Synthesis of New Fluorescent Dyes in the Benzoxazinone Series: Aminobenzoxazinones with a Rigidized Structure

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Received August 3, 1988

The structure of 7-aminobenzoxazinones was modified by enclosing their amino nitrogen atom in a julolidyl ring. This rigidization was expected to enhance the fluorescence performances in this series. Several fluorescent dyes and styryl derivatives were prepared and their spectral characteristics were investigated. Comparison with homologous benzoxazinones with a flexible amino group shows that rigidization does not improve the quantum yield and the photochemical stability, in contrast with the results reported for other classes of dyes, like coumarins or rhodamines.

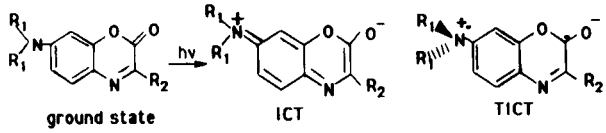
J. Heterocyclic Chem., **26**, 429 (1989).

The performances required for fluorescent dyes, especially for their use in dye lasers, have induced many chemists to synthesize new molecules possessing optimal photophysical properties (quantum efficiency, lifetime, stability). Among these compounds, aminocoumarins and rhodamines constitute very important classes of laser dyes and have been the subject of extensive investigations [1-6]. Now, the laser performances of these dyes strongly depend on the physicochemical properties of the solvents used (polarity, viscosity, temperature): their quantum yield decreases, often by a significant factor, when the temperature and/or the polarity of solvents increase, but it is recovered, for example, in viscous or glassy solvents or at low temperature.

These results are explained, in the case of coumarins, by the strong polar character of these molecules in the excited state: the presence of donor (amino) and acceptor (C=O) groups leads to a dipolar, planar intramolecular charge transfer state (ICT), which results in a large increase of dipole moment and a strong solvatochromic effect; a reduction of the emission and a bathochromic shift of the fluorescence spectrum are observed in polar solvents.

On the other hand, it was shown that these phenomena are strongly diminished, when the rigidity of the dye molecule is increased, by including the amino nitrogen atom in a planar ring, thus, for example, the quantum yields (in ethanol) of coumarin 152A, which possess an amino group free to rotate, is 0.08; for coumarin 153, with relevant rigid structure, the quantum yield rises to 0.41.

Scheme 1



These effects can be interpreted by the mobility of the amino group whose rotation causes energy dissipation, leading in some cases to the formation of a non planar twisted intramolecular charge transfer state (TICT); when the molecule is rigidized the rotation of the amino group is hindered and the emission is noticeably improved.

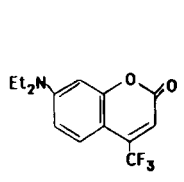
In the case of rhodamines, TICT formation takes place at higher temperature, by rotation around the *N*-aryl bonds [9]. A planar rigid molecular structure favors, also in this series, high fluorescence efficiencies; so, in the rhodamine B, the quantum yield in ethanol is dependent on the temperature and the viscosity of the solvent: from about 40% at 25°, it increases to nearly 100% if the temperature is lowered, or in glycerol, but it drops to only a few percent in boiling ethanol. On the other hand, in rigid rhodamine 101, the quantum yield is found to be 100%, independent of the temperature [2]. However, it is also possible for a dye with a non rigid structure to be highly fluorescent: this is the case, for instance, rhodamine 6G has a quantum yield of 95%, whatever the temperature [2].

It must be noted that the concept of TICT state was first described for *p*-cyanodialkylanilines, and then extended to a variety of compounds [7,8,10]; these compounds emit a dual fluorescence: one, at low energy, which prevails in the most polar solvents, the other, at high energy in the weakly polar solvents. In the case of coumarins, the alteration of their emissive properties as a function of solvent polarity has been explained by a decay *via* a non emissive TICT state [5,6,9], although, in this case, dual fluorescence was not illustrated.

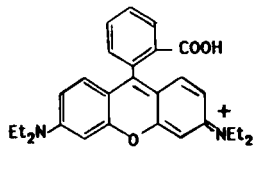
We have already described a new class of fluorescent dyes: 7-aminobenzoxazinones [11-16], which offer interesting properties, especially as laser dyes [13] and for solar concentrators [16]. These dyes, in the excited state, have a pronounced dipolar character: the donor is the amino, or dialkylamino group, whereas the acceptor is both the oxygen atom of the lactonic carbonyl and the heterocyclic nitrogen atom [15,17,18], with a large charge separation between donor and acceptor moieties. By analogy with aminocoumarins one could think that the mobility of the amino group can increase the separation of charges by

twisting of the C-N bond, with possible formation of a TICT state.

