of photofading of basic violet 3 was observed to be 210×10^{-4} when the dye was irradiated with 250-nm (λ_1) light, 8.6×10^{-4} when the dye was irradiated with 303-nm (λ_2) light, and only 1×10^{-5} with 577-nm light (λ_3). In degassed acetonitrile the trend was similar. In this instance when, $\lambda_1 = 250$ nm, the quantum yield of photoreaction was 7.1×10^{-4}, whereas for $\lambda_2 = 303$ nm and $\lambda_3 = 577$ nm it was 0.13×10^{-4} and 0.15×10^{-4}, respectively. The photoreaction of the dye in air similarly depended upon the wavelength of the irradiating light. In aerated 2-propanol and quantum yields were 1.7×10^{-4}, 0.011×10^{-4}, and 0.017×10^{-4} for the respective wavelengths $\lambda_1 = 250$ nm, $\lambda_2 = 303$ nm, and $\lambda_3 = 577$ nm. In aerated acetonitrile the respective values were 2.2×10^{-4} (λ_1), 0.18×10^{-4} (λ_2), and 0.14×10^{-4} (λ_3), again showing the trend.

Similarly, Jones and Goswami[289] found that in 2-propanol, 283-nm radiation was effective at causing the photodegradation of basic violet 3, but 546-nm excitation did not result in any significant decomposition.

Naguib et al.[608] observed that basic violet 3 showed essentially no fading in both degassed acetonitrile and 2-propanol when irradiated at 546 nm and at 366 nm. Some fading was observed in acetonitrile at 250 nm and at 313 nm in 2-propanol. In the presence of a hydrogen donor (such as 2-propanol or benzhydrol) and benzophenone, the sensitized fading of the dye was very efficient for irradiation wavelengths less than 366 nm.

D. The Nature of the Substrate

The influence of a substrate cannot be overlooked, particularly in a study on triphenylmethane dyes, which have been observed to exhibit vastly different lightfastness values in different media.[183,302c,659,683,684] Many of the ways in which a substrate influences dye fading have already been discussed (particularly in sections IV.B and IV.C), and so only a brief summary of the important factors will be given here.

Dye fading may be retarded or promoted by the agency of some chemical group within the fiber. Such a group could be a ground-state species or an excited-

state species, in the event that the substrate is able to absorb radiation. The close proximity or the ability of a dye to form a bond with this group would favor these interactions.

The porosity of the substrate is also an important factor. On the one hand, a high porosity can promote fading by facilitating penetration of moisture and gaseous reactants into the substrate, and on the other hand, this will promote dye aggregation which is generally believed to reduce photodegradation.[685]

A substrate may also act as a protective agent by screening the dye from light of wavelengths capable of causing degradation. This may also be achieved if the surface of the substrate is rough since light scattering will direct the incident radiation away from the dye.[686]

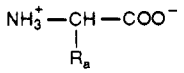
The purity of the substrate is an important consideration whenever the photochemistry of dyed technical polymers is considered. Technical-grade cotton, viscose rayon, poly(ethylene), poly(propylene), and poly(isoprene) are known to contain carbonyl group impurities. These absorb light of wavelengths greater than 300 nm, which are present in sunlight, and so excitation of these impurities may lead to reactive species capable of sensitizing dye fading.[658] Conversely, other additives such as carbon black, which can be added to nylon 6 as a dulling agent, are believed to enhance lightfastness by trapping free radicals which may initiate dye fading.[687]

VI. Sensitized Fading of Triphenylmethane Dyes in Protein Substrates

It has been pointed out in the previous discussion that the fading of triphenylmethane dyes is highly dependent upon the environment in which they exist. In particular, it was noted that this class of dye exhibits very poor lightfastness on protein substrates such as wool and silk yet moderate stability to light is achieved on poly(acrylonitrile).[1b,659] These observations suggest that some constituent of the protein substrate is responsible for the low lightfastness exhibited by these dyes.

In order to understand the complex nature of the photointeraction occurring between the dye and the wool it is worthwhile briefly examining the structure of the wool substrate.

Wool has a polymeric structure consisting of amino acids linked together in a chain by peptide (amide) bonds. Each amino acid has the following general structure:



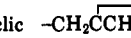
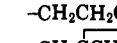
(79)

the zwitterionic form

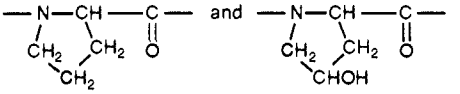
In this structure, R_a is used to classify each amino acid. For the amino acids present in wool, R_a is either aliphatic, aromatic, heterocyclic, acidic, basic, or a group containing sulfur. Table III shows the composition of wool. Thus, as a first approximation it is reasonable to assume that wool reacts as a mixture of compounds representing each amino acid.

