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A New Fluorescent Triphenodioxazine Dye Derived from 4-Aminodiphenylamine

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ABSTRACT

*A new substituent triphenodioxazine compound containing the 3,10-di(*N-*benzoyl-*N-*phenyl) amino has been synthesized. The benzoyl groups were introduced into the molecule during the cyclization of the dianilide derived from 4-amino-diphenylamine in the presence of benzoyl chloride as ring closure agent. The absorption and fluorescence spectra of the dye were measured in five solvents and it was found that the fluorescence quantum yields, Stokes shifts and molar extinction coefficients varied linearly with* E_T *of the solvents. When using* p*-toluene sulphonyl chloride as ring closure agent,* p*-toluene sulphonyl groups were also introduced.*

INTRODUCTION

It has been found that some triphenodioxazines are fluorescent compounds, and their fluorescence properties are affected by substituents. The unsulphonated triphenodioxazines have higher fluorescence quantum yields than sulphonated derivatives. The presence of phenyl groups at the 6,13-positions are advantageous to the fluorescence quantum yields, but these derivatives are difficult to synthesize.[1] Generally, triphenodioxazine compounds can be obtained, i.e by condensation of an arylamine with chloranil to form the dianilide and then cyclizing the dianilide in

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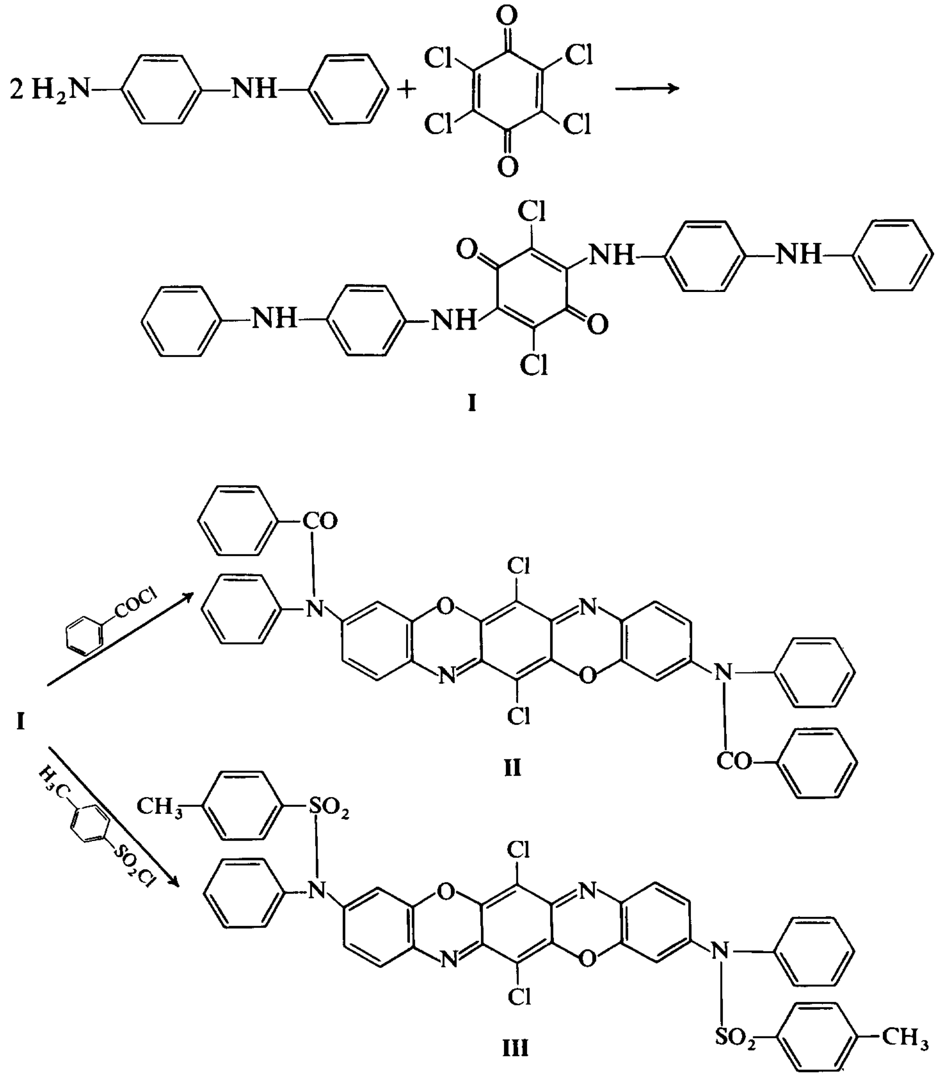
an organic solvent, such as *o*-dichlorobenzene or nitrobenzene, in the presence of a ring closure agent, e.g. benzoyl chloride or *p*-toluene sulphonyl chloride.[2,3] However, when using 4-aminodiphenylamine, in the presence of benzoyl chlorid 3,10-di-(*N*-benzoyl-*N*-phenyl)amino-6,13-dichlorotriphenodioxazine is obtained and not the expected 3,10-di-(*N*-phenyl)amino-6,13-dichlorotriphenodioxazine. Similarly, in the presence of *p*-toluene sulphonyl chloride, 3,10-di-(*N*-*p*-toluene sulfonyl-*N*-phenyl)-amino-6,13-dichlorotriphenodioxazine is obtained.



