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Fluorescent Whitening Agents—A Survey (1974–82)

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SUMMARY

This survey presents a comprehensive coverage of the literature on fluorescent whitening agents for the period 1974 to mid-1982. It is intended to serve researchers in the field by providing an up-to-date summary of the published literature on the synthesis, textile applications and analysis of fluorescent whitening agents. The survey does not cover the use of fluorescent whitening agents as additives for soaps and detergents.

The latter part of the survey describes the light fading reactions of five technologically important classes of fluorescent whitening agent. Recent progress in understanding the photochemical processes that are responsible for fading, and the factors that influence the light stability of fluorescent whitening agents in a polymeric environment, are summarized.

1. INTRODUCTION

The last detailed survey[1] of the literature on fluorescent whitening agents spanned the period 1967 to 1973. Our survey, for the period 1974 to mid-1982, includes the synthesis, textile applications, analysis and photochemical behaviour of fluorescent whitening agents. Limitations of space preclude detailed discussion of all these topics. However, the photochemistry of fluorescent whitening agents has been actively studied in recent years, and this topic has therefore been discussed in more detail.

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Several general reviews have appeared during the period under survey,[2–8] but only one of these reviews[7] has dealt with the photochemical reactions of whiteners in any detail. We have not surveyed literature on the use of fluorescent whitening agents as additives for soaps and detergents; two recent reviews of this topic are available.[9,10]

2. SYNTHESIS

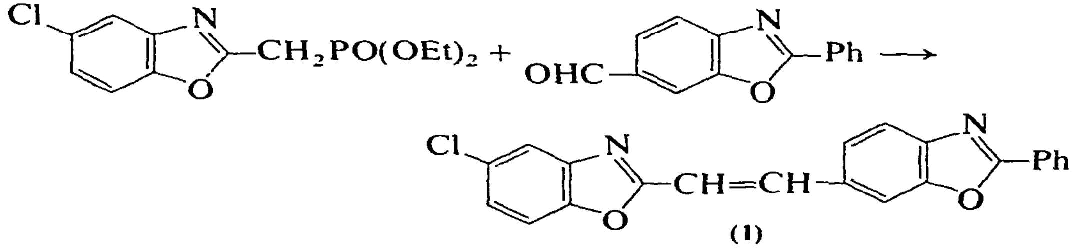
Most fluorescent whitening agents contain a stilbene, styrene or ethylene moiety supplemented by one or more heterocyclic systems. Many are unsymmetrically substituted molecules which fall into more than one of the following classifications; however in the interests of brevity no attempt at cross-referencing has been made. An extensive review[11] of synthetic approaches to fluorescent whitening agents using heterocycles as 'building blocks' was published in 1975.

2.1. Stilbenes, styrenes and ethylenes

2.1.1. With benzoxazolyl substituents

Many whiteners of this class have been synthesized using benzoxazole derivatives as starting materials. The well-known condensation reaction between diethyl benzylphosphonates or heteroarylmethylphosphonates and aromatic aldehydes has been used most frequently.[12–18] An example[17] is the synthesis of the benzoxazolylethylene **1**. Other whiteners, for example[19] the stilbene **2**, have been prepared by reaction of benzoxazolyltoluenes with suitably substituted anils.[19–23]

An alternative route to benzoxazolylstilbenes entails condensation of stilbenecarboxylic acid chlorides with 2-aminophenols, and cyclization of the resultant amides.[24–28] An example[28] is the synthesis of the bisbenzoxazolylstilbene **3**. Additional heterocyclic substituents, e.g.



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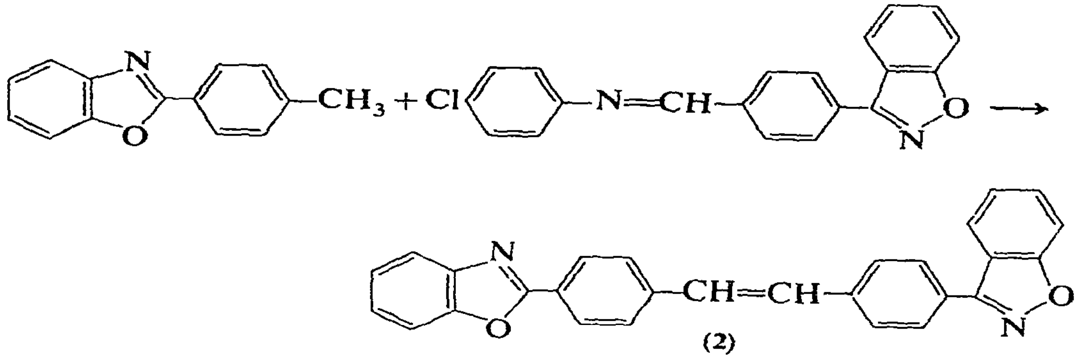

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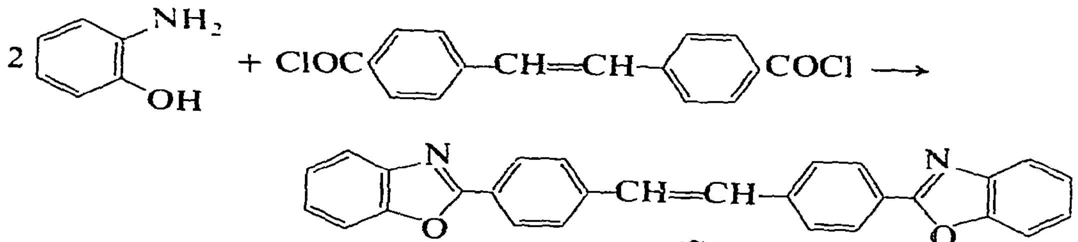

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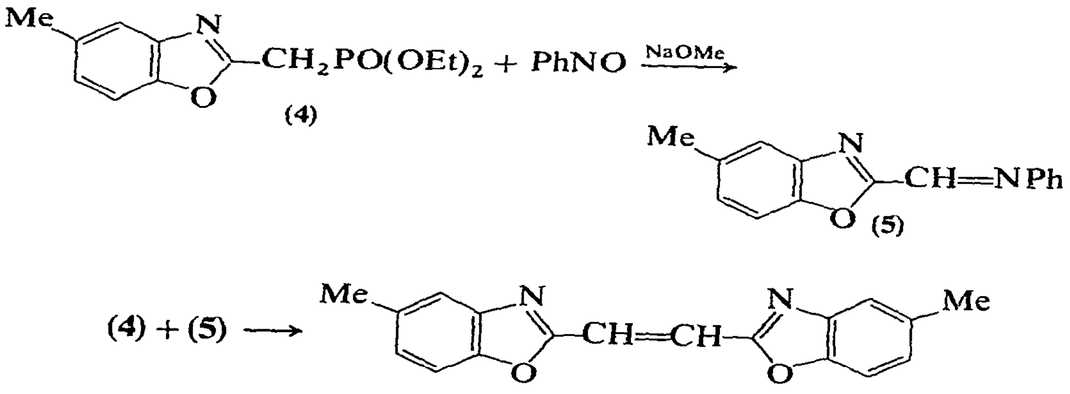
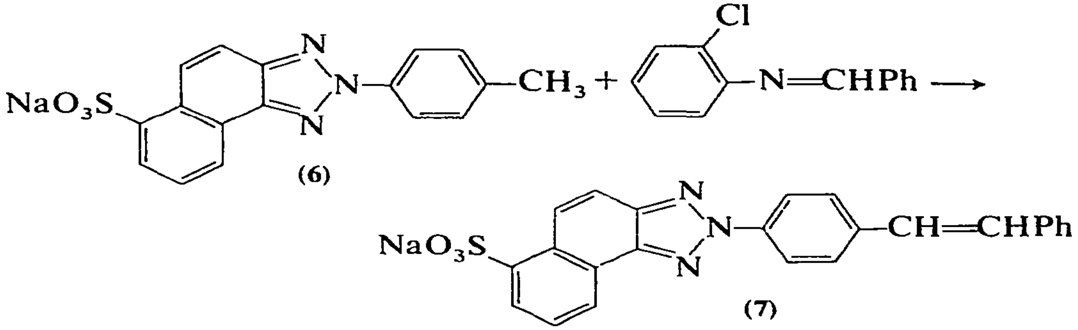
oxadiazolyl,[29,30] pyrido-oxazolyl[31,32] or benzimidazolyl,[27] have been introduced in related fashion using benzoxazolylstilbene carboxylic acid chlorides as starting materials, and by other routes.[15,17,18,33–37]

Symmetrical benzoxazolylethylenes are obtained by reaction of diethyl benzoxazol-2-ylmethylphosphonates with nitrosobenzene in the presence of sodium methoxide.[38,39] The reaction proceeds via an anil,[38] for example **5**:



2.1.2. *With* v-*triazolyl substituents*

Several new *v*-triazolyl-substituted stilbenes have been obtained using *v*-triazoles as starting materials, the stilbene moiety being built up by condensation of appropriately substituted diethyl benzylphosphonates and aromatic aldehydes.[40-44] Others have been prepared by reaction between anils of *v*-triazolyl-substituted benzaldehydes and appropriately substituted toluenes,[45-51] or between *v*-triazolyltoluenes and anils.[52-57] The conversion of **6** to **7** is an example.[52] A group of workers from Ciba–Geigy describes the synthesis of 271 *v*-triazolyl-substituted stilbenes by this route.[46]



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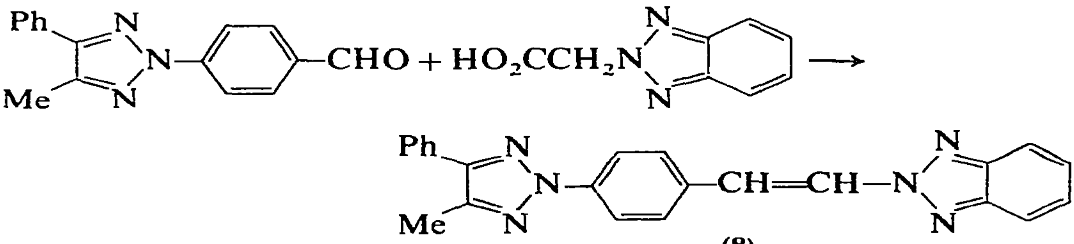
v-Triazolylacetic acid has been used as the starting material for a number of *v*-triazolylstyrene derivatives.[58,59] Reaction with substituted benzaldehydes at high temperatures in the presence of piperidine gives the desired styrenes, for example[58] the benzotriazolylstyrene **8**. Stilbenes containing *v*-triazolyl groups linked through carbon, rather than nitrogen, have also been reported;[43,49,60,61] the cyanotriazolylstilbene **9** is an example.[61] Other patents describe whiteners containing two or more *v*-triazolyl groups,[62-65] which in some cases[63] are used to link styrene chromophores together, as in **10**. Stilbenes containing 1,2,4-triazolyl



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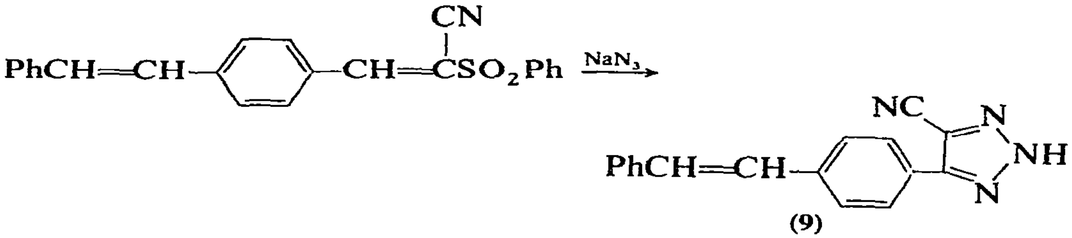

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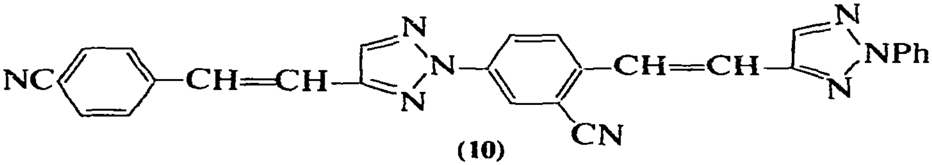

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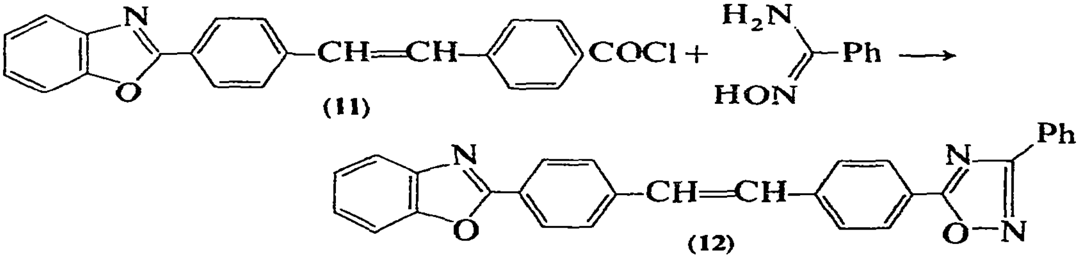
substituents, rather than *v*-triazolyl substituents, have also been reported.[66,67]

2.1.3. *With oxadiazolyl substituents*

1,2,4-Oxadiazolylstilbenes have been prepared using oxadiazolylmethyl- or oxadiazolylbenzyl-phosphonates as starting materials for stilbene synthesis,[68–70] and also by condensation of stilbene carboxylic acid chlorides with amidoximes.[29,30] An example[29] of the second route is the conversion of **11** to **12**. Alternatively, styrene or stilbene carboxylic acid chlorides can be converted to hydrazides, which are then cyclized by treatment with thionyl chloride or other reagents.[37,71–74] The conversion of **13** to **14** is an example.[37]

The symmetrically substituted oxadiazole **15** was obtained by condensation of 4-carbomethoxycinnamoyl chloride with hydrazine, and cyclization of the resultant hydrazide.[71] It is much more fluorescent and photostable than the parent compound which lacks carbomethoxy groups.