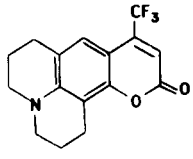
Scheme 2



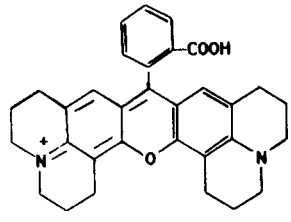
Coumarin 152A



Rhodamine B



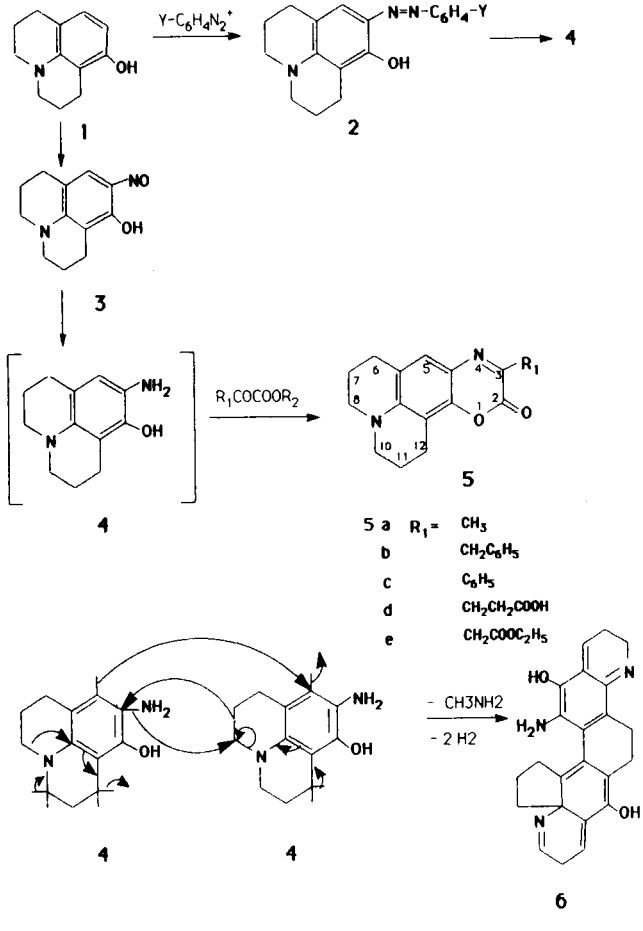
Coumarin 153



Rhodamine 101

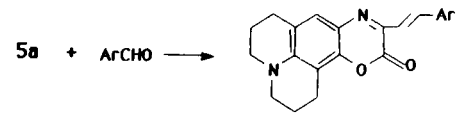
If this assumption was verified, the imposition of rigidity upon benzoxazinone molecule would lead, as in coumarins, to an improvement of the emissive properties of this class of dyes. Therefore, we have attempted to obtain the quinolizinobenzoxazinones **5**. They were prepared by heterocyclisation of aminohydroxyjulolidine **4** by *alpha*-ketoacids or esters. However, we must report that the diaminophenol **4**, obtained after the reduction of either azo dye **2** or nitroso compound **3**, is very readily oxidized: on exposure to the air it turns into an hexocyclic blue dye **6**.

Scheme 3



As for aminobenzoxazinones, the condensation of dye **5a** with araldehydes leads to styryl derivatives **7**.

Scheme 4



7 a Ar= C_6H_5
b α naphthyl
c β naphthyl
d $-=-C_6H_5$
e $C_6H_4OCOCH_3$ (3)
f C_6H_4CHO (4)

In the organic solvents, dyes **5** and **7** show deep fluorescence from green to red, and large Stokes shifts up to 100 nm.

On the other hand, the photochemical stability of these dyes is surprisingly very bad: after 2 hours exposure under a Xenon lamp (illuminance 3000W/m²) [21], their ethanolic solutions become entirely bleached; in comparison with a non rigid benzoxazinone (Scheme 2, $R_1 = R_2 = CH_3$), under the same conditions, the decrease in absorbance is only 40%.

Thus, in contrast to the previously related observations in the literature, the behaviour of julolidyl dyes **5** and **7**, that the rigidization of the amino nitrogen atom leads to a surprising photochemical instability.

