

# Aminopyrido[2,3-c]-1,2,6-thiadiazine 2,2-dioxides as laser dyes

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## Abstract

Measurements of the spectral and temporal characteristics and energy efficiency of the neutral and acidic species of 4-amino-1,7-dimethylpyrido[2,3-c]-1,2,6-thiadiazine 2,2-dioxide (compound N1) and 4-amino-7,8-dimethylpyrido[2,3-c]-1,2,6-thiadiazine 2,2-dioxide (compound N2) in dimethylsulphoxide and acetonitrile have been performed. Continuous lasing of N1 from 0 to 1 M total proton concentration reveals simultaneous lasing of the neutral (N) and acidic (A) species of N1.

*Keywords:* Dye lasers; Intermolecular proton transfer; Acid–base processes; Multifrequency lasers; Broadband lasers

## 1. Introduction

Aminopyrido[2,3-c]-1,2,6-thiadiazine 2,2-dioxides undergo acid–base processes in the ground and excited states in acetonitrile [1]. Dyes undergoing acid–base processes are useful and interesting for several reasons. An extreme case of the latter process involves intermolecular proton transfer. For example, when the acidities ( $pK$  values)<sup>1</sup> in the ground and excited states are very different, the formation of a certain species absent in the ground state can be photoinduced in the excited state [2–4], leading to a high population inversion and, consequently, to efficient laser dyes. In an intermediate case, i.e. similar  $pK$  values in the ground and excited states, the acidic and neutral species can coexist in the ground and excited states over a wide range of proton concentrations in the solution. In mixtures of these dyes, the proportions of the species can be controlled by the proton concentration in the solution, giving several advantages: if the two species involved have different emission spectra, the tuning range may be widened [5–8]; on the other hand, simultaneous lasing (two-band lasing) of the two species may be observed (multifrequency laser) [5–7].

<sup>1</sup> We talk about the  $pK$  value of a deprotonation reaction, i.e.  $A \rightleftharpoons N + H^+$ , and thus  $pK = -\log([N][H^+]/[A])$ , where  $[A]$  is the molar concentration of the protonated or acidic species,  $[N]$  is the molar concentration of the neutral species and  $[H^+]$  is the molar concentration of free protons.

We have studied [1] the spectroscopic characteristics of 4-amino-1,7-dimethylpyrido[2,3-c]-1,2,6-thiadiazine 2,2-dioxide (compound N1) and 4-amino-7,8-dimethylpyrido[2,3-c]-1,2,6-thiadiazine 2,2-dioxide (compound N2) in dimethylsulphoxide (DMSO) and acetonitrile. A single neutral species was detected in DMSO for both compounds. In acetonitrile, an acid–base process between a neutral (N) and an acidic (A) form was detected and characterized through the  $pK$  values in the ground state and  $pK^*$  values in the excited state (N1:  $pK = 2.0$ ,  $pK^* = 2.3$ ; N2:  $pK = 2.9$ ,  $pK^* = 4.0$ ). Absorption maxima in the range 326–384 nm were observed depending on the compound and species. Fluorescence maxima in the range 413–469 nm, with relatively high quantum efficiencies (0.3–0.7), were obtained.

## 2. Experimental details

### 2.1. Materials

The compounds were synthesized by the research group of P. Goya (Instituto de Química Médica (CSIC), Juan de la Cierva 3, E-28006 Madrid, Spain) with microanalytical purity [9] and were used without further purification. The structural formulae of the compounds are shown in Fig. 1. The solvents used were DMSO and acetonitrile (Uvasol quality, Merck, 0.3% maximum water content). To acidify the solutions in acetonitrile, concentrated perchloric acid (Fluka, puriss., 70%) was used [10].

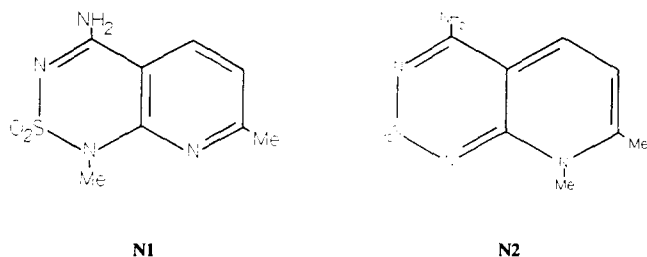


Fig. 1. Molecular formulae of the compounds studied.