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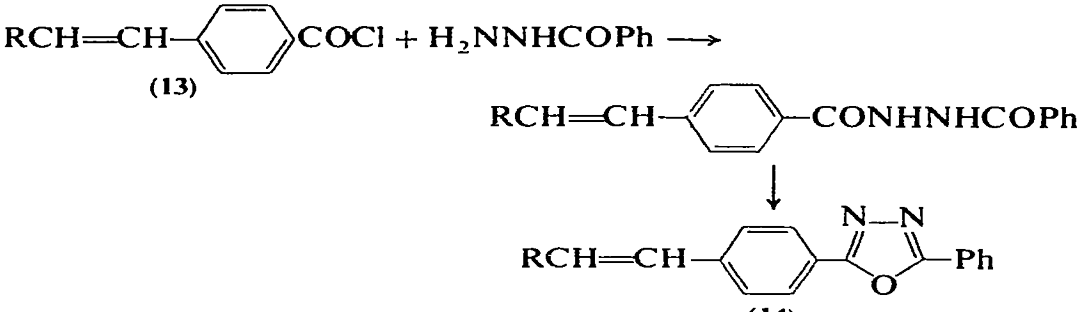

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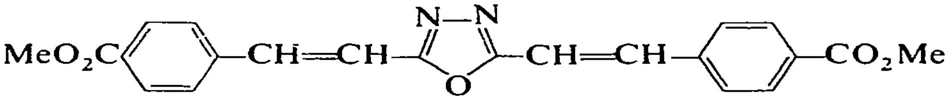

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2.1.4. With miscellaneous heterocyclic substituents

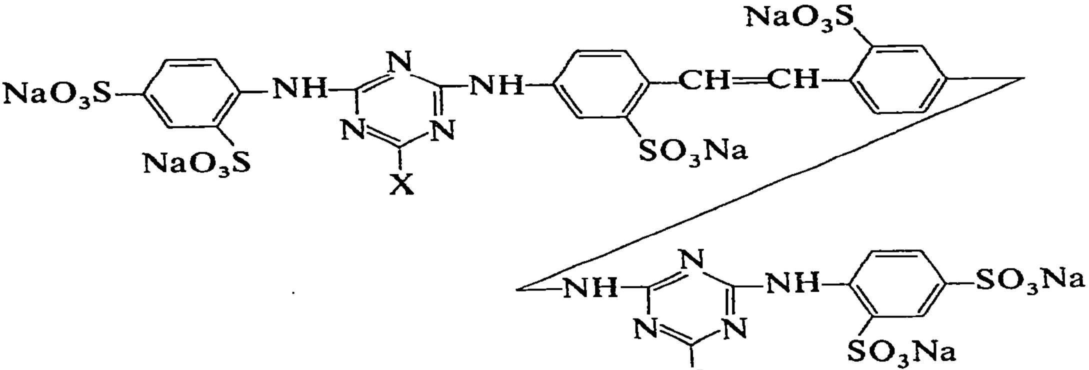
Stilbenes containing benzofuranyl substituents have been prepared by condensation of benzofuranyltoluenes with anils.[75–79] This procedure produces *trans*-stilbenes exclusively, in contrast to the reaction of an aromatic aldehyde with a diethyl arylmethylphosphonate, which may give mixtures of *cis*- and *trans*-isomers.[75] Stilbenes with benzothiophene,[76,78] benzopyrrole[76,78] and oxazolopyridine[80] groups are also reported.

2.1.5. With s-*triazinylamino substituents*

Patent activity in this area has declined. Triazinylaminostilbenes containing allylamino,[81] propargylamino,[81] cyanoethyl,[82] guanidinosulphonyl[83] and thiosulphate[84,85] groups are among those described. An improved method for introducing alkylthio groups is claimed.[86] Several bis-(4-chloro-*s*-triazinylamino)stilbenedisulphonic acids have been found to whiten cotton but not silk, although they are bound covalently to both fibres.[87] The azido derivative **16** ($X = N_3$) colours paper and nylon yellow, but is converted by light into the fluorescent whitener **16** ($X = NH_2$).[88]

2.2. Bis-styryl aromatics

Most bis-styryl aromatic whiteners have been prepared by condensing diethyl benzylphosphonates with appropriately substituted benzaldehydes.[89–104] An example[89] is the conversion of **17** to **18**. Unsymmetrical



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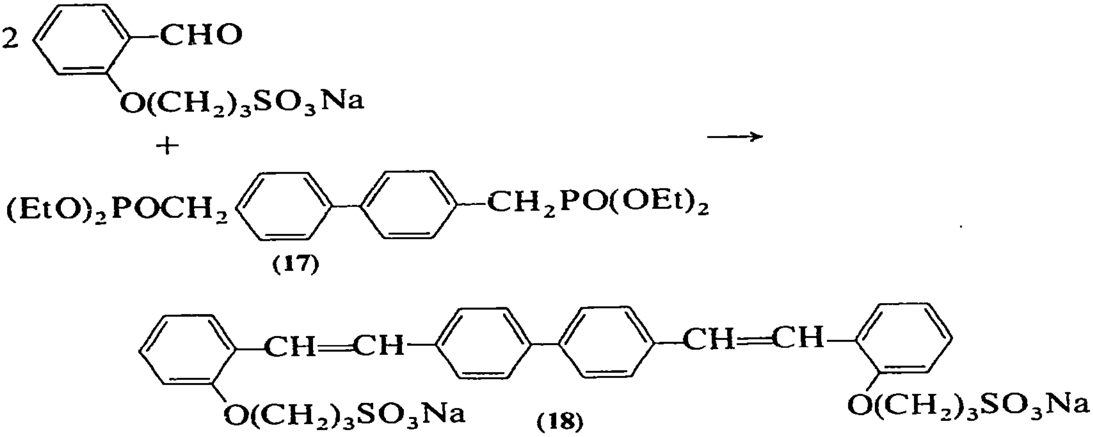
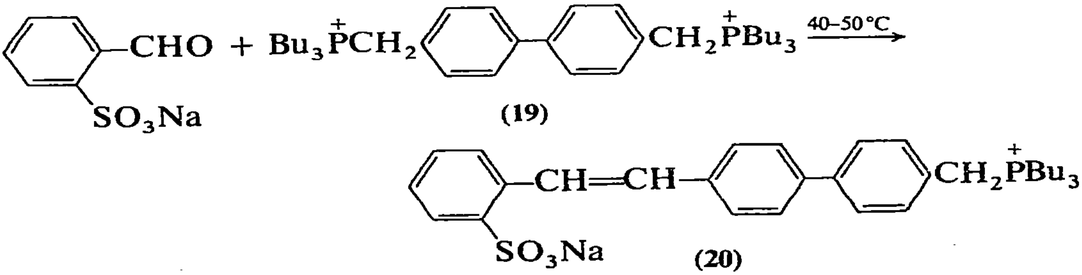


(17) **(18)**

compounds can be prepared by using the tributylphosphonium salt **19** instead of **17**; the two steps proceed at different rates, which permits the use of two different aldehydes:[105]



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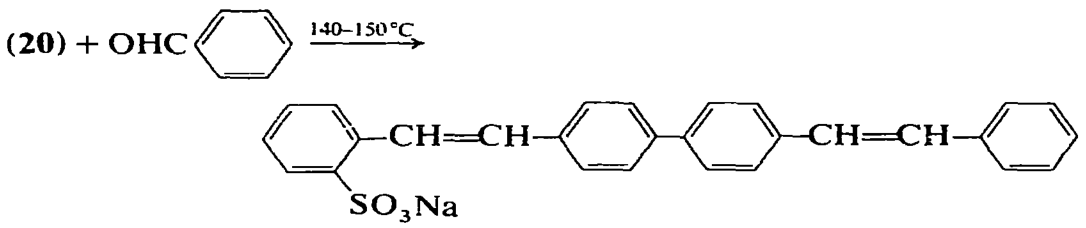
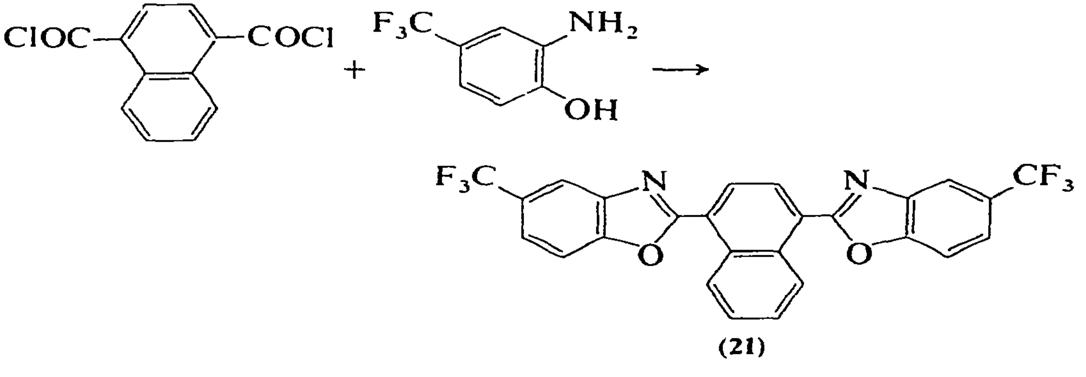


Symmetrical compounds are also prepared by this route.[106]

Other synthetic methods involve the reaction of appropriate toluene derivatives with benzaldehyde anils.[75,107] The condensation of substituted styrenes with sodium 2,5-dibromobenzenesulphonate in the presence of a palladium catalyst gives sulphonated bis-styrylbenzene whiteners.[108]

2.3. Benzoxazoles and benzimidazoles

Numerous patents claim bisbenzoxazolyl aromatic compounds as whiteners for polyester, polypropylene or acetate fibres. The method of synthesis used in each case[109–117] was condensation of an aromatic dicarboxylic acid chloride with a substituted 2-aminophenol, for example[112] the synthesis of **21**. Benzoxazoles with *v*-triazolyl,[118] cyano[113,117,119] and quaternized pyrazolyl[120] substituents are also described.



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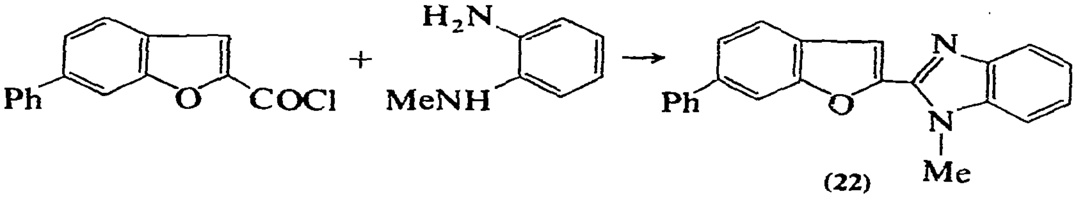
Similar condensation of acid chlorides with substituted *o*-phenylenediamines yields benzimidazoles,[121–125] for example[122] the benzofuranylimidazole **22**. Aldehydes[126] or trichloromethyl compounds[127] can be



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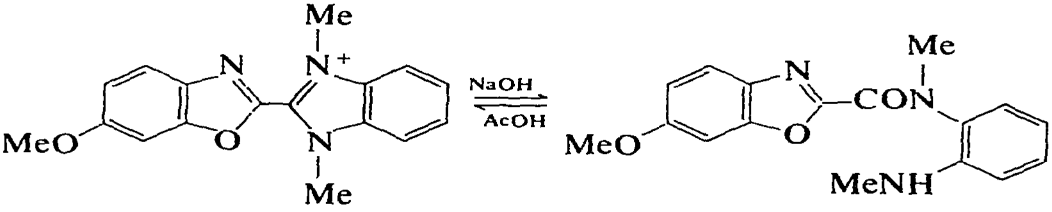
used instead of acid chlorides. Methods for introducing additional heterocyclic substituents are also described.[128] Treatment of the resultant benzimidazoles with dialkyl sulphates gives quaternary ammonium salts which are useful for whitening synthetic fibres.[122–127,129–131]

Treatment of quaternized benzimidazoles with hot alkali gives *N*-acyl *o*-phenylenediamines, which are also useful for whitening acrylic fibres;[132] the conversion of **23** to **24** is an example. The *N*-methylamide **24** can be reconverted to **23** by refluxing with acetic acid.



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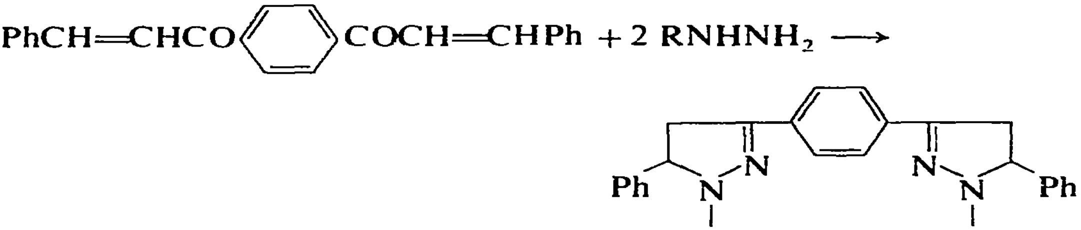
2.4. Pyrazolines

The synthesis of a wide range of cationic pyrazolines, by treating functionally reactive pyrazolines with different diamines, is described;[133–138] all are recommended for whitening acrylic fibres. Sulphonated pyrazolines are prepared by addition of bisulphite to 3-hydroxyallylsulphonylpyrazolines,[139] by reaction of pyrazolines containing acid chloride groups with taurine or its derivatives,[138,140] or by condensation of ω-chloropropiophenones with sidechain-sulphonated phenylhydrazines.[141,142] Whiteners containing sulpho groups linked to the 4-position of the pyrazoline ring are also described.[143,144] Other patents claim the introduction of thiosulphate,[145] sulphonium,[138,146] butanesulphonyl,[147–149] pyrazolyl[144] and styryl groups[148,150] into pyrazolines.

