Dyes and Pigments, Vol. 38, Nos 1-3, pp. 97-105, 1998

PII: S0143-7208(97)00114-9
0143-7208/98 $19.00+0.00

Hydrolytic Breakdown of Meso-diphenylamine Substituted Heptamethine Dye IR140 and Isomerism of the Merocyanine Breakdown Product

Robert Gray, David Walton, John Bickerton, Paul Richards & John Heptinstall*

School of Natural and Environmental Sciences, Coventry University, Priory Street, Coventry, CV1 5FB, UK

(Received 28 October 1997; accepted 21 November 1997)

ABSTRACT

Nucleophilic attack by hydroxyl ions is found to occur preferentially at the C_2 *position of the benzothiazolium heterocyclic moiety of the laser dye IR140, and not at the eneamine functionality that consists of the meso-carbon atom and the adjacent diphenylamine moiety, which is the other electrophilic site on the dye. The temperature-dependence of the absorption spectrum of the merocyanine breakdown product suggests that similar ground state isomerism is present in the breakdown product, as is found in the initial dye IR140. It is concluded that the non-fluorescent majority conformer of the merocyanine breakdown product is the one in which the meso-amine substituent is twisted so as to withdraw electron density by induction, and that the fluorescent minority conformer is that in which themeso-amine substituent is conjugated to act as an electron donor by resonance. © 1998 Elsevier Science Ltd. All rights reserved*

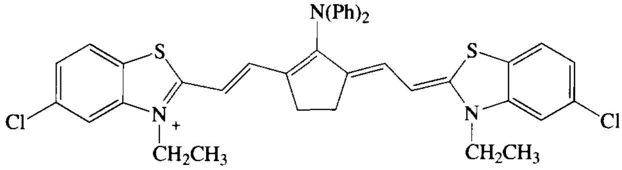
Keywords: cyanine, heptamethine, fluorescence, hydrolysis, IR140, conformers.

INTRODUCTION

Published studies on the meso-diphenylamine substituted heptamethine dye IR140 (Fig. 1), have primarily been concerned with its lasing and photographic sensitizing characteristics [1, 2]. However, our recent work on its

---

*Corresponding author.



absorption and fluorescence properties indicates that ground state isomerism of IR140 involves the twisting of the meso-diphenylamine substituent [3]. This results in two isomeric forms of the dye, with the majority of dye molecules at room temperature possessing a meso-nitrogen atom that withdraws electron density from the chromophoric chain by induction, while the minority of dye molecules possess a meso-nitrogen atom that donates electron density into the chromophoric chain by resonance. This difference in interaction between the chromophoric chain and the meso-nitrogen atom leads to the two isomeric forms possessing different absorption maxima and absorption band profiles; indeed, the isomer in which the meso-nitrogen atom donates electron density by resonance can be considered to have considerable trinuclear character. To further illustrate and investigate isomerism of this type we have synthesized the merocyanine derivative meroIR140 (Fig. 2), which is a product of breakdown of IR140 by nucleophilic substitution, and studied its absorption and fluorescence characteristics. This may help in understanding the chemistry of these commercially important dyes.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker AC250 with Me_4Si as an internal reference. IR spectra were recorded (KBr discs) on a Phillips PU9800 FTIR spectrophotometer. Fluorescence spectroscopy was performed on a Perkin Elmer LS50 spectrophotometer and absorption spectroscopy on a Shimadzu UV2100 spectrophotometer.

IR140, laser grade, was supplied by Eastman Kodak Ltd. and used without further purification: its spectroscopic properties are as follows: ^{1}H NMR, CD_3OD, 50°C:δ 1.35(t,6H,CH_3), 2.88(s,4H,CH_2), 4.23(q,4H,CH_2), 5.95(d,2H,vinyl), 6.91(d,2H,vinyl), 7.17 to 7.28(m,8m,8H, diphenylamine H), 7.37 to 7.59(m,6H, aromatic), 7.71(d,2H,diphenylamine H).