For all dyes described in this paper, the absorption and emission spectra exhibit unusual large bands and very small overlap. The values of quantum yield are weaker than, or close to these observed for benzoxazinones with a flexible amino group.

In Table 1 the data of dyes **5c** and **7f** in ethanolic solu-

Table 1

Ethanolic solution	λ abs. (nm)	λ em. (nm)	Stokes shift (cm^{-1})	φ [a]
7f	525	608	2600	0.12
9 [b]	488	590	3542	0.59
5c	472	578	3885	0.15
8 [c]	442	556	4639	0.38

[a] Fluorescence quantum yield. [b] Scheme 1: $R_2 = CH_3$, $R_1 = CH{=}CH{-}C_6H_4{-}CHO$. [c] Scheme 1: $R_2 = CH_3$, $R_1 = C_6H_5$.

tions are summarized; if we compare these data to those of the relevant non rigid dyes **8** and **9**, we observe that the Stokes shift is not markedly affected by the rigidization, whereas the quantum yield is reduced.

In conclusion, these results show that 7-amino- or dialkylaminobenzoxazinones are unlikely to lead to a TICT state.

EXPERIMENTAL

Melting points were determined on a Kofler hot plate and were uncorrected. The uv and visible spectra (ethanolic solutions) were recorded on a Uvikon 820 spectrophotometer. The ir spectra were recorded on a Perkin-Elmer 197 spectrophotometer, as potassium bromide discs. The mass spectra were determined on a VG 30 F spectrometer. Emission spectra (ethanolic solutions) were measured with a SPF 500 Aminco interfaced to a ψ 80 Kontron computer. Fluorescence spectra are depicted as: λ max, nm, (quantum yield); fluorescence quantum yields (ϕ) were determined from areas under corrected emission spectra, relative to rhodamine 640 (ϕ = 1, λm emission = 571 nm).

The ^{1}H nmr spectra (all compounds in pyridine D5) were obtained on a Perkin-Elmer R 32 spectrometer, except for less soluble substances which were studied with Cameca 350 and Brooker 200 spectrometers; chemical shifts are reported in parts per million downfield from tetramethylsilane (δ units). Since the shifts of the protons of the julolidine ring are exactly identical for both dyes **5** and **7**, these shifts have been recorded for the first described dye **5a** only.

9-Amino-8-hydroxyjulolidine (4).

The most convenient way to afford 8-hydroxyjulolidine (**1**) [19] seemed to be similar to the method leading to 1-amino-2-naphthol [20], for instance; in this method, a diazonium salt is coupled with a phenol, then the obtained azo dye undergoes a reduction giving rise to amino group. In the molecule of julolidine the coupling will proceed only on the 9 position, activated by an OH group. For this reaction the diazonium salt commonly used is 4-sulfophenyldiazonium salt, which provides water soluble dyes whose reduction is easily performed by means of sodium dithionite. In these conditions, aminohydroxyjulolidine **4** provided by reduction of azo dye **2** (Y = SO_3H) in aqueous solution is easily oxidized, even with an excess of reductor and under inert cover; oxidation is revealed by the appearance of a deep blue color.

For this reason, we have preferred the following operating process consisting in the catalytic reduction of alkohol-soluble dyes **2** (Y = Cl): this reaction was easily achieved at ordinary temperature and pressure with Raney Nickel as a catalyst. The aminophenol **4** was isolated in the form of the hydrochloride then cyclised by *alpha*-ketoacids in pyridine solution. An alternative way consisted of the direct cyclisation of **4** in the reduction solution.

8-Hydroxy-9-(4-sulfophenylazo)-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*i*,*j*]quinolizine (**2** Y = SO_3H).

The diazonium salt prepared from sulfanilic acid (3.5 g, 0.02 mole) was buffered by sodium acetate and then poured into a cold pyridine solution (60 ml) of hydroxyjulolidine **1** (3.8 g, 0.02 mole). Upon standing for 1 hour the dark red solution was acidified with hydrochloric acid. The bright red needles of dye were filtered off, washed with water and recrystallized from 40% acetic acid, mp 270°; visible spectrum (ethanol 70%): λ max, nm (ϵ) 465 (41500).

Anal. Calcd. for $C_{18}H_{19}N_3O_4S$: C, 57.91; H, 5.09; N, 11.26. Found: C, 57.96; H, 5.14; N, 11.04.

Reduction.

The dye was dissolved in 100 parts of water, heated on the steam bath under a nitrogen current; an excess of sodium dithionite was added; the red solution first became colorless, then very quickly fast blue.

