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Photophysical and Photochemical Properties of Benzoxazole Fluorescent Whitening Agents

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ABSTRACT

Some photophysical and photochemical properties of 15 benzoxazole fluorescent whitening agents in DMF have been measured. These compounds have fluorescence quantum yields greater than 0·64. With the exception of compounds containing a biphenyl residue in the structure, the compounds have laser action with laser conversion efficiencies between 9·5% and 22·4%. The photostability and the relationship between molecular structure and photophysical properties are discussed.

1 INTRODUCTION

Fluorescent whitening agents (FWAs) are organic compounds which can absorb ultraviolet light of wavelength below 400 nm and emit visible fluorescence at wavelength above 400 nm. Their physical and chemical properties are similar to near UV-band laser dyes, i.e. they have high fluorescence quantum yields and photostability. The laser properties of FWAs have been studied.[1] Because the absorption maxima of FWAs are near the emission wavelength of the nitrogen laser, and they are much cheaper than other laser dyes, other investigations of them have been made.[2]

Previous studies focused principally on FWAs containing water-soluble groups such as carboxyl and sulfonic acid groups. This present paper is concerned with the laser and photostability properties of the benzoxazole derivatives **I–IV** (Table 1).

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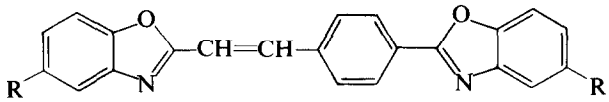
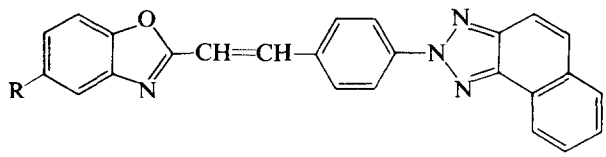
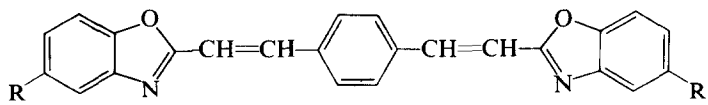
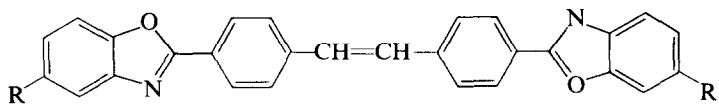
TABLE 1
Structures of the Benzoxazole FWAs

Number	*Molecular structure*
Ia–Id[a]	
IIa–IIc[a]	
IIIa–IIId[a]	
IVa–IVd[a]	

[a] **a**, R = H; **b**, R = Me; **c**, R = Cl; **d**, R = Ph.

2 EXPERIMENTAL

The benzoxazole derivatives were synthesized and purified as previously described.[3]

The absorption spectra in DMF were recorded on a Shimadzu 260 spectrophotometer and the fluorescence spectra measurements on a Hitachi 850 spectrophotofluorimeter. Fluorescence quantum yields were calculated by the relative method.[4] The fluorescent standard was quinine sulfate (0·01 M) (fluorescence quantum yield 0·55). Laser measurements were made with a 7912A nitrogen laser (China) and the laser output energies were measured using an NJ-1 laser energy meter (China). Laser conversion efficiencies were calculated by comparing the output energy of the nitrogen laser with that of an individual dye cell.

Freshly prepared solutions (absorbance *c.* 0·1) of each compound in DMF were placed into matched stopper glass tubes (15 mm internal diameter), which were laid at equal distances and aerated under a 500W high-pressure mercury lamp for 30 min. The absorbance of the samples, before and after light radiation, was then measured.

