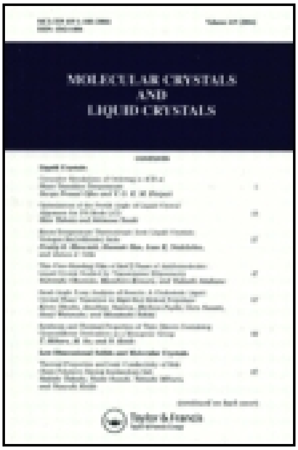


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Water Soluble Organic Photochromes: Sulphonated Spiro (Indolinonaphthoxazines)

Pietro Allegrini [a] & Vincenzo Malatesta [a]

[a] Enichem Synthesis, Via Maritano 26, 20097 San Donato Milanese, Milano, Italy

Version of record first published: 24 Sep 2006.

To cite this article: Pietro Allegrini & Vincenzo Malatesta (1994): Water Soluble Organic Photochromes: Sulphonated Spiro (Indolinonaphthoxazines), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 25-28

To link to this article: http://dx.doi.org/10.1080/10587259408037781

Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 25–28
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

WATER SOLUBLE ORGANIC PHOTOCHROMES: SULPHONATED SPIRO (INDOLINONAPHTHOXAZINES).

PIETRO ALLEGRINI , VINCENZO MALATESTA
Enichem Synthesis, Via Maritano 26, 20097 San Donato Milanese, Milano, Italy.

Abstract. Two photochromic disulphonated spiro (indolino-naphthoxazines) have been synthesized. Both compounds crystallize in the open merocyanine form. The molar extinction coefficients of the coloured forms have been calculated and the rate constant k_b for the thermal bleaching measured. The presence of sulphonic groups lowers the k_b value by two orders of magnitude with respect to that of the unsubstituted compound.

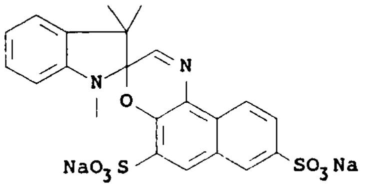
INTRODUCTION

Several studies have been carried out on spiro (indolino-naphthoxazines) because of their good photochromic properties, i.e. colourability and photochemical fatigue resistance. The mechanism of the photochemical ring opening reaction has been elucidated[1,2] and the parameters of the thermal and photochemical bleaching reaction measured[3,4]. The determination of the quantum yields of photocolouration and the characteristics of the coloured forms, i.e. their molar absorption coefficients has been attempted.

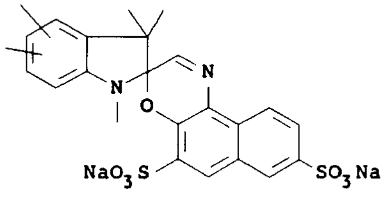
The measurement of the $\varepsilon(\lambda_{max})$ of the merocyanine forms is, in our opinion, the main outstanding matter in the spiroxazines field because it allows a correct understanding of the differences of colourability observed between different compounds of this class. Some authors[5,6,7] have proposed to measure the molar absorption coefficients of the coloured forms at low temperatures to prevent the thermal ring closure. This method assumes that the isomeric composition of the open forms is not influenced by the temperature. Other workers have determined the $\varepsilon(\lambda_{max})$ of the photomerocyanines with a modified Fischer's method[8]. In this paper we wish to report on the calculation of the molar extinction coefficients of a disulphonated spiro (indolinonaphthoxazine) in aqueous solution obtained in an independent way.

RESULTS

Compounds (1) and (2) (disodium salt of 1,3-dihydro-5',8'- disulfonated -1,3,3-trimethyl spiro [2H-indole-2,3'-[3H]naphtho-(2,1b)-(1,4)-oxazine] and disodium salt of the mixture of isomers 1,3-dihydro-5',8'- disulphonated-1,3,3,4,5- and -1,3,3,5,6-pentamethyl spiro [2H indole-2,3'-[3H]naphtho-(2,1b)-(1,4)-oxazine] respectively were synthesized by a known method[9].



(1)



(2)

The crude products were crystallized from methanol after treating the solution with active charcoal. Compounds (1) and (2) were obtained in the open form as deep blue powder and were characterized by ^{1}H NMR (d_6-DMSO and D_2O). Compound (2) was chosen for the molar extinction coefficient measurement because of its slower fading rate to spiroxazine. The molar ratio of merocyanine form was determined following the evolution of ^{1}H NMR spectrum (D_2O) with time (Fig. 1).