A Russian paper[151] describes the synthesis of several 1,4-bis(pyrazolin-3-yl)benzenes, for example **25**, by the following general method:



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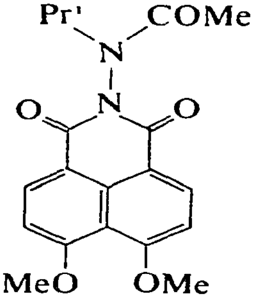
2.5. Naphthalimides

Patent activity in this area is mainly concerned with the structure of the *N*-substituent. Claims include a variety of naphthalimides with *N*-substituents containing cyano,[152] carboxyl,[152] aldehyde,[152] acyl,[152] sulpho,[153] alkoxy,[154] ureido,[155] piperidino,[156] morpholino,[156] pyridinium,[157] pyrazolium[157] or trialkylammoniumalkyl groups.[158–160] *N*-acylaminonaphthalimides[155,161–163] (e.g. **26**) and naphthalimides with benzotriazolyl[164] or naphthotriazolyl groups[164,165] (e.g. **27**) are also described. Other patents claim naphthalimides with 4-alkoxy or 4,5-dialkoxy groups containing additional ether,[166] thioether[166] or quaternary ammonium groups.[167]



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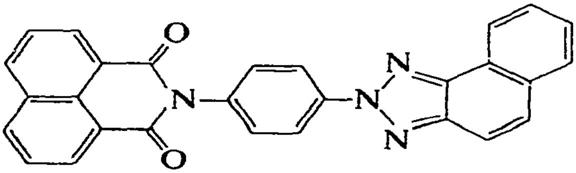

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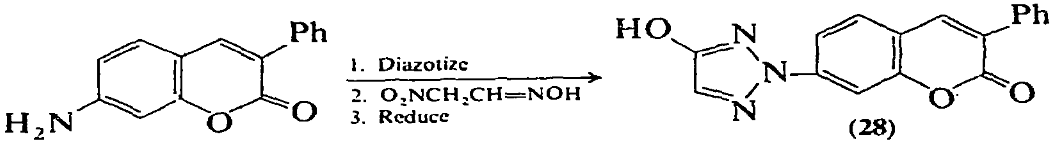
2.6. Coumarins

Several recent patents describe coumarins with 1,2,3- or 1,2,4-triazolyl substituents in either the 3- or 7-position.[168–175] The triazole group is incorporated into a coumarin intermediate in some cases,[168,169,175] for example[168] in the synthesis of **28**. In other instances, triazolyl derivatives, such as **29**, are used as starting materials to construct the coumarin system.[171,172,174]



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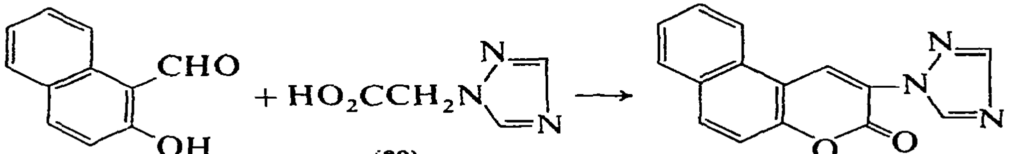

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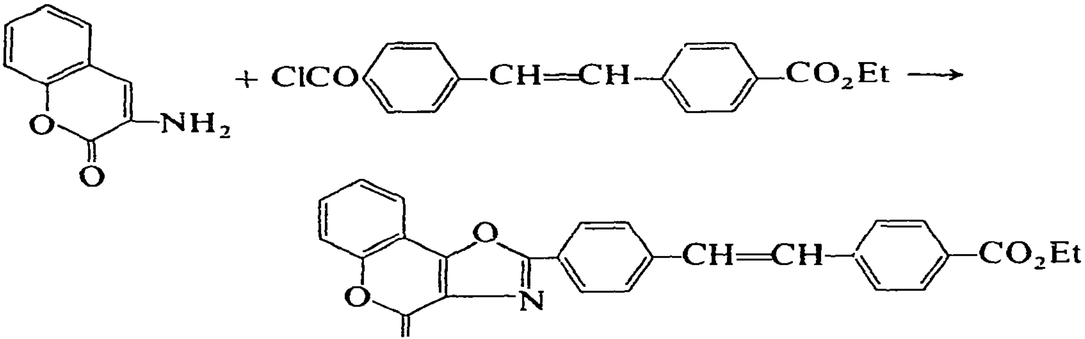
Coumarins containing benzoxazolyl,[175a] oxadiazolyl,[176] oxopiperidino,[177] oxopyrrolinyl[177] and halogeno[178] substituents are also described. The whitener **30** contains coumarin and oxazole systems fused together:[179]



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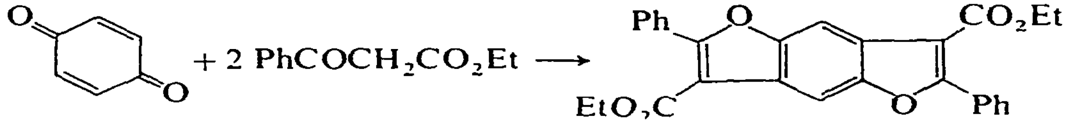
Fibre-reactive coumarins containing chlorotriazine,[180] dichloroquinoxaline,[180] chloropyrimidine[180] and sulphonylethyl sulphate[181] groups are also claimed as washfast whiteners for cotton, nylon or wool.

2.7. Benzofurans

Several methods have been described for the synthesis of benzodifurans[182,183] and bisbenzofuranyl compounds.[184–187] Examples[183,187]



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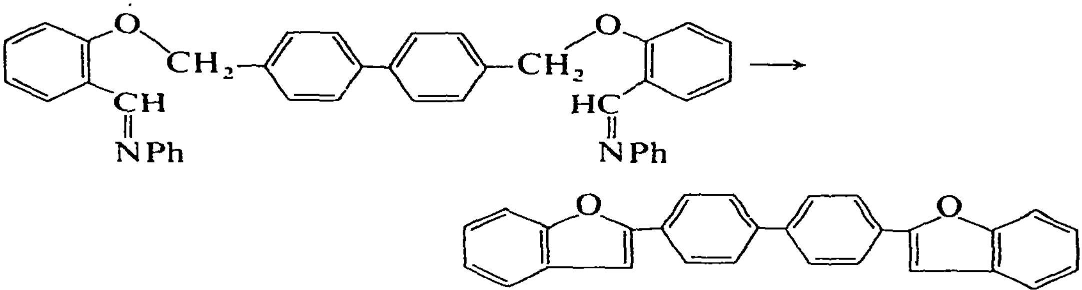

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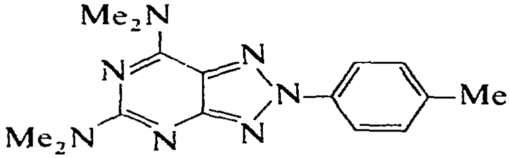
are the synthesis of the benzodifuran **31** and the bisbenzofuran **32**. Benzofurans containing a wide range of heterocyclic and other substituents have been patented.[26,183,186,187]

2.8. Miscellaneous whiteners

Miscellaneous whiteners include the *v*-triazolo[4,5-*d*]pyrimidine[188] **33**, various 1,2-di-β-naphthylethylenes,[189,190] the triazinylhydrazide[191] **34** and the diimidazopyrazine **35**, prepared by heating tetrakisbenzamidopyrazine.[192] Various whiteners containing acetylenic groups[193-195]



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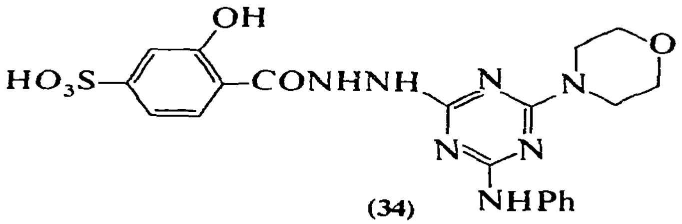

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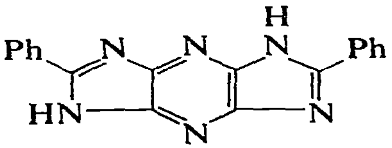

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have been described. Many substituted 2-hydroxyphenylbenzotriazoles have been claimed both as ultraviolet stabilizers and fluorescent whiteners.[196–198]

3. TEXTILE APPLICATIONS

The application of fluorescent whiteners to textiles has been discussed in a recent book[6] and review[199] by Williamson. Procedures for whitening cellulosic, polyester, polyamide and acrylic fibres with Hoechst[200] and Bayer[201] products have also been described.

Factors affecting whiteness during the pad/batch application of a bistriazinylaminostilbene whitener to cotton have been examined.[202] Whiteness is improved if the whitener is applied together with a surfactant and if the padded cloth is stored, preferably at 75 °C, before drying.[202] The improvement in whiteness is attributed to an increase in the extent of penetration of the fibre, and to enhanced binding of whitener molecules, in their planar form, to the cellulose chains. The authors postulate that this binding retards vibrational processes, thereby stimulating radiative relaxation (that is, fluorescence emission) and hindering non-radiative relaxation processes. It is also important to exclude all traces of copper and iron salts, which cause a bathochromic shift in the absorption spectra of stilbene whiteners and quench their fluorescence, thereby decreasing fabric whiteness.[203] Similar spectral effects occur if optimal whitener concentrations are exceeded, and lead to a reduction in fabric whiteness.[204] Bleaching and whitening procedures for cotton and cotton/polyester blends have been evaluated.[205]

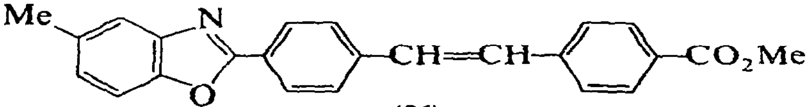
The poor light stability of fluorescently whitened wool is well known. Reasons for this behaviour, and methods to minimize it, have been reviewed.[206] Treatment of wool containing a coumarin whitener with sodium bisulphite and sodium ascorbate has recently been claimed[207] to increase the lightfastness rating from 1 to 2, while the addition of malonic or mandelic acid to the above reductants produces a further slight improvement.[208] The application of stilbene whiteners to wool in the presence of thiourea dioxide gives a product that is as white as that produced by the fluorescent whitening of peroxide-bleached wool,[209] and a little more stable to light. Despite the relatively high cost of thiourea dioxide, this one-step bleaching/whitening procedure may offer economic advantages over the more usual two-step procedures. The sensitized photoyellowing that occurs with conventionally whitened wool can be avoided by the application of a polymer film containing fluorescent whiteners to the fibre surface.[210] However, practical surface-whitening procedures still await development, as no single whitener/polymer system which confers satisfactory whiteness, light stability, washfastness and softness has been found.

Treatment of fluorescently whitened cotton fabrics with sodium thiosulphate solutions improves the lightfastness, but similar treatment of whitened wool or synthetic fabrics has no effect.[211] Application of whiteners in conjunction with hydroxyammonium sulphate to silk,[212] and in conjunction with organophosphorus compounds such as 1-hydroxyethane-1,1-diphosphonic acid to modacrylic fibres,[213] is claimed to improve light stability.

Mixtures of some fluorescent whiteners are claimed to whiten polyester more effectively than either component alone at the same total concentration.[214–224] Bisbenzoxazolyl-ethylenes,[214,220,221] -stilbenes[215,216] and -aromatics,[217,221] in particular, show synergistic whitening effects when used in conjunction with related whiteners. For example,[215] pad/heat application of a mixture of **36** and **37** whitens polyester fabric more effectively than application of either **36** or **37** alone (see Table 1).

TABLE 1
Synergistic Whitening of Polyester by the Benzoxazolyl-stilbenes **36** and **37** (from ref. 215)

Whitener	*Concentration* (g/l)	*Fabric whiteness*	
		Berger formula	*Stensby formula*
36	0·8	148	151
37	0·8	160	154
36 **37**	0·6 0·2	162	158



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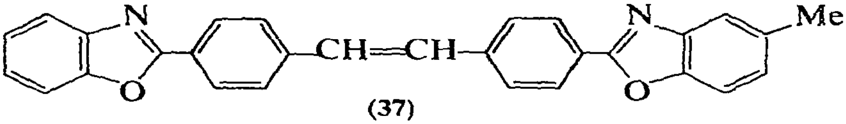

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Other classes, for example bis-styrylbenzenes and naphthalimides,[218] also show synergistic whitening effects on polyester.

4. ANALYSIS

Several papers describe procedures for the extraction of fluorescent whiteners from textiles or detergents, and their subsequent identification by thin layer chromatography.[225–229] Other papers describe the use of fluorimetry[230] and reflectance spectroscopy[231] for the determination of whiteners on thin layer chromatographic plates.