Scheme 1

EXPERIMENTAL

General

IR spectra were taken on a Nicolet FTIR 5DX, mass spectra on a MAT/SS200 and ^{1}H NMR spectra on a JEOL FX-90Q. Absorption spectra were measured using a Shimadzu UV-260, and fluorescence spectra on a Hitachi 850 fluorescence spectrophotometer at 25°C. The concentration of the samples was $1{\cdot}6 \times 10^{-6}$ M. All the solvents used were of analytical grade.

The fluorescence quantum yields were calculated according to the equation.

$$\phi = \frac{A_0}{A} \frac{F}{F_0} \frac{n^2}{n_0^2} \phi_0$$

where A is the absorption, F is the value of the integral area of the emission spectrum, n is the refractive index of the solvent and the subscript zero refers to the standard reference Rhodamine B ($\phi_0 = 0{\cdot}98$; ethanol).[4]

The Stokes shifts were calculated using the relationship:

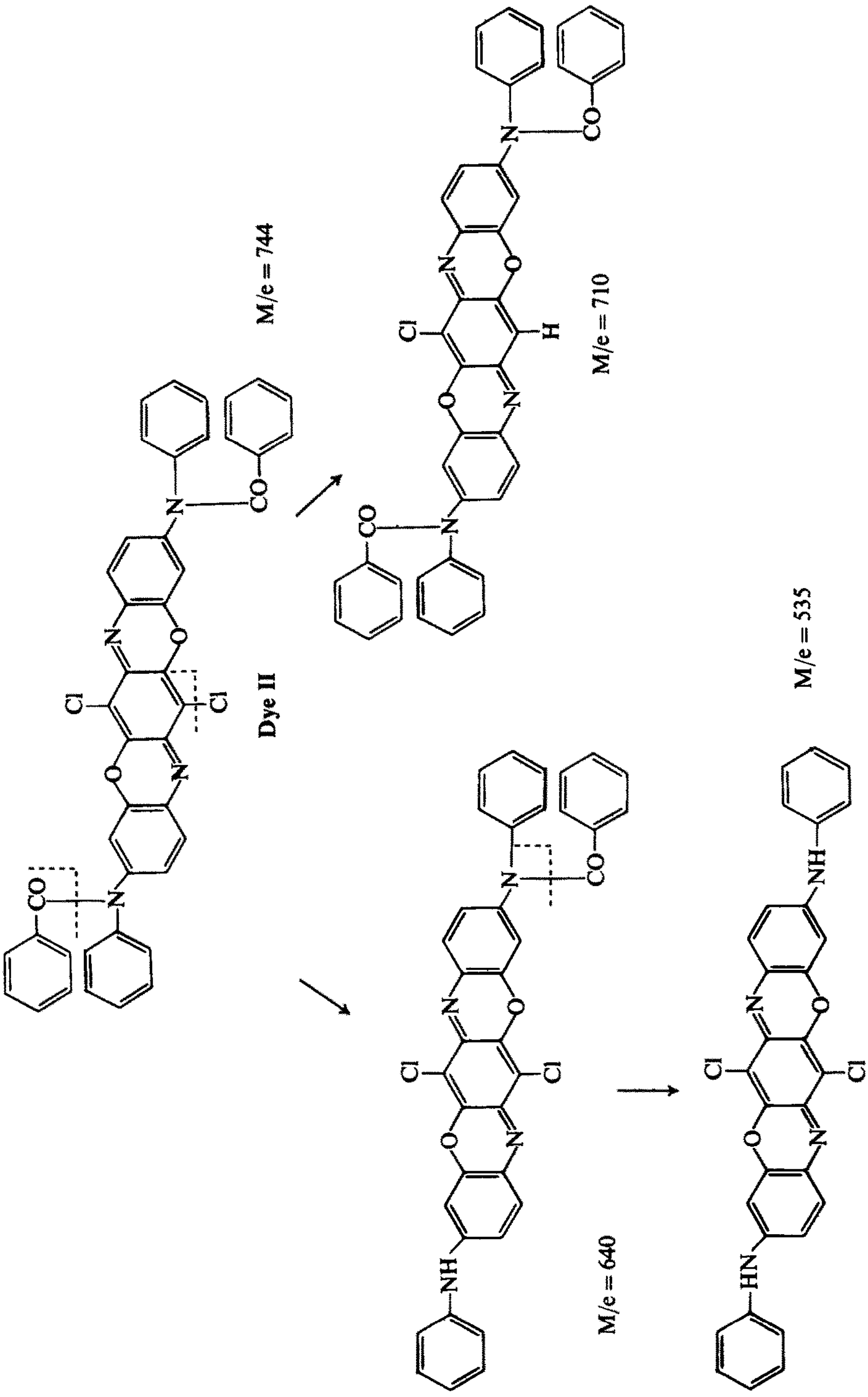
$$\Delta\nu = \left(\frac{1}{\lambda_{\max}^{\mathrm{ab}}} - \frac{1}{\lambda_{\max}^{\mathrm{em}}}\right) \times 10^7 \ (\mathrm{cm}^{-1})$$