8-Hydroxy-9-(4-chlorophenylazo)-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*i*,*j*]quinolizine (**2** Y = Cl).

A pyridine solution of 8-hydroxyjulolidine **1** (5.7 g, 0.03 mole) was cooled by addition of ice, then mixed with a buffered solution of 4-chlorophenyldiazonium chloride (0.03 mole). The coupling was instantaneous; after 30 minutes, red needles were isolated in quantitative yield and crystallized from pyridine, mp 168°; visible spectrum: λ max, nm (ϵ) 467 (60000); ir: ν cm^{-1} 2930, 2830 (CH_2), OH not detected (chelate), 1290 (C-Cl); ^{1}H nmr: 15.09 (s, OH), 7.68-7.40 (q, 4H, J = 8 Hz), 7.17 (s, 1H), 3.04 (t, 4H, J = 10 Hz), 2.64 (q, 4H, J = 10 Hz), 1.72 (t, 4H, J = 10 Hz); ms: m/e (relative intensity) 329 (M 27), 327 (78), 201 (19), 189 (14), 188 (100), 160 (14).

Anal. Calcd. for $C_{18}H_{18}ClN_3O$: C, 65.95; H, 5.50; N, 12.82. Found: C, 66.07; H, 5.44; N, 12.77.

Catalytic Reduction of Azo Dye **2** (Y = Cl).

General Procedure.

The pure, crystallized dye (3.27 g, 0.01 mole) was dissolved on heating in absolute ethanol (100 ml); on cooling, fine needles of dye were suspended in alcohol and reduced by hydrogen in the presence of Raney Nickel. The reaction was very fast and a colorless solution of the aminohydroxyjulolidine **4** obtained.

Oxidation of Aminohydroxyjulolidine **4**. Isolation of Compound **6**.

When the solution of the above aminophenol **4** (after exclusion of Ni) was stirred for several hours in the air, a deep blue solution was observed. Ethanol was removed under vacuum and the blue dye extracted with water. After removal of water, the dye was taken up with ethanol and the solution filtered and chromatographied on alumina column: the pure blue eluted fraction was collected and evaporated to dryness giving green crystals with bronze reflects, mp 270°; visible spectrum: λ max, nm (ϵ) 666 (220400); emission: λ max, nm 684; ir: ν (cm^{-1}) 3400 (large OH + NH_2), 2930, 2940 (CH_2), 1600 (large, very strong C=N, NH_2); ^{1}H nmr: (350 MHz) 2.73 (large signal, 7H), 1.95 and 1.82 (2 large signals, 8 CH_2); ms: m/e (relative intensity) 373 (M, 100) 372 (18).

Anal. Calcd. for $C_{23}H_{23}N_3O_2$: C, 73.99; H, 6.17; N, 11.26. Found: C, 74.06; H, 6.17; N, 11.06.

Working Out of the Structure of Compound **6**.

The study of the mass spectra of this dye recorded the molecular ion at m/e 373, *i.e.* (2 x **4**)-35; this mass displayed odd-numbered nitrogen atoms (other fragment-ions resulted from a complete destruction of the molecule). Analysis provided the empirical formula $C_{23}H_{23}N_3O_2$. Therefore the molecule was obtained by elimination of groups CH_3NH_2 + $2H_2$ from 2 molecules of aminophenol **4**. The infrared spectrum revealed amino and (or)

hydroxyl groups but no carbonyl group; moreover the nmr spectrum showed 3 CH and 8 CH_2 groups but no aromatic proton. Formula **6** was in good agreement with the analytical and spectral data.

Preparation of Dyes **5**.

General Procedure.

By treating the alcoholic solution of the aminophenol **4** with α-ketoacids, the benzoxazinones **5** were isolated in impure form and low yields. It is best to use the hydrochloride of this aminophenol prepared as follow: under nitrogen flushing, the alcoholic solution of **4** was filtered from nickel, then hydrogen chloride was bubbled through the filtrate, alcohol was removed, and a mixture of the hydrochlorides of chloroaniline and aminohydroxyjulolidine obtained; under magnetic stirring, ketoester (or acid), some ice, and finally pyridine were added; in all cases, the fluorescent dye crystallized instantaneously.

8-Hydroxy-7-nitrosojulolidine (**3**).