The recent development of high performance liquid chromatography has greatly facilitated whitener identification and estimation.[232–234] Separations have been made with silica columns[232] and reversed-phase ion pair systems.[233,234] The latter procedures take as little as 15 min to separate complex whitener mixtures, the results agreeing closely with those obtained using thin layer chromatography followed by densitometry.[233]

A colorimetric method for the determination of stilbene whiteners, based on oxidation to benzaldehyde derivatives, is described,[235] and the relative merits of other conventional methods are discussed.[236]

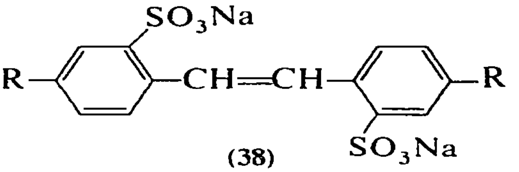
5. PHOTOCHEMICAL BEHAVIOUR

5.1. Stilbenes

Fluorescent whiteners based on the *trans*-stilbene chromophore have for many years been the cornerstone of the whitener industry, and numerous papers dealing with both mechanistic and kinetic aspects of the photochemistry of these compounds have appeared during the period of this review. The main fading reactions are isomerization to the non-fluorescent *cis* isomer, oxidative cleavage of the ethylenic bond and (in some cases) dimerization to cyclobutane derivatives.

5.1.1. Photoproducts and mechanisms

Photolysis of the model whitener, disodium 4,4′-diacetamidostilbene-2,2′-disulphonate (**38**, R = MeCONH—), results in rapid isomerization to give an equilibrium mixture of *cis* and *trans* isomers, followed by a slow irreversible conversion to the dihydroderivative **39**, the aldehyde **40** and the corresponding carboxylic acid.[237–239] There are conflicting views as to the importance of the isomerization pathway in the overall reaction scheme,[238,239] but a general survey[240] of the fading behaviour of 4,4′-diaminostilbene derivatives in water and in cellophane films has confirmed that photoisomerization is the major decomposition pathway. The dihydro compound **39** and the aldehyde **40** are formed in very low yield (2–3 %) in aqueous solution, but the conversion to the dihydro compound is reported to be as high as 39 % when wet wool fabric containing **38** is exposed to light.[238]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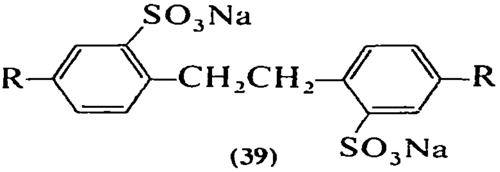
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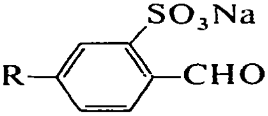
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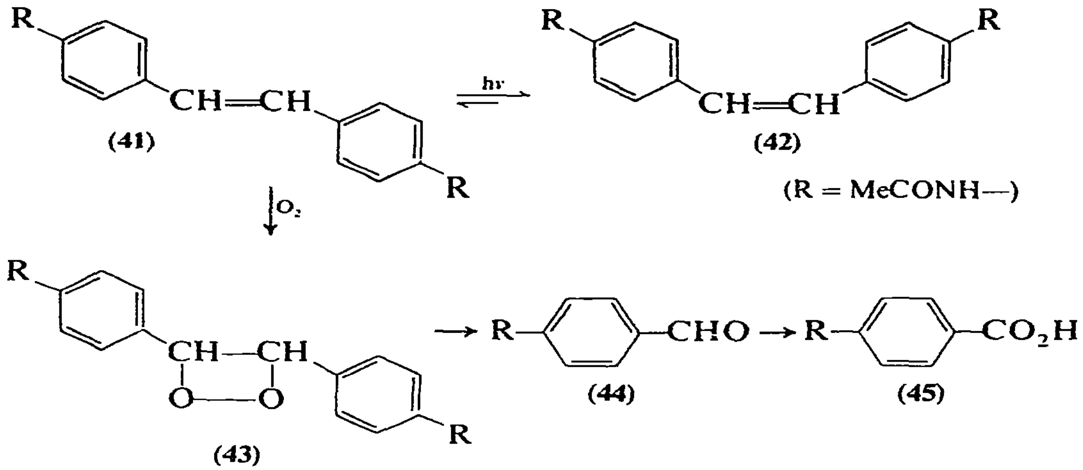
The rate of photoisomerization of **38** depends on the nature of its substituents and on its environment. The whitener **38** (R = 4-phenyltriazolyl) fades much more rapidly than **38** (R = benzoylamino) in water, whereas in cellophane films they fade at the same rate. Both are more photostable than **38** (R = triazinylamino or phenylureido) in either water or cellophane films.[240]

The photodegradation of *trans*-4,4′-diacetamidostilbene (**41**) in

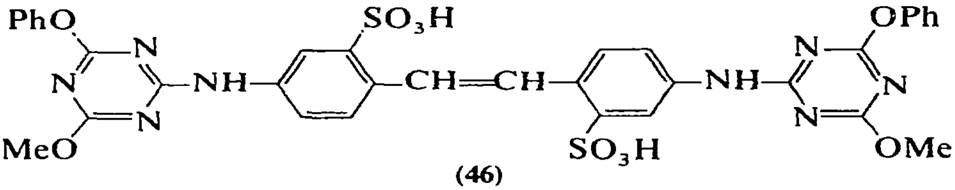


(41) (42) (43) (44) (45)

(R = MeCONH—)

solution appears to follow a similar pattern to that observed for the 2,2′-disulphonate **38**.[241,242] Photolysis of **41** in acetonitrile, acetone or ethanol results in rapid isomerization to give an equilibrium mixture of *cis* (**42**) and *trans* (**41**) isomers, followed by cleavage of the ethylenic bond to give 4-acetamidobenzaldehyde (**44**) and 4-acetamidobenzoic acid (**45**). The singlet-oxygen sensitizer, Rose Bengal, promotes the breakdown of the stilbene and increases the yield of 4-acetamidobenzaldehyde, whereas *β*-carotene, a known quencher of singlet oxygen, has the reverse effect. The proposed mechanism for fading involves attack by singlet oxygen on **41**, resulting in an unstable dioxetan intermediate (**43**) which then undergoes thermal or photochemical fission to give the aldehyde **44**. A similar photolytic pathway was proposed earlier[237] for the disulphonated derivative **38** (R = MeCONH—).

Although most commercial stilbene fluorescent whitening agents possess bulky substituents, which might be expected to suppress the photoisomerization reaction by restricting molecular rotation, the light-fading reactions of these more complex structures mirror those observed for simple model compounds[238,243–247] For example, *trans*-bis-4,4′-(4″-methoxy-6″-phenoxy-*s*-triazin-2″-ylamino)stilbene-2,2′-disulphonic acid (**46**) behaves in a very similar fashion to the diacetamidostilbene derivative **38** (R = MeCONH—). In both water and wool fabric it undergoes photoisomerization, followed by decomposition to the corresponding aldehyde, acid and dihydroderivative.[238,243,244] Adsorbed water greatly promotes the photodecomposition of **46** in wool by swelling



(46)

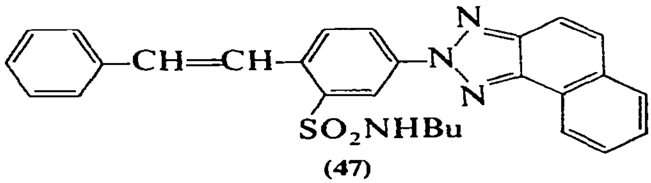
the fibre[245] and thus facilitating the photoisomerization reaction, which is the principal cause of fading.

The breakdown in sunlight of a related whitener, disodium 4,4′-bis[4-anilino-6-(*N*-methyl-*N*-2-hydroxyethyl)amino-*s*-triazin-2-ylamino]stilbene-2,2′-disulphonate, has been studied in connection with the biological degradation of fluorescent whitening agents in the environment.[246] The photochemical and biological degradation of the whitener follow similar reaction pathways.

The fading of some triazinylaminostilbenes in water can be retarded by the addition of a heavy-atom ion, such as iodide, which modifies the electronic relaxation processes in the fluorescent molecule through a spin-orbit coupling interaction.[248] Complex ions carrying phosphonic and carboxylic acid groups are also reported to retard the photodecomposition of 4,4′-diaminostilbenes in aqueous solution, without having any detrimental effect on the fluorescence properties.[249] Several Russian groups[250-252] have ranked commercial fluorescent whitening agents in order of increasing light stability, based on a consideration of their fading rates in water and in polyamide and polyester fibres.

Exposure to light brings about a dramatic decrease in the solubility of stilbene-based fluorescent whiteners in water, caused by photoisomerization of *trans*- to *cis*-isomers.[253] This differential solubility has been exploited in the preparation of pure *cis*-isomers of several bistriazinylaminostilbenes and a triazolylstilbene.[253]

The photochemistry of triazolylstilbene fluorescent whiteners has also been actively investigated in recent years.[254-257] Photolysis of *trans*-*N*-butyl-4-(2*H*-naphtho[1,2-*d*]triazolyl)stilbene-2-sulphonamide (47) in



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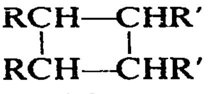
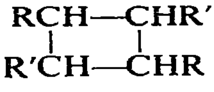
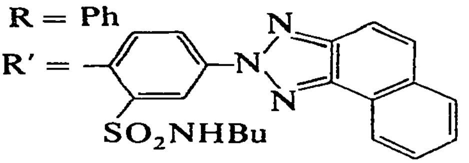


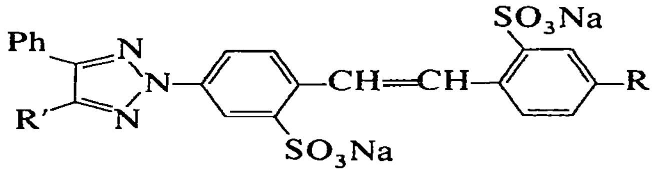
(48a)



(48b)



dioxan results in rapid isomerization to the *cis*-isomer, followed by dimerization to give the cyclobutane **48a** or **48b**; the stereochemistry of the dimer has not been established.[254–256] The *cis*-isomer is the major product obtained by photolysis of **47** in dioxane,[255] but the dimer predominates when polymer films containing **47** are exposed to light.[254] The dimer is highly fluorescent in dioxan solution, but polymer films containing both monomer and dimer exhibit only monomer fluorescence.[256] The absence of dimer fluorescence is due to long range energy transfer from the photoexcited dimer to a neighbouring molecule of monomer, which traps the absorbed energy and then re-emits this energy as normal monomer fluorescence.



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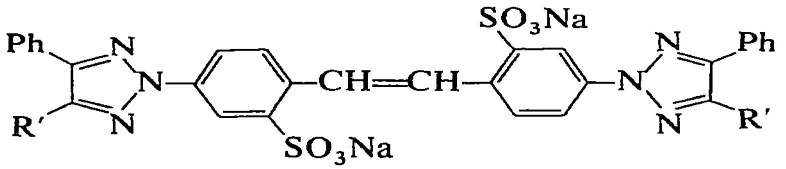
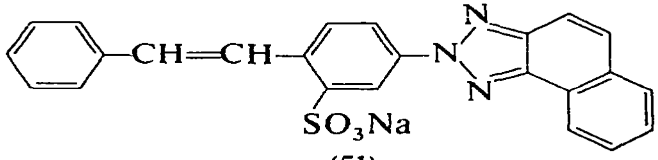


(50)

The rates of photoisomerization of *v*-triazol-2-ylstilbene disulphonates are reported[257] to depend on the symmetry of these molecules. The fluorescence and photostability of the unsymmetrical derivatives **49** (R = acetylamino, benzoylamino, phenylureido, 2,4-bis(2-hydroxyethylamino)-*s*-triazin-6-ylamino and 6-sulphonaphtho[1,2-*d*]triazol-2-yl) are generally inferior to those of the symmetrical *v*-triazolylstilbene whiteners **50** (R' = H, Me, Cl, SO_3Na) but superior to those of the corresponding symmetrical sulphonated R-substituted stilbenes.[257]

5.1.2. Photosensitizing effects in protein fibres

Another important aspect of the photochemistry of stilbene fluorescent whiteners is the photodegradative or sensitizing action of these compounds in protein fibres. Although fluorescent whiteners are frequently used to whiten wool and silk, they promote subsequent yellowing[258-261] and deterioration in tensile properties[260] during exposure to light. The histidine, tryptophan and methionine sidechains of wool proteins are selectively photo-oxidized on exposure of fibres containing naphthotriazolylstilbene or bistriazinylaminostilbene fluorescent whiteners.[261] Singlet oxygen is believed to be involved. The naphthotriazole derivative **51** does not bind in close proximity to tryptophan sidechains in wool,[245] yet it sensitizes the photo-oxidation of up to seven tryptophan residues before it is itself destroyed.[261] The overall photochemical changes, which are inhibited by sodium azide (a known quencher of singlet oxygen) follow the pattern of reactivity of singlet oxygen.