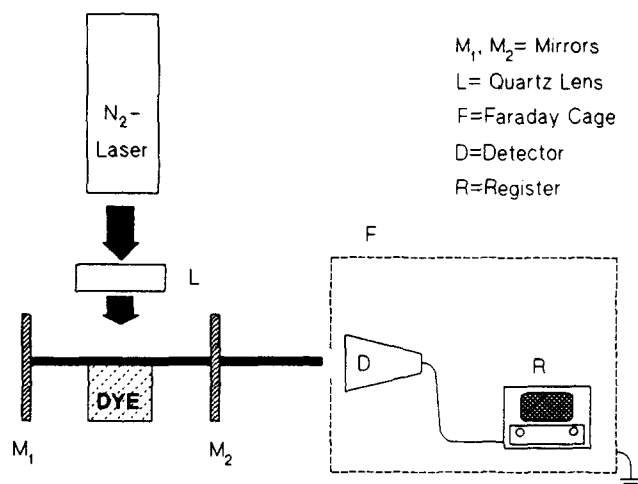


Fig. 2. Experimental set-up for laser measurements.

## 2.2. Experimental set-up

Laser measurements were performed with the geometry described in Fig. 2. Transverse pumping with a pulsed  $N_2$  laser (337 nm, 3.7 ns full width at half-maximum (FWHM), 0.5 mJ per pulse) was used. The pumping pulse was focused with a cylindrical fused silica lens (L) over the front inner face of a fused silica cell (length, 1 cm), filled with the air-saturated dye solution at room temperature. The cell was tilted by about  $10^\circ$  to avoid feedback from the cell walls. The external resonator was 3 cm in length, with two mirrors ( $M_1, M_2$ ) of reflectivities  $R_1 \approx 95\%$  and  $R_2 \approx 20\%$ . The different lasing characteristics were detected by the different detectors (D) and registered by devices (R) (Fig. 2).

In energy measurements, D is a thermopile (continuous wave sensitivity,  $10 \mu\text{W}$ ) and R is a digital voltmeter. Measurements were taken at a rate of 4 pulses  $\text{s}^{-1}$  and the lasing energy efficiency  $\Phi_1$  was calculated as the quotient between the dye output energy and the pump energy ( $N_2$  laser energy after going through lens L). The resonator was calibrated with Coumarin 500 ( $1 \times 10^{-2}$  M in ethanol), obtaining 34% energy efficiency.

The temporal shape of the dye output pulse was detected with a planar-type photocell (ITL TF 1850) (detector D) (0.1 ns rise time, S-20 spectral response),

connected ( $50 \Omega$  line matched) to a digital transient register (Tektronix SCD1000) (register R) (1 GHz real time bandwidth) in external trigger mode. Detection was performed inside a Faraday cage to avoid electric stray noise. The accuracy was 1024 points for 20 ns.

For spectral measurements, the dye pulse was guided with an optical fibre to a plain field monochromator, equipped with a diffraction grating for the blue region of the spectrum ( $1200 \text{ lines mm}^{-1}$  over 25 mm), followed by an optical multichannel analyser (OMA) (D and R) with 512 channels over 1.25 cm (total resolution, 0.1 nm). The spectral scale was calibrated with low pressure spectral lamps. Each laser spectrum was accumulated during 50 cycles and plotted in an X-Y register.

Concentrated solutions were prepared ( $1 \times 10^{-2}$  M) to ensure a situation above the estimated threshold [1]. At this concentration, for the pK values in acetonitrile [1], species N predominates in the solution. The addition of concentrated acid is required to form species A (without addition of too much water to the solution). Sometimes a thermal bath in an ultrasound container was used to aid the solubility. The absorption spectrum of a thin film of the solution inside two fused silica windows (due to the high optical density) was obtained to guarantee the composition N:A and to ensure that no degradation or dimer formation had occurred.

## 3. Results

The results are summarized in Table 1.  $M_0$  and  $A_0$  refer to the total molar concentrations of dye and acid in the solution.

### 3.1. Results in DMSO

#### Compound N1

A  $1.2 \times 10^{-2}$  M solution was initially prepared and later diluted (Table 1). In some cases, relaxation oscillations were obtained (Fig. 3). A typical blue shift with dilution was observed. In the less concentrated solution, alignment defects due to imperfections in the cuvette were more significant, and a gradual extinction of the laser pulse was observed, which was recovered by stirring the solution. This shows the influence of the viscosity of DMSO. No degradation was observed after 5000 pulses.

#### Compound N2

This compound has an absorption minimum at  $\lambda = 337$  nm and, due to its limited solubility in DMSO, an  $N_2$  laser is not appropriate for excitation.