The merocyanine breakdown product mero IR140 (Fig. 2) was prepared by the phase-transfer-catalysed hydrolysis of IR140. IR140 (80 mg) was dissolved in CH_2Cl_2(50 ml) and 1 M NaOH (50 ml) containing $(C_4H_9)_4$ N^+ Br^-(100 mg). The mixture changed colour from violet (attributable to IR140, λ_{max} = 806 nm in CH_2Cl_2) to green, probably due to a mixture of the

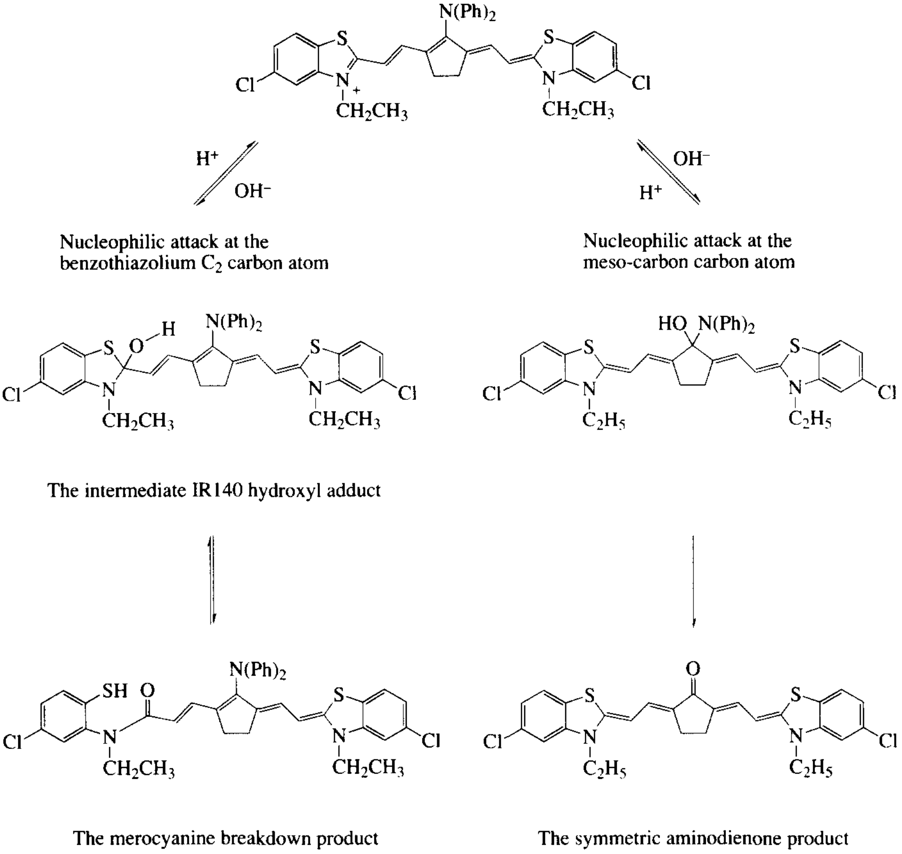


Fig. 2. Nucleophilic attack upon IR140 at either the benzothiazolium C_2 carbon atom or the meso-carbon atom.

intermediate hydroxyl adduct (Fig. 2) $\lambda_{max} = 418$ nm in CH_2Cl_2, together with unreacted IR140, and then to pink (attributable to the merocyanine product alone, $\lambda_{max} = 510$ nmin CH_2Cl_2). After 3 h the CH_2Cl_2 layer was separated, washed three times with H_2O and evaporated. The resultant green crystals were dissolved in methanol (2 ml) and recrystallized using H_2O (30 ml, 80°C). Further purification was achieved using silica gel column chromatography with methanol as eluent. Merocyanine breakdown product, mero 140 (Fig. 2), yield 85%, IR(KBr) υ 1661 cm^{-1} (conjugated ketone) ^{1}H NMR, CD_3OD, 20°C: δ1.03(t,3H,CH_3), 1.19(t,3H,CH_3), 2.33 to 2.54(M,4H,CH_2), 3.35(s,1H,SH), 3.59(q,2H,NCH_2), 3.61(q,2H,NCH_2), 4.78(d,1H,vinyl), 5.09(d,1H,vinyl), 5.77(d,1H,vinyl), 6.51(S,1H,aromatic), 6.70(d,1H,aromatic), 7.0(s,1H,aromatic), 7.01(d,1H,aromatic), 7.04 to 7.19(m,8H,diphenylamine H), 7.10(d,1H,aromatic), 7.16(d,1H,aromatic), 7.41(d,1H,vinyl), 7.49(d,2H,diphenylamine H).