2,5-Bis(4-phenylamino)anilino-3,6-dichlorobenzoquinone (I) (see Scheme 1)

A mixture of 7·4 g (0·03 mol) of chloranil and 12·4 g (0·15 mol) of anhydrous sodium acetate was stirred in 150 ml of ethanol, and 11·2 g (0·06 mol) of 4-aminodiphenylamine was then added. The mixture was heated, with stirring, under reflux for 8 h and then cooled to room temperature. The solid was filtered, washed with hot water then with ethanol, and dried, giving 15·6 g of crude product.

3,10-Di(*N*-benzoyl-*N*-phenyl) amino-6,13-dichlorotriphenodioxzine (II)

A mixture of 6·0 g (0·11 mol) of compound **I**, 11 ml of benzoyl chloride and 40 ml of nitrobenzene was heated under reflux for 8 h, giving a violet solution. Nitrobenzene was removed by vacuum distillation and the residue was washed with ethanol and water, and then dried, to give 7·3 g of a purple product, which was recrystallized from chloroform (found: C70·77, H 3·51, N 7·30%; $C_{44}H_{26}H_4O_4Cl_2$ requires C70·87, H3·49, N7·52%); MS M+ 744 (mol. wt 745); IR: 1659 cm^{-1} ($\nu_{C=O)}$) (Nujol).



Scheme 2

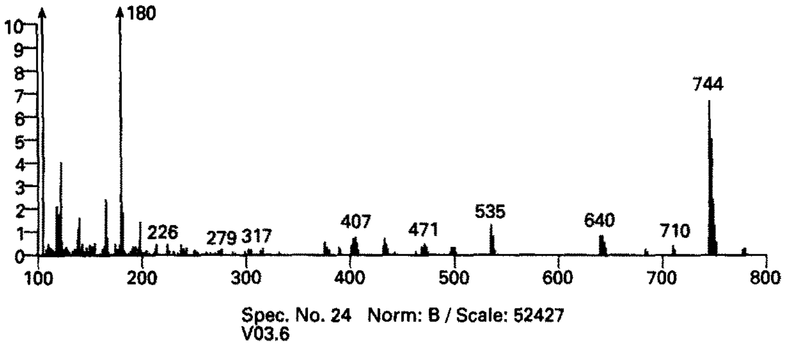


Fig. 1. Mass spectrum of compound II.