8-Hydroxyjulolidine **1**, (5 g, 0.026 mole) was dissolved in concentrated hydrochloric acid (25 ml) and 25 g of ice added; this solution was treated, under effective stirring and cooling by sodium nitrite (1.8 g, 20 ml of water). Upon standing (1 hour), the orange hydrochloride was isolated and changed into base by means of sodium acetate; this base crystallized from water as dark-red needles with bronze reflects, yield 3.4 g (60%), mp 209°; uv: λ max, nm (ε) 339 (16600), 410 (shoulder); ir: ν cm^{-1} 3430 (broad, OH, intermolecular bonds), 2950, 2860 (CH_2), 1640 (C-N), 1515 (N=O), 1350, 1200 (OH); ^1H nmr: 20.4 (s, OH chelate), 6.9 (s, 1H), 3.08 (m, 4H), 2.60 (t, 2H, J = 6.4), 2.35 (t, 2H, J = 5), 1.60 (m, 4H).

Anal. Calcd. for $C_{12}H_{14}N_2O_2$: C, 66.05; H, 6.42; N, 12.84. Found: C, 65.93; H, 6.50; N, 12.93.

3-Methyl-8*H*,12*H*-6,7,10,11-tetrahydroquinolizino[*g*,*h*]-1,4-benzoxazin-2-one (**5a**).

This dye was obtained in 70-80% yield, on treatment of **4** (0.01 mole, from reduction of the nitrosophenol **3**) with ethyl pyruvate (2.3 g, 0.02 mole); it was crystallized from diluted pyridine as gold yellow tablets, showing an orange (crystalline form) or bright yellow (ethanol) fluorescence, mp 138°; uv: λ max, nm (ε) 269.5 (14000), 431.7 (26900); emission: λ max nm (φ) 578 (0.16); ir: ν cm^{-1} 2930, 2840 (CH_2), 1710 (C=O), 1615 (C=C, C=N); ^1H nmr: 7.33 (s, H5), 3.03, 3.01 (2 t, J = 6, H8 + H10), 2.69, 2.64, (2 t, J = 6, H6 + H12), 1.72 (quintuplet, J = 6, H7 + H11), 2.5 (s, 3H); ms: m/e (relative intensity) 256 (M, 100), 228 (29), 227 (46).

Anal. Calcd. for $C_{15}H_{16}N_2O_2$: C, 70.31; H, 6.25; N, 10.94. Found: C, 70.07; H, 6.18; N, 11.05.

3-Benzyl-8*H*,12*H*-6,7,10,11-tetrahydroquinolizino[*g*,*h*]-1,4-benzoxazin-2-one (**5b**).

The aminophenol **4** was cyclised by phenylpyruvic acid (1.7 g, 0.01 mole); the dye was isolated as orange needles in 72% yield and crystallized from ethanol; its fluorescence was bright yellow in alcohols, yellow-green in acetone and green in benzene, mp 157°; uv: λ max, nm (ε) 271.3 (11500), 441.2 (22400); emission: λ max nm (φ) 562 (0.30); ir: ν cm^{-1} 2940, 2920, 2830 (CH_2), 1720 (C=O), 1615 (C=N); ^1H nmr: 7.70-7.25 (m, 5H), 4.25 (s, 2H); ms: m/e (relative intensity) 332 (M 100), 305 (17), 304 (87), 303 (48), 158 (23), 91 (51).

Anal. Calcd. for $C_{21}H_{20}N_2O_2$: C, 75.90; H, 6.02; N, 8.43. Found: C, 75.67; H, 6.04; N, 8.40.

3-Phenyl-8*H*,12*H*-6,7,10,11-tetrahydroquinolizino[*g*,*h*]-1,4-benzoxazin-2-one (**5c**).

Benzoylformic acid (1.5 g, 0.01 mole) was added to the aminophenol **4**. The bright orange needles of dye were isolated in 65% yield and crystallized from pyridine, mp 244°; uv: λ max nm (ε) 284 (10800), 472 (26200); fluorescence λ max nm (φ) 578 (0.38); ir: ν cm^{-1} 2935, 2850 (CH_2), 1715 (C=O), 1615 (C=N); ^1H nmr: 8.70 (s, 1H), 8.66 (s, 1H), 7.55-7.40 (m, 3H); ms: m/e (relative intensity) 318 (M 100), 290 (73), 289 (50), 158 (19), 77 (13).

Anal. Calcd. for $C_{20}H_{18}N_2O_2$: C, 75.47; H, 5.66; N, 8.80. Found: C, 75.27; H, 5.74; N, 8.79.