The intermediate IR140 hydroxyl adduct (Fig. 2) was prepared by dissolving IR140 in CD_3OD with addition of $NaOCD_3$ in CD_3OD dropwise until reaction was deemed complete, as evidenced by no further change to NMR spectrum. The intermediate IR140 hydroxyl adduct (Fig. 2), 1H NMR, CD_3OD, 20½C: d, 1.01(t,3H,CH_3), 1.21(t,3H,CH_3), 2.36(S,4H,CH_2), 3.01(q,2H,NCH_2), 3.67(q,2H,NCH_2), 5.23(d,1H,vinyl), 5.73(d,1H,vinyl), 5.83(d,1H,vinyl), 6.34(S,1H,aromatic), 6.60(d,1H,aromatic), 6.64(S,1H,aromatic), 6.68(d,1H,vinyl), 6.76(d,1H,aromatic), 6.93(d,1H,aromatic), 7.03 (d,1H,aromatic), 7.10 to 7.26(M,8H,diphenylamine H), 7.71(d,2H diphenylamine H).*

RESULTS AND DISCUSSION

Nucleophilic substitution of IR140 by hydroxyl ions

The preparation of meroIR140 requires nucleophilic attack of IR140 (Fig. 1) by hydroxyl ions at the benzothiazolium C_2 carbon atom; however, IR140 possesses several other electrophilic sites on the chromophoric chain due to the presence of nitrogen atoms. These may donate electrons by resonance of the lone pair into an appropriately conjugated π system,but may also withdraw by induction if orbital overlap is not favoured for steric or other reasons. It is this duality of the role of nitrogen atoms which influences the behaviour of these dye systems. Here the eneamine functionality, comprising the meso-nitrogen atom and the adjacent carbon double bond within the chromophoric chain, causes the meso-carbon atom of the chromophoric chain to be particularly electrophilic, as are the alternate carbon atoms along the chain in conjugation with it. Furthermore, the terminal heterocyclic nitrogen atoms further increase the electrophilic character of the adjacent benzothiazolium C_2 carbon atoms and alternate carbon atoms in conjugation. Therefore, both the terminal and meso-nitrogen atoms cause increased electrophilic character at the same carbon atoms along the chromophoric chain.

Nucleophilic attack by hydroxyl ions on unsubstituted cyanine dyes has been reported to occur at the benzothiazolium C_2 carbon atom [4]. The analogous reaction for IR140 would therefore be expected to give rise to meroIR140 (Fig. 2). However, nucleophilic attack by acetate ion has been reported to occur at the meso-carbon atom of the dimethylindolinium-containing meso-chlorine substituted dye (Fig. 3) [5], leading to the formation of an intermediate acetoxy derivative which hydrolyses to give a symmetric aminodienone product.

*A small amount of contamination by H_2O ensured that the hydroxyl adduct rather than the methoxy adduct resulted.

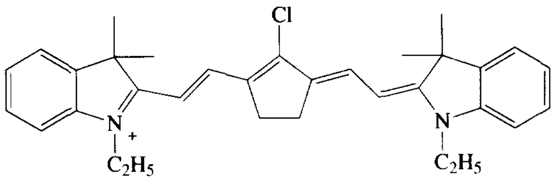


Fig. 3. The meso-chlorine substituted dye studied by Strekowski *et al.* [5].

Nucleophilic attack at the meso-carbon atom of IR140 would similarly result in the loss of the meso-diphenylamine moiety to also give a symmetric aminodienone product (Fig. 2). However, the NMR spectrum of the product of alkaline hydrolysis of IR140 shows the diphenylamine unit. Furthermore, this reaction may be reversed by acidification, indicating that nucleophilic attack of IR140 by phase transfer catalysed hydrolysis occurs primarily at the benzothiazolium C2 carbon atom to give meroIR140 (Fig. 2). In addition, the NMR spectrum of the hydrolytic breakdown product (meroIR140) gives different δ values for the two methylene carbon atoms adjacent to the terminal nitrogen atoms. If nucleophilic attack had taken place at the meso-carbon atom, these carbon atoms would be expected to possess the same δ value in the symmetric aminodienone product (Fig. 2).