3,10-Di(*N*-*p*-toluene sulphonyl-*N*-phenyl)amino-6,13-di-chlorotriphenodioxazine (III)

A mixture of 6·0 g (0·011 mol) of compound **I**, 4·5 g (0·024 mol) of *p*-toluene sulphonyl chloride and 40 ml of *o*-dichlorobenzene was heated under reflux for 8 h to give a reddish blue solution. *o*-Dichlorobenzene was removed by vacuum distillation and the residue was washed with ethanol and water, and then dried, to give a blue product (7·0 g), which was then recrystallized from chloroform and ethanol (found: S 7·40%; $C_{44}H_{30}N_4O_6S_2Cl_2$ requires S7·57%); ^{1}H NMR δ_H(90 MH$_z$, CD_3Cl; 2·28, 6H CH_3 of toluene sulphonyl and 8·2—6·3, 24H ArH); IR: 1145 and 1302 cm^{-1} ν_{SO} (Nujol).

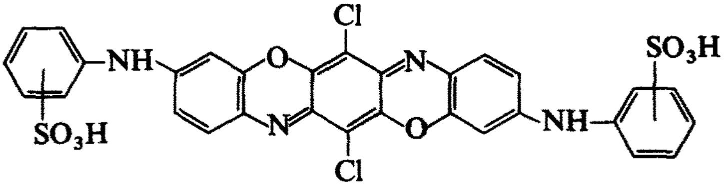
RESULTS AND DISCUSSION

Synthesis

Diphenylamine reacted with benzoyl chloride to form the amide when compound **I** was cyclizing using benzoyl chloride in nitrobenzene. The IR spectrum of compound **II** showed the C = O stretching band at 1660 cm^{-1} and no N—H at *c.* 3300 cm^{-1}. MS and elemental analysis confirmed the structure of compounds **II**.

3,10-Di(*N*-phenyl)amino-6,13-dichlorotriphenodioxazine could not be obtained under these reaction conditions. Therefore, if the cyclized product derived from 4-aminodiphenylamine was sulphonated, Sirus Light Blue FF2GL (Direct Blue 106, CI 51300) could not be obtained, as is stated in the literature.[4] Normally, this dye is produced from 4-aminodiphenylamine-2-sulphonic acid using oleum as cyclization medium.[5,6]

When compound **I** was cyclized in the presence of *p*-toluene sulphonyl chloride, *p*-toluene sulphonyl groups were introduced into the ring-closed product.



Sirus Light Blue

Most triphenodioxazine compounds have poor solubility in organic solvents. After the cyclization reaction, on cooling the reaction mixture optionally with addition of ethanol the product crystallized or precipitated. However, compounds **II** and **III** did not separate in this way, i.e. they had greater solubility, as the planar and linear properties of the molecule were degraded after introducing the benzoyl or *p*-toluene sulphonyl substituents. To obtain solid products, vacuum distillation was necessary to remove the solvents.

The influence of solvents on the absorption and fluorescence spectra of compound **II** is shown in Table 1. The Stokes shifts became larger with increasing polarity of the solvents, as the absorption spectra varied towards shorter wavelengths and the fluorescence spectra towards longer wavelength. The relationship between the Stokes shift and the E_T valve of the solvents can be expressed by

$$\Delta\nu = 0{\cdot}068E_T - 1{\cdot}482 \ (r = 0{\cdot}982, n = 5)$$

Compound **II** shows more intense absorption bands in solvents of lower polarity. The relationship between the molar extinction coefficient and the E_T value of the solvents is given by

$$\varepsilon_{max} = -0{\cdot}074\ E_T + 8{\cdot}660 \ (r = 0{\cdot}998, n = 5)$$

TABLE 1
Absorption and Emission Data of Compound **II**

Solvent	*Absorption* λ_{max} *(nm)*	*Emission* λ_{max} *(nm)*	ε_{max} *(10^4)*	ϕ	$\Delta\nu$ *($k\ cm^{-1}$)*	E_T[7]
Toluene	553·8	578·0	6·13	0·59	0·956 9	33·9
Chloroform	552·8	595·0	5·81	0·49	1·283 0	39·1
Acetone	542·8	584·8	5·49	0·30	1·323 1	42·2
DMF	545·2	596·0	5·44	0·29	1·563 4	43·8
Ethanol	541·4	609·0	4·81	0·10	2·050 3	51·9