TABLE 2
UV, FL and Laser Spectra Data, Fluorescence Quantum Yields and Laser Conversion Coefficients of Compounds **I–IV**

Number	λ^{a}_{max} (*nm*)	ε (*liter mol*$^{-1}$ *cm*$^{-1}$)	λ^{f}_{max} (*nm*)	ϕ (%)	λ^{l}_{max} (*nm*)	η (%)
Ia	362·4	52 700	429·7	86	436·9	11·0
Ib	377·0	54 000	435·2	88	438·8	13·3
Ic	347·8	45 700	422·9	72	425·1	9·5
Id	353·0	47 600	440·0	66	—	—
IIa	368·8	66 800	431·0	84	438·0	9·9
IIb	373·6	69 400	431·9	86	432·9	22·4
IIc	373·6	65 300	434·0	80	435·8	9·5
IIIa	382·0	70 600	447·4	86	449·6	11·0
IIIb	384·0	78 400	452·0	87	455·9	11·0
IIIc	383·4	72 000	450·8	71	452·6	9·5
IIId	390·6	66 800	457·1	64	—	—
IVa	354·0	76 200	433·7	79	434·5	11·0
IVb	376·0	77 300	435·7	89	436·5	20·1
IVc	375·8	72 000	436·0	83	437·5	17·9
IVd	362·4	62 500	413·9	65	—	—

3 RESULTS AND DISCUSSION

The maxima in the ultraviolet, fluorescence and laser spectra, together with molar extinction coefficients, fluorescence quantum yields and laser conversion efficiencies, are given in Table 2.

In order to determine the accuracy of the methods and the measurements used to determine the fluorescence quantum yields, the value for 1,2-bis(5,5′-dimethylbenzoxazolyl)ethylene in DMF was also determined by the same method. The value obtained was 0·78, i.e. identical to the literature value.[5]

The absorbance of compounds **Ib**, **IIb**, **IIIb** and **IVb** in DMF are given in Table 3, before and after light radiation. The decay rate D was calculated from the relationship

$$D = E_0 - E_{30}/E_0$$

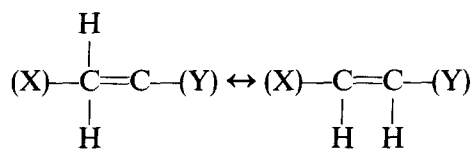
From Table 2, the absorption maxima of the compounds lie between 350 and 390 nm. The emission wavelength of the nitrogen laser is 337·1 nm. Molar extinction coefficients are from 4·5 × 10 to 7·8 × 10 mol/cm. With the exception of compounds **Id**, **IIId** and **IVd**, which contain a biphenyl moiety in their structure, the compounds have high fluorescence quantum yields (above 0·7) and exhibit laser conversion efficiencies of 0·095–0·224. The

TABLE 3
Absorbance Before and After Light Radiation and Decay Rate of **Ib**, **IIb**, **IIIb** and **IVb** in DMF

Number	*t* (*min*)	λ^{a}_{max} (*nm*)	*E*	*D* (%)
Ib	0	377	0·102	
	30	377	0·092	9·8
IIb	0	374	0·123	
	30	374	0·107	13·0
IIIb	0	384	0·099	
	30	384	0·053	46·5
IVb	0	376	0·105	
	30	376	0·044	58·1

compounds have a planar, rigid molecular structure and a greater rate of electronic transition from the first excited singlet state to the ground state may be assumed.

Since the compounds have a —CH=CH— residue in their molecular structure, there is the possibility of *cis–trans* isomerization, i.e.



where X and Y represent the terminal groups.

The *trans* form is usually more stable than the *cis* form. On the basis, therefore, that the compounds exist predominantly in the *trans* form, when this *trans* form undergoes transition from the first excited singlet state S_1 to the ground state S_0, four processes can occur simultaneously, i.e.

(1) Fluorescence emission: $t_{S_1} \xrightarrow{K_f} t_{S_0}$

(2) Radiationless internal conversion: $t_{S_1} \xrightarrow{K_{ic}} t_{S_0}$

(3) Intersystem crossing: $t_{S_1} \xrightarrow{K_{isc}} t_{T_1}$

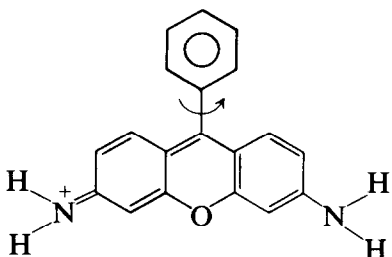
(4) Radiationless return to the *cis* form ground state: $t_{S_1} \xrightarrow{K_{ic}} C_{S_0}$

It is evident that the processes (2), (3) and (4) reduce the fluorescence quantum yields of the compounds.