3-Propanoic-8*H*,12*H*-6,7,10,11-tetrahydroquinolizino[*g*,*h*]-1,4-benzoxazin-2-one Acid (**5d**).

α-Ketoglutaric acid (1.5 g, 0.01 mole) was added to aminophenol **4** and the dye isolated in 67% yield; the orange flakes of dye were recrystallized from acetone; they showed a yellow fluorescence in alcohols, yellow-green in acetone and turquoise-blue in ether, mp 217; uv: λ max, nm (ε) 269 (11900), 429 (23000); fluoresence: λ max, nm (φ) 558 (0.21); ir: ν cm^{-1} 2940, 2880 (CH_2), 1720-1690 (C=O lactone and acid), 3200-2000 (OH chelate), 1615 (C=N); ^1H nmr: 13.70 (s large, 1H), 3.25-3.20 (m, 2H), 3.20-2.85 (m, 6H, CH_2 + H8 + H10); ms: m/e (relative intensity) 314 (M 100), 286 (23), 285 (27), 268 (35), 255 (33), 241 (28), 227 (87), 158 (25).

Anal. Calcd. for $C_{17}H_{18}N_2O_4$: C, 64.97; H, 5.73; N, 8.92. Found: C, 64.57; H, 5.77; N, 8.81.

Ethylcarboxymethylene-3-8*H*,12*H*-6,7,10,11-tetrahydroquinolizino[*g*,*h*]-1,4-benzoxazin-2-one (**5e**).

The sodium salt of ethyl oxalacetate (1.9 g, 0.01 mole) was suspended in ethanol, slightly acidified with hydrochloric acid and taken to *p*H 5 with sodium acetate; this suspension was added to an alcoholic solution of **4**. The cyclisation was allowed to occur for 4 hours under nitrogen, nickel was filtered off and 2/3 of the solvent removed; orange needles of dye were obtained in 74% yield. This dye showed a deep yellow fluorescence in the organic solvents and was recrystallized from ethanol, mp 156°; uv λ max, nm (ε) 270 (11500), 441 (22800); fluorescence: λ max nm (φ) 573 (0.14); ir: ν cm^{-1} 2940, 2840 (CH_2), 1720 (large, C=O lactone + ester), 1615 (C=N); ^1H nmr: 4.20 (q, 2H), 4.05 (s, 2H), 1.15 (t, 3H); ms: m/e (relative intensity) 328 (M 100), 300 (18), 282 (21), 256 (17), 255 (79), 227 (56).

Anal. Calcd. for $C_{18}H_{20}N_2O_4$: C, 65.85; H, 6.10; N, 8.54. Found: C, 65.89; H, 6.13; N, 8.46.

Styryl Derivatives **7**.

General Procedure.

Dye **5a** (1.28 g, 5 mmoles) was suspended in acetic anhydride (4 ml); after addition of the selected araldehyde (7.5 mmoles), the mixture was heated for 4 hours at 140° in an oil bath. After cooling, the styryl derivative was stirred with acetone (10 ml) and filtered. In this series, all ^1H nmr spectra were obtained at 350 MHz.

3-Styryl-8*H*,12*H*-6,7,10,11-tetrahydroquinolizino[*g*,*h*]-1,4-benzoxazin-2-one (**7a**).

By condensing dye **5a** with benzaldehyde (0.8 g) the dye **7a** was obtained in 65% yield and crystallized in orange rods from diluted pyridine; its fluorescence was orange-yellow in alcohols, yellow in acetone and green in ether, mp 143°; uv (ethanol): λ max, nm (ε) 313 (19000), 498 (38900); fluorescence: λ max, nm (φ) 592, (0.12); ir: ν cm^{-1} 3040 (CH=CH), 2930, 2820 (CH_2), 1715 (C=O), 1610 (C=N); ^1H nmr: 8.28 (d, 1H, J = 16 Hz), 7.85 (d, 1H, J = 16 Hz), 7.69 (d, 2H, J = 7), 7.23-7.44 (m, 3H); ms: m/e (relative intensity) 344 (100), 316 (47), 315 (43), 256 (16), 158 (19), 157 (19).

Anal. Calcd. for $C_{22}H_{20}N_2O$: C, 76.74; H, 5.87; N, 9.29. Found: C, 76.60; H, 5.79; N, 9.08.

3-(1-Naphthylvinylene)-8*H*,12*H*-6,7,10,11-tetrahydroquinolizino[*g*,*h*]-1,4-benzoxazin-2-one (**7b**).