Absorption and fluorescence characteristics of meroIR140 (Fig. 2)

Although meroIR140 and IR140 possess the same number of vinyl bonds, the convergent wavelength quality of merocyanine chromophores [6] causes meroIR140 to possess a substantially lower absorption maximum in comparison to IR140 (Table 1). Both cyanine dyes (such as IR140) and merocyanine dyes (such as meroIR140) are isoconjugate with odd-alternate hydrocarbons, which implies that substituents act upon the HOMO and LUMO in accordance with Dewar's rules [7]. Therefore, if the conformational isomerism present in IR140, due to the twisting of the meso-diphenylamine group, is also present in meroIR140, this would result in two different absorption maxima for meroIR140. This is found to be the case, as the fluorescence excitation maximum of meroIR140 does not coincide with its absorption maximum (Table 1), implying that a different species is responsible for absorption at the fluorescence excitation maximum to the one which is responsible for absorption at the absorption maximum. Therefore, like IR140, meroIR140 exists as two ground state conformers, a fluorescent minority conformer possessing a resonance donating meso-nitrogen atom leading to a hypsochromically shifted absorption maximum, in accordance with Dewar's rules, and a non-fluorescent majority conformer possessing an inductively

TABLE 1
Absorbance and Flourescence Characteristics of IR140 and its Hydrolytic Breakdown Products in Methanol

Dye	*Absorption maximum (nm)*	*Molar extinction coefficient* $(\times 10^{-5})$ $(l\ mol^{-1}\ cm^{-1})$	*Excitation maximum (nm)*	*Emission maximum (nm)*	*Flourescence intensity*[a] *(%)*
IR140 (Fig.1)	800	1.61	712	830	100
MeroIR140 (Fig.2)	516	0.42	450	645	17
Intermediate IR140 hydroxyl adduct (Fig. 2)	418[b]	—[c]	—	—	0

[a] Fluorescence output (5) relative to the output of IR140.
[b] 90% methanol/5% sodium hydroxide (1,M) as solvent.
[c] The molar extinction coefficient could not be calculated, as this compound could not be isolated without rapid reversible reaction to IR140 on removal of alkaline conditions.

electron withdrawing meso-nitrogen atom leading to a bathochromically shifted absorption maximum, also in accordance with Dewar's rules.

It is therefore apparent that ring-opening upon one side of the dye molecule, for instance in converting IR140 to meroIR140, does not relieve steric hindrance sufficiently to encourage the meso-diphenylamine to twist into a position in which it can, by resonance, donate electron density into the chromophoric chain. This is consistent with the position of the absorption maxima reported for a series of dyes possessing meso-aniline and meso-N-methylaniline substituents [8]. Despite the reduction size on one side of the amine group, the remaining phenyl moiety discourages the twisting of the meso-amine group as can be seen by the relatively higher absoption maxima for these dyes compared to the less-hindered dimethylamine sustituted analogue.

The very low fluorescence quantum yield of the minority conformer of meroIR140 containing a resonance-donating meso-nitrogen atom (Table 1) can be attributed not only to the low quantum yields generally of unsymmetrical non-rigid donor-acceptor dyes due to the greater number of modes by which vibrational relaxation can take place [9], but also to the branching of the π electron system (three resonance-donating terminal hetero atoms are involved) which is also known to cause a reduction in fluorescence output [10]. Internal absorption of the fluorescence emission by the non-fluorescent majority conformer, whose absorption profile coincides with the emission profile of the minority conformer, also accounts for some loss in the recorded fluorescence output [3].

The temperature-dependence of the absorption spectrum of the merocyanine hydrolysis product is similar to that of IR140[3], in which increasing temperature causes a decrease in absorbance at the absorption maximum,