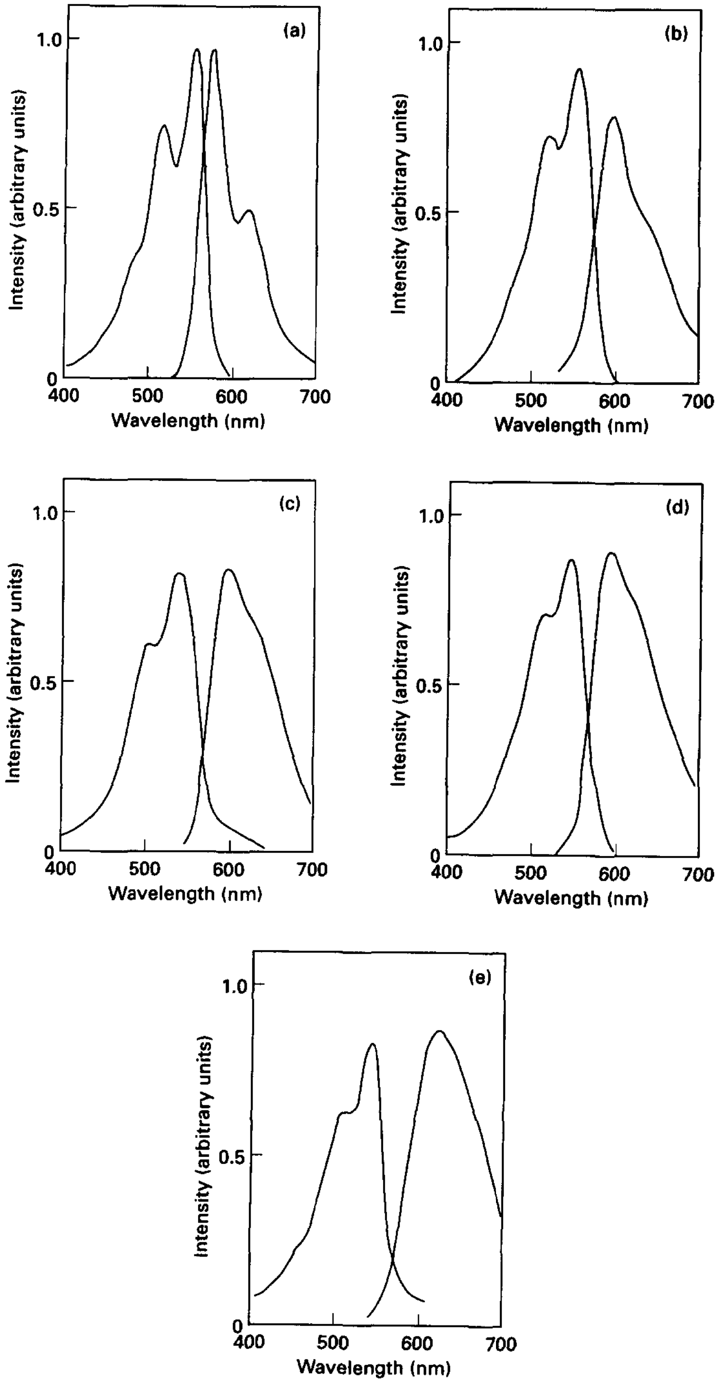


Fig. 2. Absorption and fluorescence spectra of compound II in (a) toluene, (b) chloroform, (c) acetone, (d) DMF, (e) ethanol.

TABLE 2
Absorption and Emission Data of Compound III

Solvent	*Absorption,* λ_{max} *(nm)*	*Emission,* λ_{max} *(nm)*	ε_{max} *(10^4)*	ϕ	$\Delta\nu$ *($k\ cm^{-1}$)*
Toluene	597·6	632·3	2·90	0·36	0·918 3
Chloroform	603·8	655·6	1·63	0·07	1·308 6
Acetone	603·9	661·4	1·56	0·03	1·439 6

The fluorescence quantum yields of compound **II** varied from 0·1 to 0·59, the higher values being pertinent to lower E_T values of the solvent. The relationship between the fluorescence quantum yield and the E_T value of the solvent is shown by the expression

$$\phi = -0{\cdot}029\ E_T + 1{\cdot}548\ (r = 0{\cdot}980,\ n = 5)$$

The absorption and emission spectra of compound **II** showed good mirror image relationships in solvents of lower polarity. With increasing polarity, the fine structure of the emission spectra disappeared (see Fig. 2).

Introduction of *p*-toluene sulphonyl groups in place of the benzoyl groups in compound **II** resulted in bathochromic shifts of both the absorption and fluorescence spectra, and both ϕ and ε_{max} decreased.

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