To further underline the complexity of the photochemistry of the dyed-wool system it should be briefly noted that wool itself is a photoactive substrate.

Table III. Amino Acid Composition of Wool (Keratin) (Adapted from ref 691. Copyright 1971 Butterworth Publishers)

type of amino acid	amino acid residue (R_a)	name of amino acid	approximate grams of amino acid per 100 grams of dry protein[a]
	$-H$	glycine	5.5
	$-CH_3$	alanine	4.3
	$-CH_2OH$	serine	10.6
aliphatic	$-CH(CH_3)_2$	valine	5.7
	$-CH(OH)CH_3$	threonine	7.15
	$-CH_2CH(CH_3)_2$	leucine	9.0
	$-CH(CH_3)CH_2CH_3$	isoleucine	3.6
aromatic	$-CH_2C_6H_5$	phenylalanine	4.1
	$-CH_2C_6H_4OH(1,4)$	tyrosine	5.5
sulfur	$-CH_2SSCH_2-$	cystine	13.0
containing	$-CH_2CH_2SCH_3$	methionine	0.55
heterocyclic	$-CH_2$ 	tryptophan	0.95
	$-CH_2CH_2CH_2-$[b]	proline	6.8
	$-CH_2CH(OH)CH_2-$[b]	hydroxyproline	0.0
acidic	$-CH_2COOH$	aspartic acid	6.8
	$-CH_2CH_2COOH$	glutamic acid	14.5
basic	$-CH_2$ 	histidine	1.2
	$-(CH_2)_3NHC(NH)NH_2$	arginine	9.8
	$-(CH_2)_4NH_2$	lysine	3.3

[a] There is considerable variation due to diet and breed of sheep. [Maclaren, J. A.; Milligan, B. *Wool Science. The Chemical Reactivity of the Wool Fibre*; Science Press: Marrickville, 1981; p 137.] These values are assessed from various sources.[691] [b] The amino acid residues of proline and hydroxy proline have the following cyclic structures, respectively



Between the wavelengths 250 to 300 nm the absorbance of wool agrees to within 10% of the estimated absorbance based on the amino acid composition and the individual amino acid absorbances. The aromatic amino acids tyrosine and tryptophan are the major absorbers, with cystine and phenylalanine making minor contributions. Above the wavelength of 300 nm and below 250 nm, the absorbance of wool is larger than can be accounted for by the amino acid composition. The additional absorbance has been attributed to a photochemically active but as yet unidentified species.

Since this review is primarily concerned with the interaction of light with triphenylmethane dyes, the photophysical and photochemical reactions of wool will not be discussed any further. Instead the reader is referred to the review article written by Nicholls,[688] where more detailed discussions can be found.

Apart from the above-mentioned variations in lightfastness with different substrates, there is also additional evidence to suggest that triphenylmethane dyes interact with protein substrates. It has been found that when wool, dyed with the triphenylmethane dye basic violet 14, is irradiated with ultraviolet radiation (300–340 nm) with a peak output at 310 nm, the electron-spin resonance signal obtained may be attributed entirely to the wool.[689] In contrast, when this dye is applied to polyamide, the electron-spin resonance signal obtained after exposure to 310-nm radiation is characteristic of the dye.[689,690] Coles and Nicholls[689,690] explained the interaction between the dye and the wool in terms of the photoconductivity of the dye. Tri-

phenylmethane dyes behave like *n*-type conductors, with mobile electrons acting as charge carriers. When they are applied to wool the mobile electrons photoejected from the dye are scavenged by the disulfide groups of cystine, at the same time enhancing the cystine electron-spin resonance signal of the wool.[689]

The above discussion implies that triphenylmethane dyes are photooxidized on wool, but previous work by Cumming et al.[563] indicates that photoreduction is also possible on protein substrates. In order to ascertain whether the amino acids, tyrosine, tryptophan, and histidine could act as reducing agents in protein substrates they examined the fading of a number of triphenylmethane and azo dyes in cellofas A (methyl ethyl cellulose, a nonprotein substrate), both in the presence and absence of these amino acids, and compared the observed fading with that obtained in gelatin (a protein substrate). From this study it was concluded that histidine was probably the reducing agent in protein substrates. Tyrosine did not appear to cause photoreduction and the results with tryptophan were inconclusive.