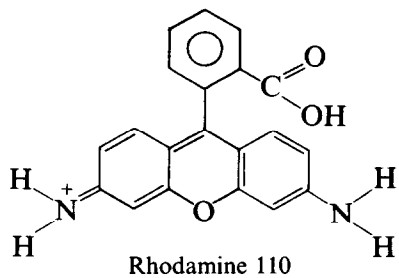
The presence of two benzoheterocycles at the terminal substituents of the —CH=CH— group makes the *cis–trans* isomerization difficult because of

steric hindrance. Hence, the fourth process contributes little to the reduction of fluorescence quantum yields.

The fluorescence quantum yields of compounds **Id**, **IIId** and **IVd** are lower than those of the parent compounds. This can be attributed to an increase in the rate of internal conversion of the phenyl groups in the molecule, as illustrated by the dyes Rosamine 4 and Rhodamine 110.[6] In the latter, the carboxyphenyl group is held in a position nearly perpendicular to the xanthene chromophore because of the presence of the bulky carboxyl group, thus allowing little, if any, mobility. In the case of Rosamine 4, however, the phenyl group can rotate to a certain degree, thus reducing the fluorescence quantum yield from 85% (Rhodamine 110) to 60% (Rosamine 4) in ethanol at 25°C.



Rosamine 4



Rhodamine 110

In addition, substituting a phenyl group in the 5-position of the molecule introduces a biphenyl moiety into the molecule. In biphenyl the two benzene rings are not in the same plane and its geometric arrangement changes during transition from the ground state to the excited state, making its absorption and emission spectra devoid of mirror-image symmetry, as shown in Fig. 1.[7] Such deviation from mirror-image symmetry usually indicates a different geometric arrangement of nuclei in the excited state as compared with the ground state. Nuclear displacement can occur prior to emission because of the relatively long lifetime of the excited state. The absorption and emission spectra of compounds **Id**, **IIId** and **IVd** are, like those of biphenyl, devoid of the symmetry. As illustrations, the absorption and emission spectra of compound **IIId** are shown in Fig. 2. The introduction of a phenyl group into the 5-position of the molecule thus greatly contributes to the reduction of the fluorescence quantum yield.

Introduction of a methyl group into the 5-position, i.e. as in compounds **Ib**, **IIb**, **IIIb** and **IVb**, results without exception in a higher fluorescence quantum yield than the parent compound, due to extension of conjugation. Similar introduction of a chloro substituent at the 5-position enhances some of the first and second series compounds, because of the heavy atom effect.

Laser light, like fluorescence, is emitted by a molecule during transition from the first excited singlet state to the ground state. Hence, three of the

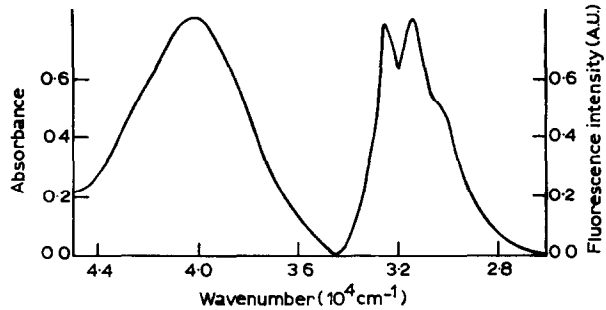


Fig. 1. Absorption and emission spectra of biphenyl.

processes mentioned above can affect the laser emission. One of the differences between fluorescence and laser emission is the lifetime of the first excited singlet state, S. In the case of the latter, the lifetime must be less than 10 ns.[8] As mentioned earlier, nuclear displacement can occur prior to the emission because of the relative long lifetime of the excited state; therefore, the three phenyl substitute derivatives **Id**, **IIId** and **IVd** have no laser action.