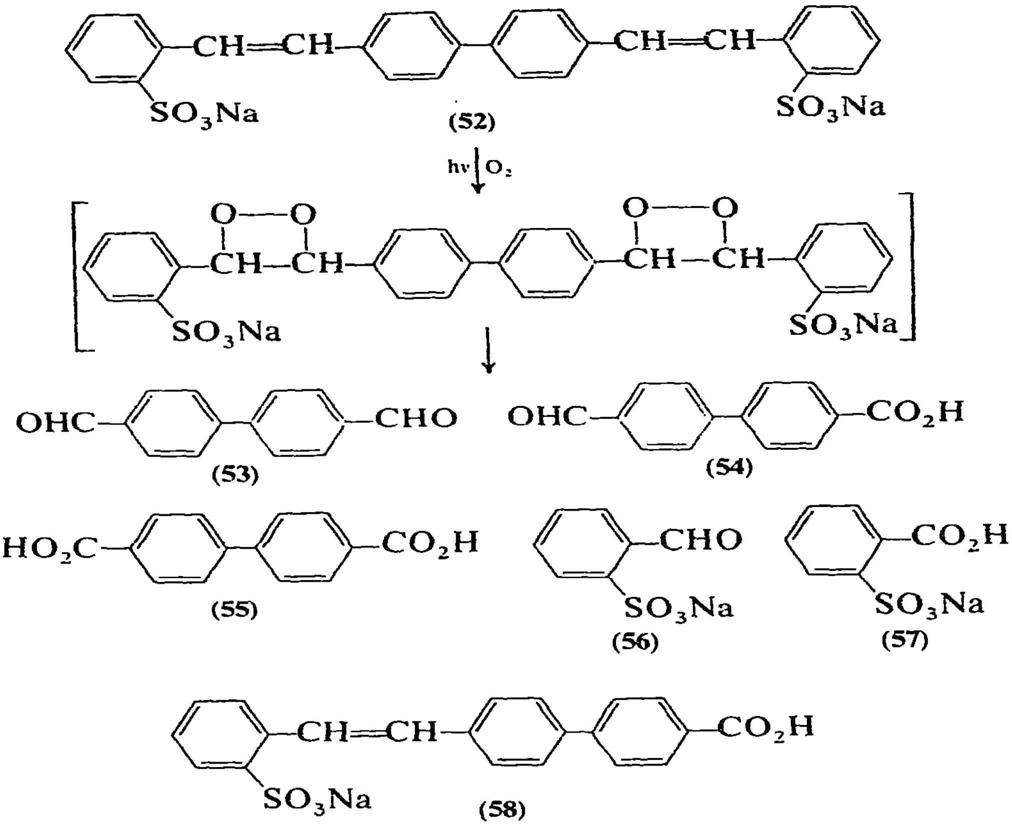


(51)

In some instances photodegradation products of the fluorescent whitener may be responsible for sensitizing the deterioration of whitened wool. Irradiation of the triazinylstilbene whitener **46** leads to formation of an aldehyde derivative[243] (see section 5.1.1), which promotes the photoyellowing of wool, especially in the presence of water.[258] Spectral studies on single wool fibres have confirmed that whitener decomposition and tryptophan photo-oxidation are not parallel processes, and that sensitized photo-oxidation can still occur after most of the whitener has been destroyed.[261] The oxidative processes that lead to yellowing can be retarded by immersing the whitened fabric in an aqueous solution of a reducing agent such as sodium sulphite, but this treatment does not affect the rate of photodecomposition of the whitener.[259]

5.2. Bis-styrylbiphenyls

Various physiochemical techniques have been employed[246] to study the photodecomposition of the bis-styrylbiphenyl fluorescent whitener **52**. Its



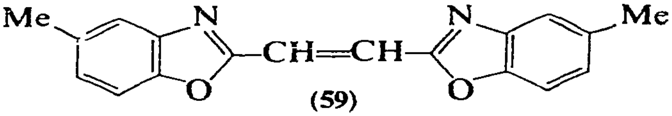
(52) (53) (54) (55) (56) (57) (58)

fluorescent *trans–trans* isomer initially isomerizes to give an equilibrium mixture of *cis–trans* and *cis–cis* isomers. Further irradiation gives a range of photo-oxidation products, possibly via a bis-dioxetane derivative; water-insoluble products (**53**–**55**) and water-soluble products (**56**–**58**) are formed.[246]

5.3. Bisbenzoxazolylethylenes

The main photochemical reactions of bisbenzoxazolylethylene whiteners are photodimerization to cyclobutane derivatives and photoisomerization. Interest in this topic has centred around the development of suitable kinetic schemes to describe the complex fading behaviour of these whiteners in solution and in polymer films.[262–266]

The rate of fading of the disperse-type whitener **59** in ethanol and in


(59)

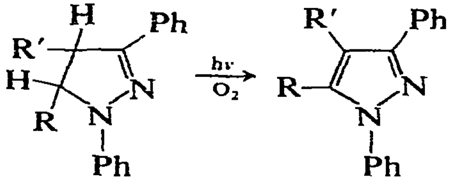
polyester films increases with increasing concentration,[265] and therefore the characteristic fading (CF) curves, which show the relationship between light stability and whitener concentration, have anomalous (negative) slopes. Two kinetic schemes have been considered for the fading of **59** in ethanol.[265] One is based on the premise that the isomerization and dimerization reactions proceed only via the singlet excited state. The second, more general scheme postulates that isomerization occurs via the singlet excited state and the lowest triplet state, while dimerization proceeds exclusively through the triplet state. The observed fading-rate curves and the CF curve for **59** in ethanol are in accord with the theoretical predictions of the second scheme.

A more sophisticated model has been developed to explain the anomalous fading behaviour of **59** in polymer films.[263,266] In this case the whitener molecules were assumed to be distributed randomly in 'holes' throughout the polymer film, in numbers according to the Poisson distribution. Fading can occur either by photoisomerization or photodimerization when two or more whitener molecules occupy a hole, but solely by isomerization if only one molecule is present. This model adequately explains the unusual shape of the CF curve for **59** in poly(ethylene terephthalate) films. A comparison of the theoretical and the observed fading behaviour at different temperatures has led to the unexpected finding that the number of holes in the film decreases as the temperature is raised, thus increasing the probability of dimerization.

Heat setting and dyeing treatments alter the physical state of the whitener **59** in poly(ethylene terephthalate), and affect its fading behaviour.[262,264] For example, there is a discontinuity in the relationship between fading rate and dyeing temperature at 130 °C for polyester films containing **59**. This observation is ascribed to a change in the fine structure of the polymer at this temperature, accompanied by a redistribution of the whitener.[264,266]

5.4. Pyrazolines

Because they are easy to synthesize, pyrazoline whiteners provide a good opportunity to investigate the relationships between structure, spectral



(60a–d) **(61a–d)**

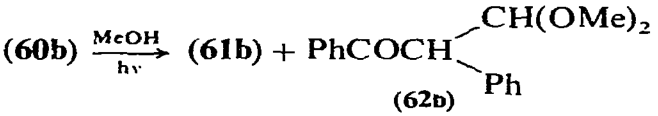
	R	R′
a	H	H
b	H	Ph
c	Ph	H
d	Ph	Ph

properties and photostability. The main reaction in both the direct[267,268] and the sensitized[269,270] photodecomposition of 1,3-diphenyl-2-pyrazoline (**60a**) is dehydrogenation to the corresponding pyrazole (**61a**). The reaction is strongly dependent on the nature of the substituents and on solvent polarity. Pyrazole yields range from 40 to 80 %. Several diagnostic tests have confirmed the intermediacy of singlet oxygen in the pyrazoline/pyrazole transformation,[268,269] but the precise mechanism of the reaction has yet to be established.

Numerous other products are formed during the photodecomposition of pyrazoline whiteners.[269] The *dye-sensitized* photo-oxidation of **60a** in methylene chloride yields the pyrazole **61a** in high yield (76 %), whereas *similar photooxidation in methanol gives a mixture containing the* pyrazole and β,β-dimethoxypropiophenone (**62a**). 1,3,4-Triphenyl-2-pyrazoline (**60b**) behaves similarly,[270] yielding a mixture of the pyrazole (**61b**) and benzoylphenylacetaldehyde dimethylacetal (**62b**) when photolysed in methanol but only the pyrazole in methylene chloride. In contrast, 1,3,5-triphenyl-2-pyrazoline (**60c**) yields only the pyrazole (**61c**) in methanol solution, and in methylene chloride it forms a red compound whose spectral properties are consistent with one of the four stereoisomers of structure **63**. Dye-sensitized photo-oxidation of 1,3,4,5-tetraphenyl-2-pyrazoline (**60d**) yields the corresponding pyrazole **61d**

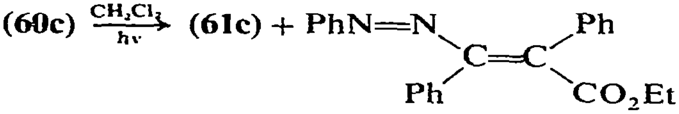
$$(\mathbf{60a}) \xrightarrow[h\nu]{\text{MeOH}} (\mathbf{61a}) + \text{PhCOCH}_2\text{CH(OMe)}_2$$

(62a)



$$(\mathbf{60b}) \xrightarrow[h\nu]{\text{MeOH}} (\mathbf{61b}) + \text{PhCOCH}\begin{matrix}\diagup\text{CH(OMe)}_2\\ \diagdown\text{Ph}\end{matrix}$$

(62b)

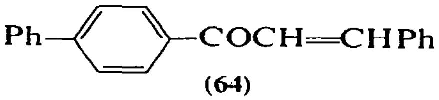


$$(\mathbf{60c}) \xrightarrow[h\nu]{\text{CH}_2\text{Cl}_2} (\mathbf{61c}) + \text{PhN{=}N(Ph)C{=}C(Ph)CO}_2\text{Et}$$

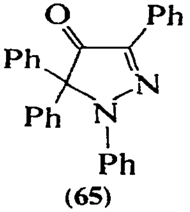
(63)

exclusively, whereas the 1,3,5,5-tetrasubstituted isomer undergoes a phenyl group migration to form 1,3,4,5-tetraphenylpyrazole (**61d**), and *N*,*N*′-dibenzoylphenylhydrazine.[270]

The major pathway in the photolysis of pyrazolines **60a–d** in the absence of a sensitizer is dehydrogenation[267,268] to the pyrazoles **61a–d**. Oxygen-containing products are also formed in small amounts, but they are different from the products from dye-sensitized photo-oxidation.[268] For example, a minor pathway in the photodecomposition of 1,3,5-triphenyl-2-pyrazoline (**60c**) in methanol is oxidation to the chalcone **64**. When photodehydrogenation is blocked by disubstitution at the 5-position, as in the case of 1,3,5,5-tetraphenyl-2-pyrazoline, photolysis results in a complex mixture of photoproducts containing biphenyl, benzophenone, benzoic acid and the orange ketone **65**.



(**64**)



(**65**)

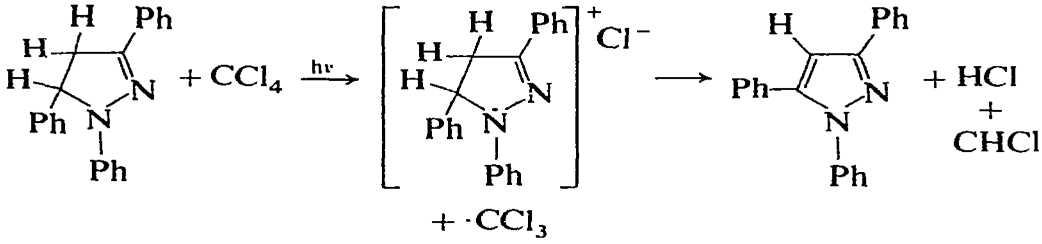
Steric factors play an important role in determining the fluorescence[271] and photochemical[268] properties of the above pyrazolines. The introduction of a phenyl group in either the 4- or the 5-position of 1,3-diphenyl-2-pyrazoline leads to increased photostability; 4-substitution is more effective than 5-substitution.[268] Disubstitution leads to a further improvement in stability, *trans*-1,3,4,5-tetraphenyl-2-pyrazoline being the most stable derivative (Table 2). The introduction of an imidazol-1-yl, pyrazol-1-yl or 1,2,4-triazol-1-yl substituent into the *para*-position of the 3-phenyl group of the pyrazoline molecule causes a large bathochromic shift in absorption and an increase in fluorescence yield (in methanol), but has little effect on photostability.[272] The main photoproduct of the triazolylphenyl-substituted pyrazoline is the pyrazole, although significant oxidation to the corresponding chalcone also occurs.

Pyrazoline photodecomposition is greatly accelerated in the presence of carbon tetrachloride or other halomethanes.[273,274] The principal reaction of 1,3,5-triphenyl-2-pyrazoline (**60c**) in solvents containing halomethanes is dehydrogenation to the pyrazole (**61c**). The quantum yield increases when chlorine-substituted methanes are replaced by

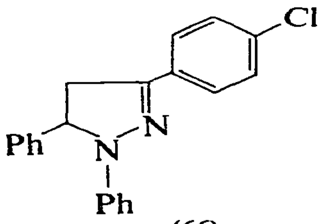
TABLE 2
Fluorescence Quantum Yields[271] and Photostability Data[268] for some 2-Pyrazoline Derivatives in Air-Saturated Solutions

2-Pyrazoline derivative	*Relative photostability*		*Fluorescence quantum yield*	
	Cyclohexane	*Methanol*	*Cyclohexane*	*Methanol*
1,3-Diphenyl	1·00	1·15	0·80	0·21
1,3,4-Triphenyl	2·18	4·85	0·78	0·22
1,3,5-Triphenyl	1·29	2·2	0·83	0·39
trans-1,3,4,5-Tetraphenyl	6·9	12·7	0·82	0·65
1,3,5,5-Tetraphenyl	6·0	5·8	0·19	0·37

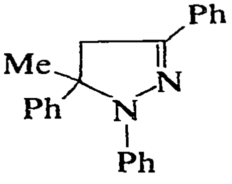
bromine-substituted methanes, and also when the number of halogen atoms in the molecule is increased (Table 3). The reaction pathway is believed to involve electron transfer from the singlet excited state of the pyrazoline molecule to the halomethane, which then undergoes dissociative electron attachment, resulting in rupture of the carbon-halogen bond:



Yamada *et al.* have extended their earlier investigation[275] of the interactions between pyrazolines and dyes.[276–278] Addition of either **66** or **67** to a methanol solution containing a triphenylmethane dye accelerates fading of the dye, while the dye quenches the fading reactions



(66)