Dye **5a** was reacted with 1-formylnaphthalene (1.2 g) resulting in a red dye in 75% yield; it was crystallized from pyridine giving red tablets showing a vermillon (dry) to orange (acetone, alcohols) or yellow (ether) fluorescence, mp 201°; uv: λ max, nm (ε) 255 (11800), 336 (12900), 506 (39600); fluorescence: λ max, nm (φ) 609 (0.15); ir: ν cm^{-1} 3035 (CH=CH), 2930, 2830 (CH_2), 1720 (C=O), 1610 (C=N); ^1H nmr: 8.42 (d, 1H, J = 16), 8.04 (d, 1H, J = 16), 7.96 (d, 1H, J = 16), 7.90 and 7.49 (m, 6H); ms: m/e (relative intensity) 394 (M, 100), 366 (24), 365 (36), 256 (44), 228 (29), 227 (39), 79 (77).

Anal. Calcd. for $C_{26}H_{22}N_2O_2$: C, 79.19; H, 5.58; N, 7.11. Found: C, 78.97; H, 5.69; N, 7.27.

3-(2-Naphthylvinylene)-8*H*,12*H*-6,7,10,11-tetrahydroquinolizino[*g*,*h*]-1,4-benzoxazin-2-one (**7c**).

In the same way as above, using 2-formylnaphthalene, the dye was obtained in 70% yield and crystallized from pyridine giving dark red tablets with an orange-yellow (ethanol, acetone) or yellow (ether) fluorescence, mp 204; uv: λ max, nm (ε 276 (15700), 329 (22900), 508 (37700); fluorescence: λ max, nm (φ) 603 (0.14); ir: ν cm^{-1} 3040 (CH=CH), 2930, 2835 (CH_2), 1710 (C=O), 1615 (C=N); ^1H nmr: 9.12 (d, 1H, J = 16), 8.49 (d, 1H, J = 16), 7.95 (m, 2H), 7.90 (d, 1H, J = 16), 7.53 (m, 4H); ms: m/e (relative intensity) 394 (M, 100), 366 (36), 365 (29), 158 (11).

Anal. Calcd. for $C_{26}H_{22}N_2O_2$: C, 79.19; H, 5.58; N, 7.11. Found: C, 78.99; H, 5.64; N, 7.16.

3-(bis-Vinylenephenyl)-8*H*,12*H*,6,7,10,11-tetrahydroquinolizino-[*g*,*h*]-1,4-benzoxazin-2-one (**7d**).

This dye was isolated after condensation of **5a** with cinnamaldehyde (1 g) in 82% yield; it was crystallized from pyridine giving garnet-red tablets; its fluorescence was orange-yellow (alcohol or acetone) or yellow (ether), mp 172°; uv: λ max, nm (ε) 260 (8700), 334 (32900), 513 (54800); fluorescence: λ max, nm (φ) 599 (0.14); ir: ν cm^{-1} 3040 (CH=CH), 2930, 2840 (CH_2), 1710 (C=O), 1615 (C=N); ^1H nmr: 8.11 (d, 1H, J = 16), 8.08 (d, 1H, J = 16), 7.25-7.45 (m, 5H), 7.30 (d, 1H, J = 16), 6.91 (d, 1H, J = 16); ms: m/e (relative intensity) 370 (M, 52), 294 (20), 293 (100), 265 (31).

Anal. Calcd. for $C_{24}H_{22}N_2O_2$: C, 77.84; H, 5.95; N, 7.57. Found: C, 77.69; H, 5.84; N, 7.42.

3-(3-Acetoxystyryl)-8*H*,12*H*,-6,7,10,11-tetrahydroquinolizino[*g*,*h*]-1,4-benzoxazin-2-one (**7e**).

Dye **5a** was reacted with 3-hydroxybenzaldehyde (1 g), giving a dark-red dye, crystallizing from diluted pyridine as brown-red prisms. Its fluorescence is orange-red (ethanol, acetone), or green (ether). As the reaction was proceeded in acetic anhydride, the hydroxyl group underwent an acylation, mp 171°; uv: λ max, nm (ε) 310 (20500), 499 (35400); fluorescence: λ max, nm (φ) 600 (0.14); ir: ν cm^{-1} 3050 (CH=CH), 2940, 2830 (CH_2), 1750, 1715 (C=O lactone and ester), 1610 (C=N); ^1H nmr: 8.2 (d, 1H, J = 16), 7.8 (d, 1H, J = 16), 8.52-7.14 (m, 4H), 2.30 (s, 3H); ms: m/e (relative intensity) 402 (M, 100), 374 (29), 373 (11), 332 (16), 331 (19), 256 (12), 158 (10).

