

N. F. Haley

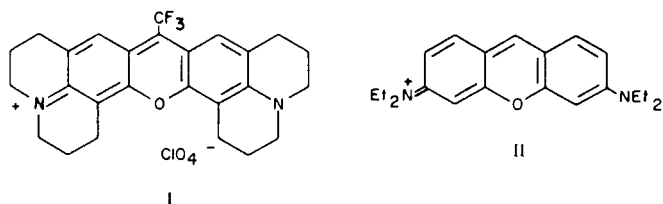
Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

Received March 4, 1977

A one-step procedure is described for the preparation of the title compound I, an efficient laser dye operating in the red region.

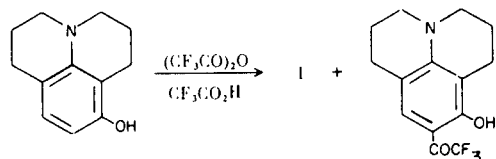
*J. Heterocyclic Chem.*, 14, 683 (1977).

In our search for a more efficient laser dye operating in the red region of the spectrum, we have designed the pyronine dye I, whose molecular structure incorporates several of the more important features which have been suggested for efficient lasing (1). We basically have modified Pyronine B (II) in two ways. We have increased the lone pair electronic interaction of the amino nitrogen



atoms with the  $\pi$ -system by making the *N*-ethyl groups rigid through bonding to the aromatic rings. Also, substitution of a trifluoromethyl group at the 9-position of Pyronine B (II) was expected to dramatically increase the light stability of I as has been demonstrated previously for a series of coumarin laser dyes (2). The fact that the *N*-ethyl groups were rigidly coupled with the electron withdrawing nature of the trifluoromethyl group shifted the absorption maximum of I compared to Pyronine B (II) toward the red region of the spectrum [552 nm (II) to 647 nm (I)]. We report in this note a simple, one-step synthesis of I from commercially available starting materials.

The preparation starting from 8-hydroxy-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizine (8-hydroxyjulolidine) (3) employs a condensation with trifluoroacetic anhydride in the presence of a catalytic amount of trifluoroacetic acid to produce the title compound (I) along with 8-hydroxy-9-trifluoroacetyl-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizine as a minor by-product. The separation of I from III presents no problem since I crystallizes from the reaction mixture upon addition of perchloric acid. The optical properties of I will be presented elsewhere.



#### EXPERIMENTAL (4)

8-(Trifluoromethyl)-2,3,5,6,11,12,14,15-octahydro-1*H*,4*H*,10*H*, 13*H*-diquinolizino[9,9*a*,1-*bc*:9'*a*',1-*hi*]xanthylium perchlorate (I).

8-Hydroxy-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizine (1.9 g., 0.01 mole), trifluoroacetic anhydride (8.4 g., 0.04 mole), trifluoroacetic acid (0.5 ml.) and methylene chloride (15 ml.) were stirred together for 72 hours at 20° under a dry nitrogen atmosphere. The solvent was evaporated under vacuum and ethanol (25 ml.) containing 70% perchloric acid (3.0 g.) was added with stirring. Filtration gave purple-bronze needles, 2.0 g. (74%), m.p. 203-205° dec.; nmr (deuteriochloroform):  $\delta$  2.1 (m, 8, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.9 (bt, 8, CH<sub>2</sub>CH<sub>2</sub>Ar), 3.6 (t, 8, J = 5 Hz, N-CH<sub>2</sub>CH<sub>2</sub>), 7.5 (bs, 2, aromatic); ir (potassium bromide): 1580, 1475, 1280, 1080 (ClO<sub>4</sub><sup>-</sup>) cm<sup>-1</sup>; mass spectrum: m/e 439 (M<sup>+</sup>); absorption max (ethanol): 647 nm ( $\epsilon$ , 98,000), 595 nm ( $\epsilon$ , 40,700).

*Anal.* Calcd. for C<sub>26</sub>H<sub>26</sub>ClF<sub>3</sub>N<sub>2</sub>O<sub>5</sub>: C, 57.9; H, 4.9; N, 5.2; F, 10.6. Found: C, 57.8; H, 4.7; N, 5.3; F, 10.5.

8-Hydroxy-9-trifluoroacetyl-2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizine (III) (5).

The filtrate from the above reaction was poured into water (200 ml.) and extracted with 200 ml. of diethylether. The ether layer was separated and evaporated *in vacuo*. The residue was chromatographed on silica gel eluting with methylene chloride. Evaporation of the methylene chloride yielded a yellow oil which deposited yellow crystals from cyclohexane. Filtration gave 0.3 g. m.p. 85.4-86.5°; nmr (deuteriochloroform):  $\delta$  1.9 (pentuplet, 4, J = 6 Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.6 (t, 4, J = 6 Hz, CH<sub>2</sub>CH<sub>2</sub>Ar), 3.3 (t, 4, J = 6 Hz, CH<sub>2</sub>CH<sub>2</sub>N), 7.1 (bs, 1H, aromatic), 13.6 (s, 1H, OH); ir (potassium bromide): 3200-2700 (H-bonded OH), 1630 (C=O) cm<sup>-1</sup>; mass spectrum: m/e 285 (M<sup>+</sup>).

*Anal.* Calcd. for C<sub>14</sub>H<sub>14</sub>F<sub>3</sub>NO: C, 58.9; H, 4.9; N, 4.9; F, 20.0. Found: C, 58.6; H, 4.7; N, 4.6; F, 19.9.

#### REFERENCES AND NOTES

- (1) K. H. Drexhage in "Topics in Applied Physics", Vol. 1, "Dye Lasers", F. P. Schaffer, Ed., Springer-Verlag, 1973, p. 144-193.
- (2) P. R. Hammond and R. L. Atkins, *J. Heterocyclic Chem.*, 12, 1061 (1975).
- (3) Available from Eastman Organic Chemicals, Eastman Kodak Company, Rochester, N.Y.
- (4) Melting points are uncorrected. Infrared spectra were determined by means of a Perkin-Elmer 137 spectrometer, ultraviolet and visible spectra by means of a Cary 17 spectrometer, nmr spectra by means of a Varian T-60 spectrometer and mass spectra by means of a Hitachi RMS-4 spectrometer.
- (5) It is probable that the minor by-product is the 8-trifluoroacetoxy derivative which is hydrolyzed during the separation to III.