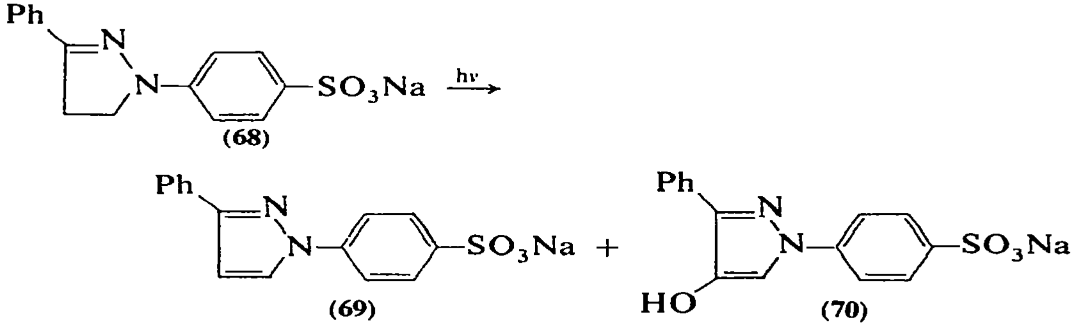
(67)

TABLE 3
Quantum Yields for the Photodegradation of 1,3,5-Triphenyl-2-Pyrazoline in Ethanol Containing Various Halomethanes[273]

Halomethane	*Halomethane concentration*		
	0·04 M	*0·25* M	*4·0* M
CBr_4	0·32	—	—
$CHBr_3$	0·19	—	—
CCl_4	0·08	0·2	—
CH_2Br_2	—	0·022	—
$CHCl_3$	—	0·001	0·02
CH_2Cl_2	—	—	0·001 3

of the whitener. Competitive inhibition experiments showed that the singlet oxygen quencher, 1,4-diazabicyclo[2.2.2]octane, did not interfere with the photosensitization reaction, and thus a mechanism involving singlet oxygen can be excluded. A kinetic analysis indicated that the pyrazolines promote the fading of dyes by a reaction involving nonradiative transfer of triplet excitation energy from the photoexcited pyrazoline molecule to the dye. The sensitization reaction occurs with a range of azo, triphenylmethane and anthraquinone dyes.[276–278]

The photochemistry of 2-pyrazolinesulphonic acids parallels that of the corresponding unsulphonated pyrazolines,[279–281] pyrazoles being the major photoproducts. Photolysis of **68** in aqueous solutions gives the pyrazole **69** in yields ranging from 25 to 85% depending upon the pH.[279–280] Small amounts of the 4-hydroxypyrazole are also formed. Yields of the pyrazole are increased by the addition of lysozyme, due to binding of the whitener to the protein.[280] The pyrazole **69** is also the



(68)

(69) **(70)**

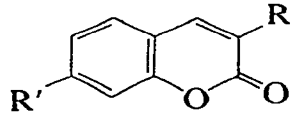
major product when poly(vinyl alcohol) films or wool fabrics containing **68** are exposed to light.[279]

The photochemical stability of **68** can be improved by attaching phenyl substituents to the 4- and 5-positions of the pyrazoline ring.[282] For example, the sulphonic acid derivative of 1,3,4,5-tetraphenyl-2-pyrazoline is twice as stable to light as the corresponding 1,3,5-triphenyl-2-pyrazoline, which in turn is 2·5 times more stable than the parent compound **68**. However, these modified fluorescent whitening agents offer no advantage for whitening wool fabric, because the improvement in lightfastness that results from increased photostability is offset by increased photoyellowing of the wool substrate, due to the longer lifetimes of the more stable whiteners.

Sulphonated 1,3,5-triphenyl-2-pyrazolines containing an imidazol-l-yl, pyrazol-l-yl or 1,2,4-triazol-l-yl substituent in the *para*-position of the 3-phenyl ring have been synthesized.[272] These compounds have excellent whitening properties on wool, but their lightfastness is no better than that of the unsubstituted sulphonic acid derivative.

5.5. Coumarins

Coumarins are well known for their propensity to dimerize under the influence of light. Exposure of 7-(2′,4′-di-*n*-butylamino-*s*-triazin-6′-ylamino)-3-phenylcoumarin (**71**) to light, either in solution or in polymer films, results in the formation of four dimers.[254,255] These correspond to the *syn*- and *anti*-isomers of the head-to-head dimer **72a** and the head-to-tail dimer **72b**. The dimers are non-fluorescent, but when exposed to wavelengths below 300 nm they rapidly dissociate to the fluorescent



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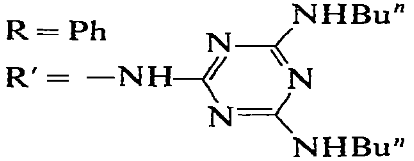
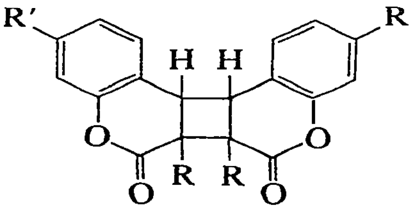
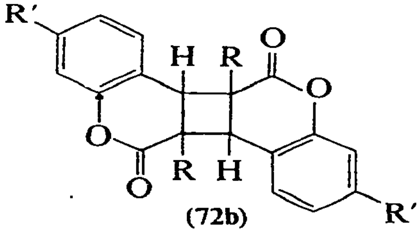




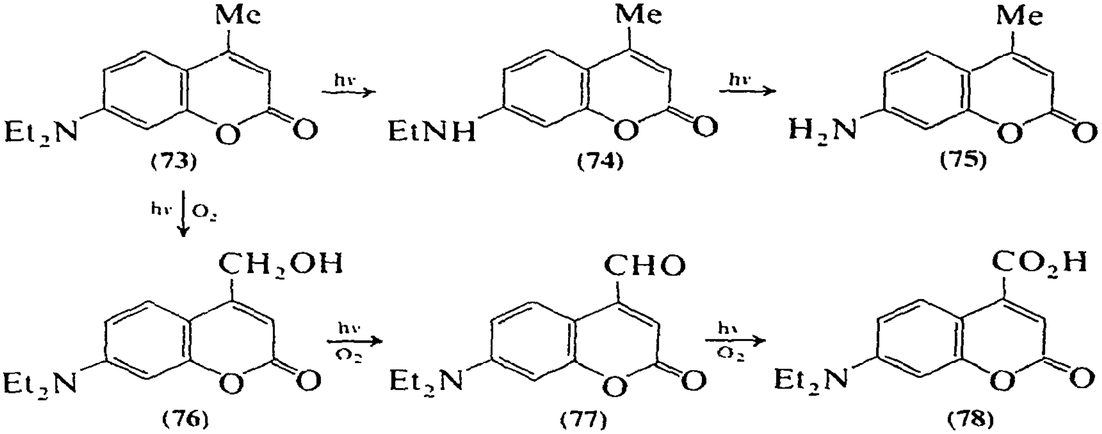
(72a)



(72b)

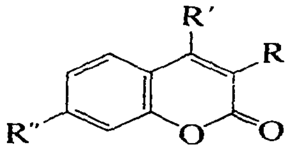
monomer (**71**). A minor photoproduct, which is formed on prolonged irradiation of **71**, has been identified[255] as the dealkylation product, 7-(2′-amino-4′-*n*-butylamino-*s*-triazin-6′-ylamino)-3-phenylcoumarin.

The use of coumarin derivatives in chemical dye lasers has prompted several workers to investigate the photochemical processes that inhibit laser action.[283–285] The breakdown of 7-diethylamino-4-methylcoumarin (**73**) in ethanol occurs via two different reaction pathways[283] Dealkylation is the main pathway: this reaction is independent of the presence of oxygen, and leads eventually to the formation of 7-amino-4-methylcoumarin (**75**), via the monoethylamino compound **74**.



The second pathway involves oxidation of the methyl group, the main products being the alcohol **76**, the aldehyde **77** and the carboxylic acid **78**. The acid was identified as the chief inhibitor of laser action. The primary photochemical reactions of another laser dye, 7-hydroxy-4-methylcoumarin, have been investigated by gain spectroscopy[284] and flash photolysis[285] techniques.

The photostability of the 7-aminocoumarin whiteners **79a–d** is strongly dependent on their environment,[286] being much higher in plastic



(79a–d)

	R	R′	R″
a	H	Me	NEt$_2$
b	Ph	H	NH$_2$
c	Ph	H	NHCO$_2$Et
d	Ph	H	NHX

X =

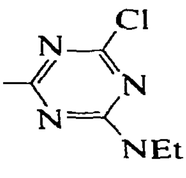


TABLE 4

Fading Rates ($\times 10^4$ min^{-1}) of 7-Aminocoumarins in Solutions and in Polymers[286]

Compound	*Solution*			*Polymer*[a]					
	Cyclohexane	*Ethanol*	*Ethylene chloride*	*PE*	*PC*	*PMMA*	*HIPS*	*ABS*	*PS*
79a	250	30	3 600	23	16	3	8	14	6
79b	221	100	520	11	7	<1	4	3	3
79c	33	23	64	10	9	1	5	6	3
79d	63	20	67	6	10	2	6	7	4

[a] PE, polyethylene; PC, polycarbonate; PMMA, poly(methyl methacrylate); HIPS, high density polystyrene; ABS, acrylonitrile/butadiene/styrene copolymer; PS, polystyrene.

materials than in fluid solutions. The light stability is generally poorer in polyethylene than in more polar polymers. The fading rates in solution do not correlate well with those in polymers when wavelengths <350 nm are present in the light source (Table 4), but a better correlation is observed when wavelengths <350 nm are excluded. This effect is attributed to the competitive light screening action of some polymers.

REFERENCES

1. D. Barton and H. Davidson, *Rev. Prog. Color. Rel. Topics*, 5, 3 (1974).
2. F. Coulston and F. Korte (eds.), *Environmental quality and safety*, Suppl. Vol. IV: *Fluorescent whitening agents*. Stuttgart, Thieme (1975).
3. E. Siegel, *Int. Rev. Sci.: Org. Chem.*, Ser. 2, ed. H. Zollinger, p. 259. London, Butterworths (1976).
4. E. A. Kleinheidt and H. Theidel, *Handb. Textilhilfsmittel*, eds. A. Chwala, V. Anger and C. Chwala, p. 645. Weinheim, Verlag Chemie (1977).
5. R. Zweidler and H. Hefti, *Kirk-Othmer encycl. chem. technol.*, 3rd edn., vol. 4, p. 213 (1978).
6. R. Williamson, *Textile science and technology*, Vol. 4: *Fluorescent whitening agents*. Amsterdam, Elsevier (1980).
7. N. A. Evans, in *Photochemistry of dyed and pigmented polymers*, ed. N. S. Allen and J. F. McKellar, p. 93. London, Applied Science (1980).
8. Y. Hashida and K. Matsui, *Senryo To Yakuhin*, **25**, 128 (1980).
9. A. E. Siegrist, *J. Am. Oil Chem. Soc.*, **55**, 114 (1978).
10. P. S. Stensby, *Surfactant Sci. Ser.*, **5** (Deterg.: Theory Test Methods, Pt 3), 729 (1981).

11. A. Dorlas, C. W. Schellhammer and J. Schroeder, *Angew. Chem.*, **87**, 693 (1975).
12. Ciba-Geigy, German Offen. 2848193 (1979); *C.A.*, **91**, 75723.
13. Ciba-Geigy, German Offen. 2848149 (1979); *C.A.*, **91**, 92996.
14. Ciba-Geigy, German Offen. 2756883 (1978); *C.A.*, **89**, 131049.
15. Ciba-Geigy, Japan. Kokai 80 152748 (1980); *C.A.*, **95**, 44743.
16. Bayer, German Offen. 3003540 (1981); *C.A.*, **95**, 188642.
17. Bayer, German Offen. 2650456 (1978); *C.A.*, **89**, 112426.
18. Bayer, German Offen. 2730644 (1979); *C.A.*, **90**, 153494.
19. Ciba-Geigy, German Offen. 2750575 (1978); *C.A.*, **90**, 40210.
20. Ciba-Geigy,German Offen. 2525681 (1974); *C.A.*, **84**, 91663.
21. Sandoz, Swiss Patent 555848 (1974); *C.A.*, **83**, 116985.
22. Ciba-Geigy,German Offen. 2535613 (1976); *C.A.*, **84**, 181616.
23. Ciba-Geigy, German Offen. 2525684 (1976); *C.A.*, **84**, 91666.
24. Ciba-Geigy, Swiss Patent 561746 (1975); *C.A.*, **83**, 195245.
25. Ciba-Geigy, British Patent 1418572 (1975); *C.A.*, **84**, 152230.
26. Ciba-Geigy, Swiss Patent 612817 (1980); *C.A.*, **93**, 27738.
27. Nippon Chem., Japan. Kokai 74 30868 (1974); *C.A.*, **83**, 61740.
28. Eastman Kodak, Canadian Patent 967569 (1975); *C.A.*, **83**, 99225.
29. Hoechst, German Offen. 2709924 (1977); *C.A.*, **88**, 24258.
30. Hoechst, German Offen. 2820322 (1979); *C.A.*, **92**, 130618.
31. Hoechst, German Offen. 2712942 (1977); *C.A.*, **90**, 40211.
32. Eastman Kodak, US Patent 3873531 (1975); *C.A.*, **83**, 12226.
33. Ciba-Geigy, German Offen. 2750576 (1978); *C.A.*, **90**, 7598.
34. Osaka Seika Chem., Japan. Kokai 75 22051 (1975); *C.A.*, **84**, 91660.
35. Hoechst, Eur. Patent Appl. 2042 (1979); *C.A.*, **92**, 60336.
36. Nippon Chem., Japan. Kokai 75 118084 (1975); *C.A.*, **84**, 19196.
37. Osaka Seika Chem., US Patent 3840528 (1974); *C.A.*, **83**, 195244.
38. Mitsui Toatsu, Japan. Kokai 77 66531 (1977); *C.A.*, **88**, 24257.
39. Mitsui Toatsu, Japan. Kokai 77 68229 (1977); *C.A.*, **87**, 186085.
40. Ciba-Geigy,German Offen. 2712409 (1977); *C.A.*, **88**, 51973.
41. Ciba-Geigy, German Offen. 2724408 (1977); *C.A.*, **88**, 192759.
42. Ciba-Geigy, German Offen. 2816511 (1978); *C.A.*, **90**, 73310.
43. Mitsui Toatsu Chem., Japan. Kokai 76 81826 (1976); *C.A.*, **85**, 110109.
44. Mitsui Toatsu Chem., Japan. Kokai 75 126743 (1975); *C.A.*, **84**, 32606.
45. Ciba-Geigy, German Offen. 2750577 (1978); *C.A.*, **90**, 24794.
46. A. E. Siegrist, G. Kormany, G. Kabas and H. Schlaepfer, *Helv. Chim. Acta*, **60**, 2334 (1977).
47. Ciba-Geigy, German Offen. 2535615 (1976); *C.A.*, **84**, 166274.
48. Ciba-Geigy, German Offen. 2535614 (1976); *C.A.*, 181618.
49. Hoechst, German Offen. 2540236 (1976); *C.A.*, **85**, 48288.
50. A. E. Siegrist, G. Kormany and G. Kabas, *Helv. Chim. Acta*, **59**, 2469 (1976).
51. Ciba-Geigy, German Offen. 2535612 (1976); *C.A.*, **84**, 181617.
52. Ciba-Geigy, Swiss Patent 596299 (1978); *C.A.*, **89**, 131075.
53. Ciba-Geigy, Swiss Patent 618058 (1981); *C.A.*, **95**, 99341.