Anal. Calcd. for $C_{24}H_{22}N_2O_4$: C, 71.64; H, 5.47; N, 6.96. Found: C, 71.46; H, 5.56; N, 7.13.

3-(4-Formylstyryl)-8*H*,12*H*-6,7,10,11-tetrahydroquinolizino[*g*,*h*]-1,4-benzoxazin-2-one (**7f**).

On reacting with terephthalcarboxaldehyde (1 g) the dye **5a** led to the styryl derivative in 95% yield; the crystallization was performed from pyridine as dark-red needles; this dye displays a deep red fluorescence in various organic solvents, mp 256°; uv: λ max, nm (ε) 263 (6500), 332 (11900), 522 (28400); fluorescence: λ max, nm (φ) 621 (0.12); ir: ν cm^{-1} 3040 (CH=CH), 2930, 2840 (CH_2), 1710, 1690 (C=O lactone and aldehyde), 1615 (C=N); ^1H nmr: 8.16 (d, 1H, J = 16), 7.62 (d, 1H, J = 16), 7.95-7.60 (m, 4H); ms: m/e (relative intensity) 372 (M, 100), 344 (21), 343 (20), 171 (5).

Anal. Calcd. for $C_{23}H_{20}N_2O_3$: C, 74.19; H, 5.38; N, 7.53. Found: C, 74.20; H, 5.30; N, 7.53.

We thank Thierry SACAZE for his excellent technical assistance.

BIBLIOGRAPHY AND NOTES

* Unité associée au CNRS N° 1103 "Physico-Chimie Organique appliquée".

[1] G. A. Reynolds and K. H. Drexhage, *Opt. Commun.*, **13**, 222 (1975).

[2] K. H. Drexhage, "Topics in Applied Physics", Vol **1**, Dye Lasers", 147, F. P. Schäfer, ed, Springer Verlag, Berlin, 1973.

[3] K. H. Drexhage, *Laser Focus*, **9**, 35 (1973).

[4] K. H. Drexhage, *J. Res. Nat. Bur. Stand. A*, **80A**, 421 (1973).

[5] G. Jones II, W. R. Jackson and A. M. Halpern, *Chem. Phys. Letters*, **72**, 391 (1980).

[6] G. Jones II, W. R. Jackson, C. Y. Choi and W. R. Bergmark, *J. Phys. Chem*, **89**, 294 (1985).

[7] Z. R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, D. J. Cowley and W. Bauman, *Nouv. J. Chim.*, **3**, 443 (1979).

[8] Z. R. Grabowski and J. Dobkowski, *Pure Appl. Chem.*, **55**, 245 (1983).

[9] W. Rettig, *Angew. Chem., Int. Ed. Engl.*, **25**, 971 (1986).

[10] K. Rotkiewicz and G. Köhler, *J. Lumin.*, **37**, 219 (1987).

[11] M. T. Le Bris, *J. Heterocyclic Chem.*, **21**, 551 (1984).

[12] M. T. Le Bris, *J. Heterocyclic Chem.*, **22**, 1275 (1985).

[13] F. Dupuy, C. Rulliere, M. T. Le Bris and B. Valeur, *Opt. Commun.*, **51**, 36 (1984).

[14] M. T. Le Bris and C. Rulliere, French Patent 83 11863 (1983).

[15] M. T. Le Bris, J. Mugnier, J. Bourson and B. Valeur, *Chem. Phys. Letters*, **106**, 124 (1984).

[16] J. Mugnier, Y. Dordet, J. Pouget, M. T. Le Bris and B. Valeur, *Solar Energy Materials*, **15**, 65 (1987).

[17] A. Declemy, C. Rulliere and Ph. Kottis, *Chem. Phys. Letters*, **101**, 401 (1983).

[18] A. Declemy, C. Rulliere and Ph. Kottis, *Chem. Phys. Letters*, **133**, 448 (1987).

[19] This compound was prepared according to U. S. Patent 4,005,092 (1977).

[20] L. F. Fieser, *Org. Synth.*, Coll Vol **II**, 35 (1943).

[21] Photochemical stability was measured by means of Suntest apparatus (Supplier: Original Hanau).