Table 1  
Lasing characteristics of aminopyrido[2,3-c]-1,2,6-thiadiazine-2,2-dioxides

Compound (solvent), species	Concentration (M)	Efficiency $\phi_1$ (%)	$\Delta\tau$ (ns)	$\lambda_{\max}$ (nm)	$\Delta\lambda$ (nm)
N1 (DMSO)	$M_0 = 1.2 \times 10^{-2}$		0.9 <sup>a</sup>	414	6
	$M_0 = 0.8 \times 10^{-2}$	6	0.8 <sup>a</sup>	412	6
	$M_0 = 0.53 \times 10^{-2}$	2	1.0	411	7
N1 (Acetonitrile), species N	$M_0 = 1.1 \times 10^{-2}$	8	2.6 <sup>a</sup>	410	6
	$M_0 = 0.7 \times 10^{-2}$	7	0.7 <sup>a</sup>	410	6
	$M_0 = 0.5 \times 10^{-2}$	7	0.7 <sup>a</sup>	410	6
N1 (acetonitrile), species A	$M_0 = 1.1 \times 10^{-2}, A_0 = 0.55$	5	0.7 <sup>a</sup>	406	5
	$M_0 = 1.1 \times 10^{-2}, A_0 = 1.12$	3	1.2 <sup>a</sup>	408	6
N2 (acetonitrile), species A	$M_0 = 1 \times 10^{-2}, A_0 = 1.3$	14	3.0 <sup>a</sup>	463	8

<sup>a</sup> With relaxation oscillations.

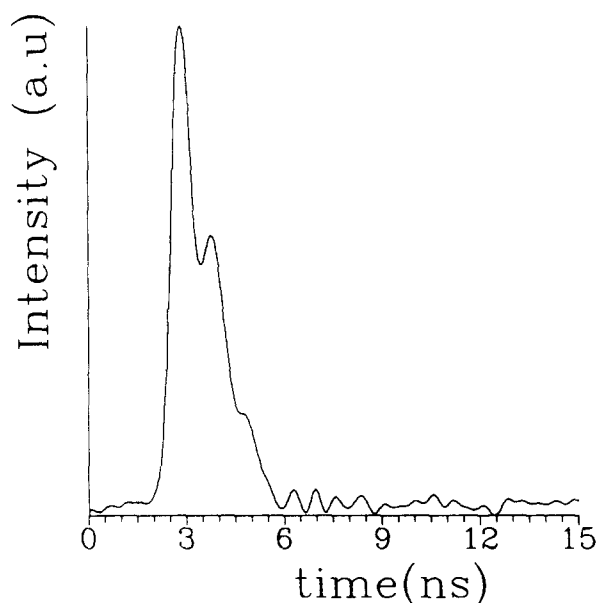


Fig. 3. Temporal evolution of the laser emission of compound N1 in DMSO.  $M_0 = 1.2 \times 10^{-2}$  M.

### 3.2. Results in acetonitrile

At concentrations of approximately  $10^{-2}$  M, only species N is present in the solution, as calculated from the corresponding pK value. The addition of concentrated perchloric acid leads to acidic species A. Relaxation oscillations are frequently encountered in the temporal shapes and no degradation is observed after 5000 pulses.

#### Compound N1

Species N was prepared at a concentration of  $1.1 \times 10^{-2}$  M with later dilution, and showed laser emission with the characteristics summarized in Table

1. The addition of perchloric acid (0.55 M) led to a mixture of species N and A; further addition of acid up to  $A_0 = 1.1$  M resulted in a solution containing only the protonated species A; both solutions exhibited the laser characteristics described in Table 1.

#### Compound N2

Form N does not reach sufficient solubility (saturation concentration less than  $1.3 \times 10^{-2}$  M) and the excitation radiation is not sufficiently absorbed. The addition of acid aids solubility and leads to form A, which prepared at  $M_0 = 1 \times 10^{-2}$  M and  $A_0 = 1.3$  M lases efficiently (Table 1).

### 4. Conclusions

The characteristics of the laser emission of aminopyrido[2,3-c]-1,2,6-thiadiazine 2,2-dioxides reveal a new family of laser dyes which are reasonably efficient and stable. The most outstanding characteristic is the simultaneous lasing of the neutral and acidic species of derivative N1 in acetonitrile, but as the fluorescence spectra of the two species overlap, it cannot be used as a multifrequency laser. Other substituents in positions 1 and/or 7 could lead to this possibility.

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