54. Ciba–Geigy, German Offen. 2539461 (1976); *C.A.*, **85**, 110108.
55. Ciba–Geigy, German Offen. 2539537 (1976); *C.A.*, **85**, 48287.
56. Ciba–Geigy, German Offen. 2525682 (1976); *C.A.*, **84**, 75717.
57. Sandoz, Swiss Patent 562812 (1975); *C.A.*, **83**, 133399.
58. Bayer, German Offen 2842686 (1980); *C.A.*, **93**, 73787.
59. German Offen. 2917619 (1980); *C.A.*, **94**, 85675.
60. Hoechst, US Patent 4039531 (1977); *C.A.*, **87**, 186088.
61. Hoechst, Swiss Patent 615164 (1980); *C.A.*, **93**, 73786.
62. Sandoz, German Offen. 2535069 (1976); *C.A.*, **84**, 181615.
63. Sandoz, Swiss Patent 562228 (1975); *C.A.*, **83**, 99223.
64. Sandoz, Swiss Patent 561708 (1975); *C.A.*, **83**, 99222.
65. Sandoz, Swiss Patent 566326 (1975); *C.A.*, **83**, 195247.
66. Hoechst, German Offen. 2524677 (1976); *C.A.*, **84**, 91665.
67. Ciba–Geigy, Swiss Patent 557917 (1975); *C.A.*, **83**, 29887.
68. Sandoz, British Patent 1550440 (1979); *C.A.*, **92**, 199758.
69. Hoechst, German Offen. 2833470 (1980); *C.A.*, **92**, 199760.
70. Ciba–Geigy, German Offen. 2525637 (1976); *C.A.*, **84**, 91667.
71. Eastman Kodak, US Patent 4095939 (1978); *C.A.*, **89**, 164945.
72. Ciba–Geigy, Swiss Patent 577535 (1976); *C.A.*, **85**, 125806.
73. Ciba–Geigy, Swiss Patent 577536 (1976); *C.A.*, **85**, 125807.
74. Nippon Kayaku, Japan. Kokai 76 11835 (1976); *C.A.*, **84**, 181614.
75. A. DeBuman and A. E. Siegrist, *Helv. Chim. Acta*, **57**, 1352 (1974).
76. Sterling Drug, US Patent 3993645 (1976); *C.A.*, **86**, 56762.
77. Ciba–Geigy, German Offen. 2525683 (1976); *C.A.*, **84**, 123420.
78. Sterling Drug, US Patent 3932301 (1976); *C.A.*, **84**, 123423.
79. Sterling Drug, German Offen. 2454855 (1975); *C.A.*, **83**, 116990.
80. Sterling Drug, US Patent 3935195 (1976); *C.A.*, **84**, 123424.
81. Showa Chem., Japan. Kokai 77 78235 (1977); *C.A.*, **87**, 186087.
82. Sandoz, French Demande 2235935 (1975); *C.A.*, **83**, 116991.
83. Sumitomo Chem., Japan. Kokai 75 154325 (1975); *C.A.*, **84**, 123422.
84. Ciba–Geigy, German Offen. 2443577 (1975); *C.A.*, **83**, 44736.
85. Hoechst, German Offen. 2325582 (1974); *C.A.*, **83**, 61741.
86. Ciba–Geigy, German Offen. 2828852 (1979); *C.A.*, **90**, 153495.
87. M. Tanaka, S. Sakuma, S. Sekiguchi and K. Matsui, *Nippon Kagaku Kaishi*, 885 (1975).
88. Showa Chem., Japan. Kokai 78 102329 (1978); *C.A.*, **90**, 7599.
89. Showa Chem., German Offen. 2721730 (1977); *C.A.*, **88**, 91057.
90. Bayer, German Offen. 2901480 (1980); *C.A.*, **94**, 85673.
91. Ciba–Geigy, Eur. Patent Appl. 14177 (1980); *C.A.*, **93**, 241198.
92. BASF, German Offen. 3001065 (1981); *C.A.*, **95**, 117072.
93. Bayer, German Offen. 2807497); *C.A.*, **92**, 60335.
94. Ciba–Geigy, German Offen. 2730246 (1978); *C.A.*, **88**, 122673.
95. Ciba–Geigy, Eur. Patent Appl. 30917 (1981); *C.A.*, **95**, 117073.
96. Ciba–Geigy, Swiss Patent 580193 (1976); *C.A.*, **85**, 194101.
97. Ciba–Geigy, Swiss Patent 568349 (1975); *C.A.*, **84**, 46062.
98. Ciba–Geigy, Swiss Patent 560736 (1975); *C.A.*, **83**, 61745.

99. Ciba–Geigy, Swiss Patent 558768 (1975); *C.A.*, **83**, 195243.
100. Ciba–Geigy, Swiss Patent 566420 (1975); *C.A.*, **83**, 195246.
101. Ciba–Geigy, Swiss Patent 580702 (1976); *C.A.*, **86**, 18375.
102. Mitsubishi, Japan. Kokai 74 50020 (1974); *C.A.*, **83**, 61734.
103. Ciba–Geigy, Swiss Patent 567607 (1975); *C.A.*, **84**, 46063.
104. Ciba–Geigy, US Patent 4013713 (1977); *C.A.*, **86**, 173082.
105. Ciba–Geigy, Eur. Patent Appl. 1991 (1979); *C.A.*, **92**, 7841.
106. Sandoz, German Offen. 2602750 (1976); *C.A.*, **85**, 161886.
107. Ciba–Geigy, German Offen. 2525679 (1976); *C.A.*, **84**, 123421.
108. Nippon Kayaku, German Offen. 2535102 (1976); *C.A.*, **85**, 22780.
109. Bayer, German Offen. 2636090 (1978); *C.A.*, **88**, 192760.
110. Hoechst, Japan. Kokai 77 137431 (1977); *C.A.*, **89**, 112425.
111. Hoechst, German Offen. 2621169 (1977); *C.A.*, **88**, 75314.
112. Hoechst, German Offen. 2750947 (1979); *C.A.*, **91**, 92995.
113. Sandoz, US Patent 3940410 (1976); *C.A.*, **84**, 166273.
114. Hoechst, German Offen. 2526230 (1976); *C.A.*, **86**, 91756.
115. Sandoz, Swiss Patent 559737 (1975); *C.A.*, **83**, 44735.
116. Ciba–Geigy, US Patent 3993659 (1976); *C.A.*, **86**, 56761.
117. Sandoz, Swiss Patent 560206 (1975); *C.A.*, **83**, 61744.
118. Sandoz, Swiss Patent 554891 (1974); *C.A.*, **83**, 61738.
119. Sandoz, German Offen. 2442887 (1975); *C.A.*, **83**, 81240.
120. Nippon Chem., Japan. Kokai 76 12841; *C.A.*, **84**, 152232.
121. Sumitomo, Japan. Kokai 74 133418 (1974); *C.A.*, **83**, 12225.
122. Ciba–Geigy, German Offen. 2733156 (1978); *C.A.*, **89**, 61044.
123. Hoechst, German Offen. 2715567 (1978); *C.A.*, **90**, 205795.
124. Bayer, German Offen. 2852531 (1980); *C.A.*, **93**, 221923.
125. Bayer, German Offen. 2821116 (1979); *C.A.*, **92**, 130616.
126. Ciba–Geigy, German Offen. 2807008 (1978); *C.A.*, **90**, 7597.
127. Sandoz, German Offen 2733439 (1978); *C.A.*, **89**, 7601.
128. Sandoz, German Offen. 2522139 (1975); *C.A.*, **84**, 91661.
129. Ciba–Geigy, Swiss Patent 593967 (1977); *C.A.*, **88**, 137906.
130. Ciba–Geigy, Swiss Patent 560277 (1975); *C.A.*, **83**, 81239.
131. Ciba–Geigy, US Patent 4009994 (1977); *C.A.*, **86**, 173081.
132. Ciba–Geigy, German Offen. 2946481 (1980); *C.A.*, **93**, 151666.
133. Sandoz, Swiss Patent 602660 (1978); *C.A.*, **89**, 164943.
134. Sandoz, Swiss Patent 609977 (1979); *C.A.*, **91**, 6411.
135. Bayer, German Offen. 2700996 (1978); *C.A.*, **90**, 73309.
136. Ciba–Geigy, German Offen. 2827749 (1979); *C.A.*, **90**, 170168.
137. BASF, German Offen. 2534180 (1977); *C.A.*, **86**, 157057.
138. Sandoz, German Offen. 2434162 (1975); *C.A.*, **83**, 61742.
139. BASF, German Offen. 2560051 (1980); *C.A.*, **94**, 85674.
140. Ciba–Geigy, German Offen. 2441158 (1975); *C.A.*, **83**, 29889.
141. Sandoz, German Offen. 2516053 (1976); *C.A.*, **84**, 137231.
142. Sandoz, German Offen. 2524927 (1976); *C.A.*, **84**, 91664.
143. Sandoz, German Offen. 2534185 (1976); *C.A.*, **84**, 166271.
144. Minnesota Mining, US Patent 3883549 (1975); *C.A.*, **83**, 81243.

145. Ciba–Geigy, German Offen. 2441226 (1975); *C.A.*, **83**, 61743.
146. Ugine Kuhlmann, US Patent 3852275 (1974); *C.A.*, **83**, 29890.
147. Sandoz, German Offen. 2502434 (1975); *C.A.*, **83**, 149113.
148. Bayer, German Offen. 2352245 (1975); *C.A.*, **83**, 81242.
149 Bayer, German Offen. 2310446 (1974); *C.A.*, **83**, 61737.
150. Ciba–Geigy, US Patent 3796706 (1974); *C.A.*, **83**, 61730.
151. G. P. Tokmakova, Y. M. Udachin, N. S. Patalakha, L. K. Denisov, A. M. Lantsov and I. I. Granberg, *Khim. Geterotsikl. Soedin.*, 79 (1980).
152. BASF, German Offen. 2753152 (1979); *C.A.*, **91**, 109009.
153. Mitsubishi, Japan. Kokai 77 31465 (1977); *C.A.*, **88**, 51974.
154. Sumitomo, Japan. Kokai 74 26584 (1974); *C.A.*, **83**, 61731.
155. BASF, German Offen. 2443664 (1976); *C.A.*, **85**, 22781.
156. BASF, German Offen. 2331307 (1975); *C.A.*, **83**, 12224.
157. BASF, German Offen. 2507459 (1976); *C.A.*, **86**, 44770.
158. Nippon Kayaku, Japan. Kokai 77 04680 (1977); *C.A.*, **88**, 63270.
159. BASF, German Offen. 2641001 (1978); *C.A.*, **89**, 181226.
160. Hoechst, German Offen. 2944867 (1981); *C.A.*, **95**, 82398.
161. BASF, German Offen. 4139532 (1979); *C.A.*, **90**, 205796.
162. BASF, German Offen. 2639649 (1978); *C.A.*, **89**, 7596.
163. Sumitomo, Japan. Kokai 74 59844 (1974); *C.A.*, **83**, 61735.
164. Z. Jankowski and R. Stolarski, Polish Patent 78458 (1975); *C.A.*, **86**, 74420; Polish Patent 96977 (1978); *C.A.*, **90**, 153493.
165. Z. Jankowski and R. Stolarski, Polish Patent 107741 (1980); *C.A.*, **95**, 82397.
166. Sumitomo, Japan. Kokai 74 54452 (1974); *C.A.*, **83**, 61733.
167. Nippon Kayaku, Japan. Kokai 74 43688 (1974); *C.A.*, **83**, 116986.
168. Ciba–Geigy, German Offen. 2712408 (1977); *C.A.*, **88**, 51972.
169. Bayer, German Offen. 2816028 (1979); *C.A.*, **92**, 78110.
170. Kanegafuchi. Japan. Kokai 78 134926 (1978); *C.A.*, **90**, 188431.
171. Ciba–Geigy, German Offen. 2712496 (1977); *C.A.*, **88**, 38962.
172. Bayer, German Offen. 2704825 (1978); *C.A.*, **89**, 164944.
173. Ciba–Geigy, Japan. Kokai 76 36369 (1976); *C.A.*, **86**, 107946.
174. Bayer, German Offen. 4005098 (1977); *C.A.*, **86**, 122955.
175. Ciba–Geigy, Swiss Patent 580192 (1976); *C.A.*, **85**, 194102.
175a. K. U. Joseph and V. V. Somayajulu, *J. Indian Chem. Soc.*, **56**, 505 (1979).
176. Ugine Kuhlmann, German Offen. 2503439 (1975); *C.A.*, **83**, 165830.
177. Daito Chem., Japan. Kokai 74 61482 (1974); *C.A.*, **83**, 133396.
178. BASF, German Offen. 2659698 (1978); *C.A.*, **89**, 112430.
179. Ciba–Geigy, German Offen. 2450258 (1975); *C.A.*, **84**, 32603.
180. Showa Chem., Japan. Kokai 75 05681 (1975); *C.A.*, **83**, 81237.
181. Showa Chem., Japan. Kokai 75 20079 (1975); *C.A.*, **83**, 81238.
182. Ciba–Geigy, German Offen. 2839595 (1979); *C.A.*, **91**, 6410.
183. Bayer, German Offen. 2306515 (1974); *C.A.*, **83**, 61729.
184. Hoechst, German Offen. 2937231 (1981); *C.A.*, **95**, 8818.
185. Nippon Kayaku, Japan. Kokai 75 40627 (1975); *C.A.*, **83**, 116988.
186. Hoechst, German Offen. 2509514 (1976); *C.A.*, **86**, 31016.