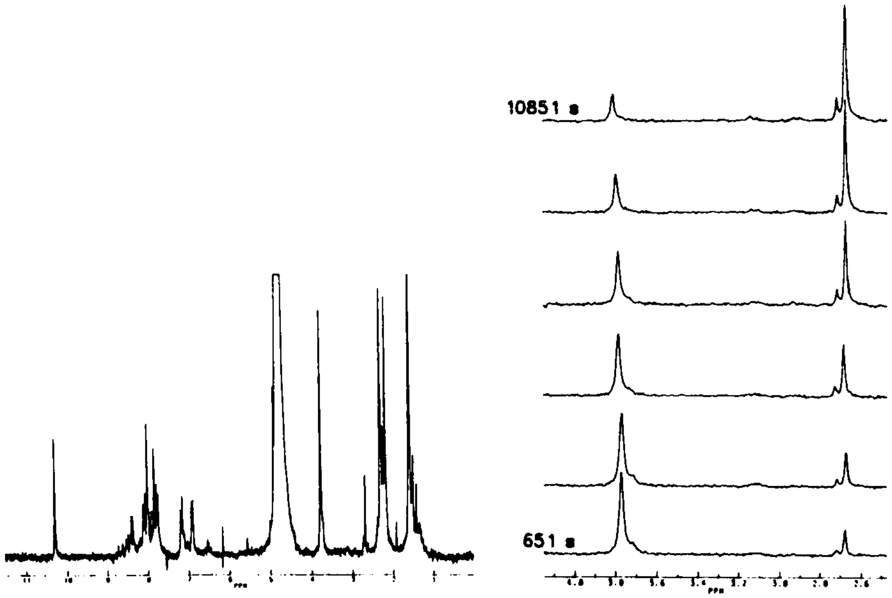


FIGURE 1 ^{1}H-NMR of (2) and kinetic NMR experiment

The results were interpolated using the following equation :

$$Xo(t) = Xo(0) \cdot e^{-kt} \quad \text{where:}$$

Xo(t) is molar fraction of the open form at time t; Xo(0) is molar fraction of the open form at time 0 ; k is the thermal bleaching rate constant.

The Xo(t) were calculated from the intensity of the NCH_3 signals of the open and closed form respectively. Extrapolating the value of molar fraction of the open form to t=0 (time at which the solvent i.e. deuterium oxide was added to compound (2)) we determined that the content of open form in the powder was 92.7 % .

The kinetic experiment was then repeated at lower concentration and followed by monitoring the variations of the UV-VIS spectrum. Plotting the decrease of absorption at λ_{max} of the open form versus time , we were able to extrapolate the absorption value to the initial time and then calculate the ε value at maximum of absorption of the coloured form with the Lambert Beer law. The relevant data are presented in Table 1.

TABLE 1 Values of ε(600nm) and thermal bleaching rate constants (k)

COMPOUND	ε (dm^3 mol^{-1}cm^{-1})·10^4	k (s^{-1})	conc. (M)
2 $^{(b)}$	–	1.65 10^{-4}	3.6 10^{-2}
2 $^{(a)}$	3.77	1.29 10^{-3}	1.2 10^{-5}
2 $^{(a)}$	4.06	1.94 10^{-3}	2.59 10^{-6}
3 $^{(c)}$	–	0.67	2.5 10^{-5}

a) determined by UV in water
b) determined by ^{1}H–NMR in deuterium oxide
c) determined by UV in ethanol[3]

DISCUSSION

Compound (1) and (2) can be crystallized in the open form from methanol. The low rate of the bleaching reaction of compound (2), allowed us to determine the molar extinction coefficients for this product. The values we obtained in our work are not comparable with those already calculated by other authors because of structures and solvents differences, although they are of the same order of magnitude (3.77-4.06 x 10^4 versus 5.1 x 10^4 for unsubstituted spiro (indolino naphthoxazine) (3)[8]).

The decrease of both the $\varepsilon(\lambda_{max})$ and the thermal bleaching rate constant observed when the dye concentration was increased, can be easily ascribed to the formation of aggregates of the open form. The effect is particularly detectable in the ^{1}H-NMR kinetic experiment in which we measured a k_b value of 1.65 x 10^{-4} s^{-1} at a concentration of about 3.6 x 10^{-2} M.

A comparison of k_b values of Table 1 with that already reported by Guglielmetti and coworkers[3] for compound (3) in ethanol (k_b=0.67 s^{-1}) shows that ring closure is about 500 times slower in the case of compound (2). This big variation is probably due to entropic effects deriving from a drastic reorganization of the solvatation shell required for the ring closure to spiroxazine, rather than to a stabilizing interaction by the sodium cation of the open merocyanine form[10].

ACKNOWLEDGEMENTS

We thank Mr. L. Lanzini for NMR analyses and dr. D. Fabbri for helpful discussions. The financial support of M.U.R.S.T. is also gratefully acknowledged.

REFERENCES

1. S. Aramaki and G. H. Atkinson, Chem. Phys. Lett., 170, 181 (1990).
2. S. Schneider, A. Mindl, G. Elfinger and M.Melzig, Ber. Bunseges. Phys. Chem., 91, 1222 (1987).
3. E. Pottier, R. Dubest, R. Guglielmetti, P. Tardieu, A. Kellmann, F. Tfibel, P. Levoir and J. Aubard, Helv. Chim. Acta, 73, 303 (1990).
4. C. Bohne, M. G. Fan, Z. Li, J. Lusztyk and J. Scaiano, J. Chem. Soc. Chem. Commun. 571 (1990).
5. N. Y. C. Chu, Can. J. Chem., 61, 300 (1983).
6. A. S. Kholmanskii and K.M. Dyumaev, Dokl. Akad. Nauk. SSSR, 303, 1189 (1988).
7. A. G. Ovcharenko, A. V. Lyubimov, V. Yu. Nedoshivin, V. S. Marevtsev and M.I. Cherkashin, Izv. Akad. Nauk. SSSR, Ser. Khim., 3, 543 (1990).
8. F. Wilkinson, J. Hobley and M. Naftaly, J. Chem. Soc. Faraday Trans., 88, (11) 1511 (1992).
9. T. Yoshihara, K. Kagawa and H. Yoshinaga, JP 48023787 (1973).
10. T. Tamaki and K. Ichimura, J. Chem. Soc. Chem. Commun., 1477 (1989).