Hida *et al.*[9] have investigated the photochemical reaction of 1,2-bis(5,5′-dimethylbenzoxazolyl)ethylene (Uvitex ERN, CI Fluorescent Brightener 135) in several organic solvents. It was found that the carbon–carbon double bond in the molecule would be broken after exposure to intense light and

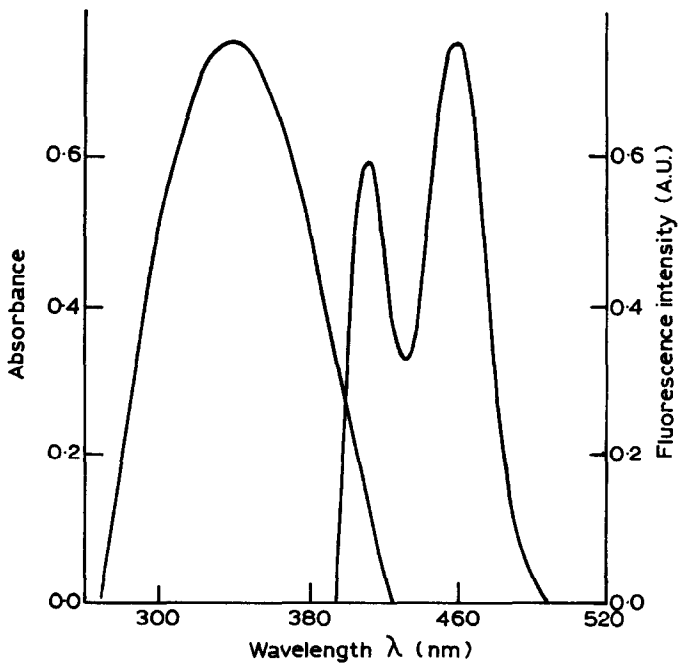


Fig. 2. UV absorption and fluorescence emission spectra of compound **IIId**.

TABLE 4
Electron Density of Carbon Atoms in —CH=CH— Groups of Compounds **Ib**, **IIb**, **IIIb** and **IVb** in the Ground and the Excited States

Number	*Ground state*				*Excited state*			
	C_1	C_2	C_3	C_4	C_1	C_2	C_3	C_4
Ib	0·985	0·937			1·040	1·016		
IIb	1·038	0·913			1·058	1·176		
IIIb	0·992	0·933	0·933	0·992	1·029	1·012	1·012	1·029
IVb	0·996	0·996			1·021	1·021		

that photodimerization would take place. On the basis of the experimental results of Hida and ourselves, we propose that the absorbance reduction can be attributed to the photochemical reaction. However, it can be seen from the data in Table 3 that the photochemical reaction is related to the structural symmetry of the molecules. Compounds which have symmetry have a photostability much lower than that of compounds which do not have structural symmetry. It is of interest to note that the absorbance of a solution of 1,2-bis(5,5′-methylbenzoxazolyl)ethylene in DMF decreases by 50% after only 9 min exposure under the same conditions. Relative to this, compounds **I**–**IV** have a generally better photostability.

To some extent, this observation can be attributed to the difference in electron density between the two carbon atoms of the —CH=CH— group. Values for four compounds, viz. **Ib**, **IIb**, **IIIb** and **IVb**, are given in Table 4, the values being derived from PPP–MO calculations. No difference in electron density is apparent in compound **IVb**, which has structural symmetry, but a difference is observed in the compounds which do not have structural symmetry. Although a difference is observed in a single —CH=CH— group of compound **IIIb** (which has two —CH=CH— groups), no difference is apparent between the two carbon atoms, in the same position in the two —CH=CH— groups. In addition, the photochemical reaction probability should be double that of the other compounds, because of the two —CH=CH— groups.

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