This conclusion, however, must be queried as histidine was employed in the form of the free amino acid. Under physiological conditions the free α-amino group and the carboxylate group of the amino acid would participate in the formation of a peptide bond. Thus, the photochemistry of the free amino acid may differ from when it is in a protein-bound state. The work presented by Mason et al.[600] provides a good illustration that this may occur. In this study the free amino acid tryptophan was observed to sensitize the fading of acid blue 7 and acid green 9 incorporated into poly(vinyl alcohol), but tryptophan derivatives in which the free α-amino and carboxylate groups are involved in peptide bonds showed no sensitization. It became apparent that the indole group of tryptophan must be linked to a free carboxylate anion for sensitized dye fading to occur. Dye fading involved the excited triplet state of tryptophan which was quenched by oxygen and Mn^{2+}. Mn^{2+} was also observed to quench the excited triplet state of the dye. Electron transfer was observed to occur, but not between the dye and tryptophan, since the amino acid was not consumed during the reaction. Accordingly, two mechanisms were suggested to explain these results:

Scheme III

$$\mathrm{Trp} \xrightarrow{h\nu} {}^1\mathrm{Trp}^* \quad \text{absorption} \tag{80}$$

$${}^1\mathrm{Trp}^* \rightarrow {}^3\mathrm{Trp}^* \quad \text{intersystem crossing} \tag{81}$$

$${}^3\mathrm{Trp}^* + \mathrm{D} \rightarrow \mathrm{Trp} + {}^3\mathrm{D}^* \quad \text{energy transfer} \tag{82}$$

$${}^3\mathrm{D}^* + \mathrm{PVA} \rightarrow \mathrm{PVA}^+ + \mathrm{D}^- \quad \text{degradation} \tag{83}$$

where Trp, D, and PVA represent tryptophan, dye, and poly(vinyl alcohol), respectively.

Scheme IV

$$\mathrm{Trp} \xrightarrow{h\nu} {}^1\mathrm{Trp} \quad \text{absorption} \tag{84}$$

$${}^1\mathrm{Trp}^* + \mathrm{D} \rightarrow {}^1(\mathrm{TrpD})^* \quad \text{exciplex formation} \tag{85}$$

$${}^1(\mathrm{TrpD})^* \rightarrow {}^3(\mathrm{TrpD})^* \quad \text{intersystem crossing} \tag{86}$$

$${}^3(\mathrm{TrpD})^* \rightarrow {}^3\mathrm{D}^* + \mathrm{Trp} \quad \text{dissociation} \tag{87}$$

$${}^3\mathrm{D}^* + \mathrm{PVA} \rightarrow \mathrm{PVA}^+ + \mathrm{D}^- \quad \text{degradation} \tag{88}$$

Reaction Scheme IV was considered to be the most likely mechanism since the carboxylate anion of the free amino acid tryptophan would influence the formation of the exciplex but would be less likely to influence direct energy transfer.

On the basis of these findings it was concluded that tryptophan was unlikely to sensitize dye fading in wool. It also seems unlikely that protein-bound tyrosine would sensitize the fading of triphenylmethane dyes, since in comparison to tryptophan, the free amino acid form of tyrosine barely enhances the fading of acid blue 7 and acid green 9 in poly(vinyl alcohol).[601] This is in agreement with the conclusion by Cumming et al.[563] regarding the effect of this amino acid on dye fading.

Duxbury[183] also considered the possibility that dye fading in the presence of a free amino acid may not be indicative of dye fading in the presence of a protein bound amino acid. In this study it was found that neither protein-bound histidine nor protein-bound lysine are likely to sensitize fading of the triphenylmethane dyes acid blue 1, acid green 9, acid blue 15, and acid violet 17 in wool, whereas protein-bound glutamic and aspartic acids and arginine enhance dye fading. Furthermore, it was found that the α-carboxyl group of the free amino acids arginine and glutamic acid was able to sensitize dye fading. In contrast, the α-amino group of both free amino acids did not enhance dye fading except in the case of acid blue 1. The α-amino group appeared to enhance dye fading only when it was attached to a carboxyl group (such as in L-glutamic acid) or a guanidino group (such as in L-arginine) and this appears to suggest that the *o*-phenyl ring SO_3^-, on the dye, facilitates fading by interacting with the positively charged α-amino group.

Both one-step transfer (of an electron and a hydrogen atom) and exciplex mechanisms were proposed by Duxbury[183] for sensitized fading of the dye monomers. The likelihood of energy transfer occurring between the dye and amino acid was precluded because the requirement that the absorption spectrum of the amino acid overlaps the fluorescence spectrum of the dye (which is necessary for energy transfer) was not fulfilled. Subsequent electron-spin resonance measurements supported these proposals for dye fading in the presence of acetate groups, but not for dye fading in the presence of guanidino groups.