187. Hoechst, German Offen. 2361338 (1974); *C.A.*, **83**, 61728.
188. Ciba-Geigy, German Offen. 2749902 (1978); *C.A.*, **89**, 112428.
189. Hoechst, German Offen. 2363416 (1975); *C.A.*, **83**, 116992.
190. Hoechst, German Offen. 2636424 (1978); *C.A.*, **89**, 199094.
191. Albright and Wilson, Australian Patent 465496 (1975); *C.A.*, **84**, 32605.
192. Du Pont, US Patent 3959277 (1976); *C.A.*, **85**, 144717.
193. Ciba-Geigy, Swiss Patent 576502 (1976); *C.A.*, **85**, 79700.
194. Ciba-Geigy, German Offen. 2525680 (1976); *C.A.*, **84**, 91662.
195. Hoechst, German Offen. 2320528 (1974); *C.A.*, **83**, 61739.
196. Ciba-Geigy, Swiss Patent 615165 (1980); *C.A.*, **93**, 8181.
197. Ciba-Geigy, Swiss Patent 615166 (1980); *C.A.*, **93**, 8179.
198. Ciba-Geigy, Swiss Patent 615167 (1980); *C.A.*, **93**, 8180.
199. R. Williamson, *Int. Dyer. Text. Printer*, **157**, 359, 408 (1977).
200. G. Roesch, *Tinctoria*, **72**, 260 (1975).
201. W. Guth, *Melliand Textilber.*, **61**, 715 (1980).
202. R. Levene and S. Magrizo, *Text. Res. J.*, **51**, 559 (1981).
203. I. Soljacic and R. Cunko, *Melliand Textilber., Eng. Edn.*, **8**, 1032 (1979).
204. A. M. Grancaric and I. Soljacic, *Melliand Textilber.*, **62**, 876 (1981).
205. W. Schuerings, *Textilveredlung*, **15**, 236 (1980).
206. B. Milligan, *Proc. Int. Wool Text. Res. Conf., Pretoria*, **V**, 167 (1980).
207. S. Imai and T. Hanyu, Japan. Kokai 75 155783 (1975); *C.A.*, **84**, 152108.
208. S. Imai and T. Hanyu, Japan. Kokai 75 155782 (1975); *C.A.*, **84**, 166187.
209. L. A. Holt and B. Milligan, *J. Text. Inst.*, **71**, 117 (1980).
210. L. A. Holt, B. Milligan and L. J. Wolfram, *Text. Res. J.*, **45**, 257 (1975).
211. S. Hidaka, *Senshoku to Kako*, **24**, 5 (1981).
212. M. Minagawa and Y. Yoshida, *Osaka-shiritsu Daigaku Seikatsukagakubu Kiyo*, **27**, 91 (1979).
213. Monsanto, US Patent 4126412 (1978); *C.A.*, **90**, 88687.
214. Ciba-Geigy, US Patent 4008166 (1977); *C.A.*, **90**, 56268.
215. Hoechst, German Offen. 2721084 (1978); *C.A.*, **90**, 88686.
216. Hoechst, German Offen. 2839936 (1980); *C.A.*, **93**, 151588.
217. Hoechst, German Offen. 2629703 (1978); *C.A.*, **88**, 137844.
218. BASF, German Offen. 3001066 (1981); *C.A.*, **95**, 152101.
219. Hoechst, German Offen. 2929591 (1981); *C.A.*, **94**, 210216.
220. Ciba-Geigy, German Offen. 2441102 (1975); *C.A.*, **83**, 29774.
221. Nippon Kayaku, Japan. Kokai 75 25876 (1975); *C.A.*, **83**, 116788.
222. Mitsui Toatsu, Japan. Kokai 76 07026 (1976); *C.A.*, **84**, 181527.
223. Nippon Chem., Japan. Kokai 75 102621 (1975); *C.A.*, **84**, 19072.
224. M. Baltorowicz, E. Higersberger, J. Rzescowski, B. Graczyk, M. Bielski, L. Michalczyk and B. Lakowska, German Offen. 2524801 (1975); *C.A.*, **84**, 75716.
225. H. Bloching, W. Holtmann and M. Otten, *Seifen, Oele, Fette, Wachse*, **105**, 33 (1979).
226. T. Ano, Y. Ohno and K. Kitamori, *Sen'i Seihin Shohi Kagaku*, **18**, 335, 468 (1977).
227. A. Abe and H. Yoshimi, *Water Res.*, **13**, 1111 (1979).

228. H. Theidel, in *Environmental quality and safety*, Suppl. Vol. IV: *Fluorescent whitening agents*, eds. F. Coulston and F. Korte, p. 94. Stuttgart, Thieme (1975).
229. A. J. Mehta, R. K. Shah, A. S. Divetia and S. S. Trivedi, *Colourage*, **25**, 29 (1978).
230. G. Anders, in *Environmental quality and safety*, Suppl. Vol. IV: *Fluorescent whitening agents*, eds. F. Coulston and F. Korte, p. 104. Stuttgart, Thieme (1975).
231. H. Theidel, in *Environmental quality and safety*, Suppl. Vol. IV: *Fluorescent whitening agents*, eds. F. Coulston and F. Korte. p. 111. Stuttgart, Thieme (1975).
232. D. Kirkpatrick, *J. Chromatogr.*, **121**, 153 (1976); **139**, 168 (1977).
233. B. P. McPherson and N. Omelczenko, *J. Am. Oil Chem. Soc.*, **57**, 388 (1980).
234. A. Nakae, M. Morita and M. Yamanaka, *Bunseki Kagaku*, **29**, 69 (1980).
235. I. A. Pinigina and A. Kh. Galuzinskaya, *Gig. Sanit.*, (2) 88 (1976).
236. B. S. Assoldekar and V. A. Kamath, *Text. Dyer Printer*, **10**, 37 (1977).
237. R. P. Seiber and H. L. Needles, *J. Chem. Soc., Chem. Commun.*, 209 (1972).
238. L. A. Holt and B. Milligan, *Text. Res. J.*, **44**, 181 (1974).
239. H. L. Needles and R. P. Seiber, *Text. Res. J.*, **44**, 183 (1974).
240. Y. Yamashita and K. Yoshida, *Yuki Gosei Kagaku Kyokaishi*, **36**, 322 (1978).
241. K. Yoshida and Y. Yamashita, *Yuki Gosei Kagaku Kyokaishi*, **36**, 406 (1978).
242. H. Oda, N. Kuramoto and T. Kitao, *J. Soc. Dyers Colour.*, **97**,462 (1981).
243. B. Milligan and L. A. Holt, *Aust. J. Chem.*, **27**, 195 (1974).
244. L. A. Holt and B. Milligan, *Aust. J. Chem.*, **27**, 23 (1974).
245. I. H. Leaver, *Austr. J. Chem.*, **30**, 87 (1977).
246. L. Guglielmetti, *Environmental quality and safety*, Suppl. Vol. IV: *Fluorescent whitening agents*, eds. F. Coulston and F. Korte, p. 180. Stuttgart, Thieme (1975).
247. Y. Yamashita and K. Yoshida, *Kochi Daigaku Gakujutsu Kenkyu Hokoku, Shizen Kagaku*, **28**, 33 (1979).
248. T. V. Proskuryakova, O. P. Studzinskii and Yu. A. Makashev, *Zh. Obshch. Khim.*, **51**, 715 (1981).
249. O. P. Studzinskii, N. M. Dyatlova and Yu. A. Makashev, *Zh. Prikl. Khim. (Leningrad)*, **54**, 1823 (1981).
250. I. N. Bykova, A. B. Pakshver and L. I. Belen'kii, *Zh. Prikl. Khim. (Leningrad)*, **52**, 378 (1979).
251. O. P. Studzinskii and V. M. Grebenkina, *Zh. Prikl. Spectrosk.*, **33**, 1117 (1980).
252. O. P. Studzinskii, Yu. A. Makashev, V. F. Evdokimov and Y. N. Seleznev, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **24**, 723 (1981).
253. W. T. Weller, *J. Soc. Dyers Colour.*, **95**, 187 (1979).
254. L. A. Holt, I. H. Leaver and B. Milligan, *Text. Res. J.*, **46**, 539 (1976).

255. B. Milligan, L. A. Holt and I. H. Leaver, *Proc. Int. Wool Textile Res. Conf., Aachen*, **III**, 607 (1975) (Pub. 1976).
256. I. H. Leaver, B. Milligan and L. A. Holt, *Aust. J. Chem.*, **29**, 437 (1976).
257. Y. Yamashita and K. Yoshida, *Yuki Gosei Kagaku Kyokaishi*, **35**, 285 (1977).
258. L. A. Holt and B. Milligan, *Text. Res. J.*, **44**, 452 (1974).
259. L. A. Holt, B. Milligan and L. J. Wolfram, *Text. Res. J.*, **44**, 846 (1974).
260. H. L. Needles, *Text. Res. J.*, **46**, 39 (1976).
261. I. H. Leaver, *Photochem. Photobiol.*, **27**, 451 (1978).
262. K. Suganuma, *Text. Res. J.*, **47**, 361 (1977).
263. M. Hida, *Senshoku Kenkyu*, **23**, 16 (1979).
264. K. Suganuma, M. Hida and A. Yabe, *Sen'i Gakkaishi*, **35**, T388 (1979).
265. M. Hida and A. Yabe, *Sen'i Gakkaishi*, **36**, T85 (1980).
266. M. Hida and A. Yabe, *Sen'i Gakkaishi*, **36**, T132 (1980).
267. L. Schrader, *Tetrahedron Lett.*, 2977 (1971).
268. N. A. Evans, D. E. Rivett and J. F. K. Wilshire, *Aust. J. Chem.*, **27**, 2267 (1974).
269. N. A. Evans and I. H. Leaver, *Aust. J. Chem.*, **27**, 1797 (1974).
270. N. A. Evans, *Aust. J. Chem.*, **28**, 433 (1975).
271. I. H. Leaver and D. E. Rivett, *Mol. Photochem.*, **6**, 113 (1974).
272. J. Lin, D. E. Rivett and J. F. K. Wilshire, *Aust. J. Chem.*, **30**, 629 (1977).
273. I. G. Bykova, O. V. Butrimovich, L. A. Isachenkova and A. M. Sarzhevskii, *Khim. Vys. Energ.*, **13**, 240 (1979).
274. I. G. Bykova, O. V. Butrimovich, L. A. Isachenkova and A. M. Sarzhevskii, *Deposited Doc.*, VINITI 1759–79 (1979).
275. K. Yamada, H. Shosenji, M. Uchida and H. Igarashi, *Nippon Kagaku Kaishi*, (3), 563 (1974).
276. K. Yamada, H. Shosenji and K. Gotoh, *J. Soc. Dyers Colour*, **93**, 219 (1977).
277. H. Shosenji, H. Igarashi and K. Yamada, *Nippon Kagaku Kaishi*, (2), 271 (1978).
278. K. Yamada, H. Shosenji, Y. Nakano, M. Uemura, S. Uto and M. Fukushima, *Dyes and Pigments*, **2**, 21 (1981).
279. I. H. Leaver, G. C. Ramsay and L. J. Stephens, *Aust. J. Chem.*, **28**, 2083 (1975).
280. N. A. Evans, L. A. Holt and B. Milligan, *Aust. J. Chem.*, **30**, 2277 (1977).
281. K. F. Langley, *Aust. J. Chem.*, **28**, 1301 (1975).
282. N. A. Evans, D. E. Rivett and P. J. Waters, *Text. Res. J.*, **46**, 214 (1976).
283. B. H. Winters, H. I. Mandelberg and W. B. Mohr, *Applied Phys. Lett.*, **25**, 723 (1974).
284. A. M. Trozzolo, A. Dienes and C. V. Shank, *J. Am. Chem. Soc.*, **96**, 4699 (1974).
285. T. P. Zhestkova, G. G. Ryabchikova and A. K. Pikaev., *Zh. Prikl. Spektrosk.*, **33**, 934 (1980).
286. K. Amano, T. Hinohara and K. Matsui, *Shikizai Kyokaishi*, **50**, 61 (1977).