On the basis of the electron-spin resonance measurements and mechanistic studies which suggest triphenylmethane dyes undergo photoreduction on wool, Duxbury[183] proposed an alternative explanation for the absence of a dye electron-spin resonance signal and the enhanced cystine electron-spin resonance signal

observed in wool by Coles and Nicholls.[689] This being that the cystinyl radical cation formed upon ultraviolet irradiation of cystine as shown in reaction 89, combines with the dye radicals to produce colorless dye photoproducts.

$$RCH_2SSCH_2R \xrightarrow{h\nu} RCH_2S^+S^\cdot CH_2R + e^- \quad (89)$$

The photoejected electron would react with cystine according to reaction 90, thereby enhancing the cystine electron-spin resonance signal.

$$RCH_2SSCH_2R + e^- \rightarrow RCH_2S^\cdot S^-CH_2R \quad (90)$$

$$\rightarrow RCH_2S^\cdot + S^-CH_2R \quad (91)$$

where R = $^+NH_3CHCOO^-$.

On the basis of the work by Jori et al.,[590] it seems likely that the thiyl free radicals recombine to form cystine since they report that cystine is unaffected by radiation in the presence of basic violet 3.

It would be interesting to examine these possibilities in more detail in future research. In this context, it would also be useful to study the electron-spin resonance signal of triphenylmethane-dyed silk, since like gelatin (and unlike wool) silk contains a low proportion of cystine.[691]

In summary, it is noted that protein-bound tyrosine, histidine, and lysine do not sensitize the fading of triphenylmethane dyes. On the other hand, the free carboxyl groups of protein bound glutamic acid and aspartic acid enhance the fading of triphenylmethane dyes. In wool, there will also be α-carboxyl groups at the beginning and end of the polymer chain which will be capable of sensitizing dye fading. Terminal α-amino groups attached to guanidino or carboxyl groups may be able to sensitize the fading of triphenylmethane dyes which have a SO_3^- group in the ortho position of a phenyl ring. The guanidino group of protein-bound arginine has also been observed to sensitize dye fading but to a lesser extent than that observed for free carboxyl groups. Protein-bound tryptophan does not sensitize triphenylmethane dye fading unless the indole ring is attached to a carboxyl group. This would occur when tryptophan was located at the end of the protein polymer chain. In the most general sense, sensitized fading of triphenylmethane dyes by the protein-bound amino acids studied by Duxbury,[183] apparently involves hydrogen atom or electron transfer, the excited triplet state dye molecule, and possibly an excited triplet state exciplex. Mason et al.[600] proposed reaction Schemes III and IV to account for dye fading sensitized by tryptophan, with reaction scheme IV, involving an exciplex being considered the most likely mechanism.

In a study by Jori and co-workers,[588,590] basic violet 3 was found to selectively sensitize photooxidation of cysteine both in the protein-bound and free states. The selectivity of this reaction was previously noted by Bellin and Yankus[589] and has been observed by Jori et al.[590] to extend over the pH range 2.5–9. In acidic solutions cysteine is quantitatively converted to cysteic acid and hydrogen peroxide is formed as an end product whereas in neutral or alkaline media the photooxidation process competes with a dark reaction which oxidizes cysteine to cystine. It was proposed by Jori et al.[590] that the thiol group of the cysteinyl side chain was probably attacked during photooxidation. A mechanism has been proposed which suggests that the triplet dye abstracts a hydrogen atom from the thiol group of cysteine:[588]

$$^3D^* + R\text{-}SH \rightarrow DH^\cdot + RS^\cdot \quad (92)$$

$$RS^\cdot + O_2 \rightarrow RSO_2^\cdot \quad (93)$$

$$RSO_2^\cdot + O_2 \rightarrow RSO_4^\cdot \quad (94)$$

$$RSO_4^\cdot + RSH \rightarrow RSO_4H + RS^\cdot \quad (95)$$

$$RSO_4H + H_2O \rightarrow RSO_3H + H_2O_2 \quad (96)$$

where R = $CH_2C(COOH)HNH_2$.

In support of this mechanism Fischer and co-workers[528] have observed an enhanced electron-spin resonance signal originating from the semireduced carbon-centered dye radical when aqueous degassed solutions of basic violet 3 in the presence of cysteine were photolyzed with light of wavelengths greater than 500 nm.

Furthermore, Gennari et al.[588] claim that the $DH^\cdot$ is probably reoxidized to form the original dye as they did not observe appreciable dye fading in their experiments.

Apart from the above mentioned studies it appears that the number of photochemical studies specifically devoted to considering the interactions between triphenylmethane dyes and protein-bound amino acids is very small and further work in this area would be a benefit to the textile industry in particular.

VII. Acknowledgments

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