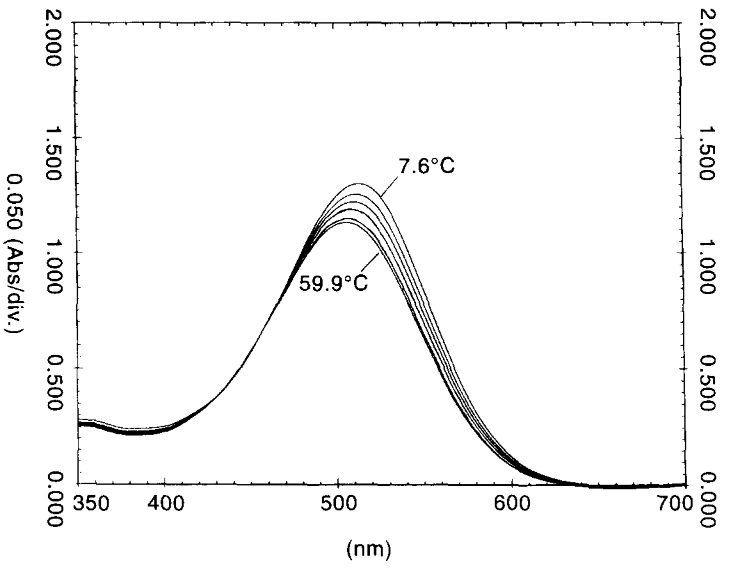


Fig. 4. The temperature dependence of the absorption spectrum of meroIR140 (Fig. 2) in methanol.

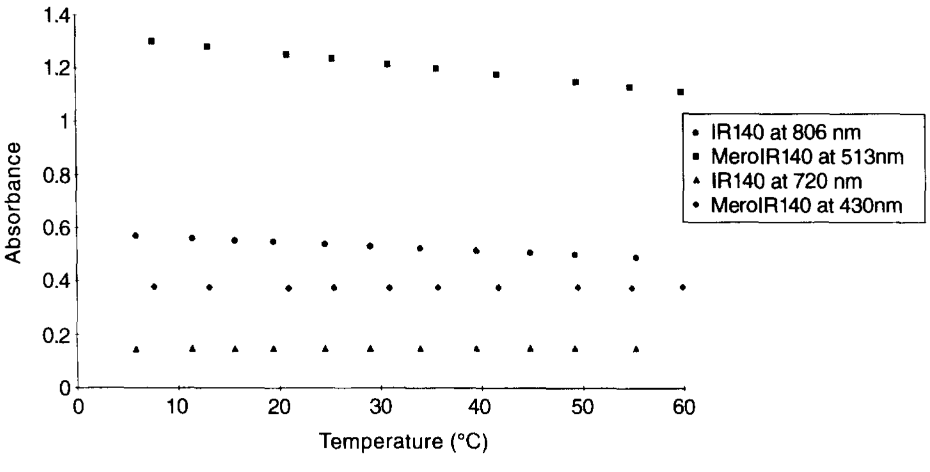


Fig. 5. The variation of the absorbance of IR140 and meroIR140 with temperature.

and a corresponding but smaller increase in the region of the excitation maximum (Fig. 4). These absorption intensity changes are reversible over the temperature range shown, although beyond 60°C there is a loss of some absorption intensity upon reversal, presumably due to irreversible chemical breakdown of the dye. This temperature dependence is consistent with two species in equilibrium, a non-fluorescent species converting to the hypsochromically absorbing fluorescent species as the temperature is increased. It is likely that the extinction coefficient of the fluorescent species is lower than that of the non-fluorescent species, because the decrease in absorbance near the absorbance maximum is not matched by the increase in absorbance near the hypsochromic shoulder (Figs 4 and 5). The lower extinction coefficient of the conformer containing resonance donation from the meso-nitrogen atom is to be expected, because of enhanced bond alternation in this conformer as opposed to the lower bond alternation in the other conformer which contains an inductively electron-withdrawing meso-nitrogen atom. The greater bond alternation due to the presence of a resonance-donating meso-substituent manifests itself in a broader bandwidth, and consequently in a lower extinction coefficient.

CONCLUSIONS

It has been found that IR140, despite containing a meso-enamine group susceptible to nucleophilic attack, reacts with hydroxyl ions preferentially at the C_2 carbon atom, in a similar manner to that reported for unsubstituted benzothiazolium cyanine dyes [5]. Both IR140 (a symmetrical cyanine dye) and its merocyanine breakdown product exhibit a similar isomerism, analogous to the allopolar isomerism found in holomeropolar cyanine dyes [11, 12], due to the twisting in or out of conjugation of a branched π electron system, leading to changes in the absorption and fluorescence characteristics of the differentially twisted isomers. The fluorescence properties of the merocyanine derivative of IR140 are due to the minor, 3-way conjugated conformer and not to the major conformer.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support for this project of a CASE award to R. G. from SERC and Northumbria Biologicals Limited.

REFERENCES

1. Webb, J., Webster, J. and Plaude, B., *Eastman Organic Bulletin*, 1974, **46**, 1.
2. Eastman Kodak Ltd., UK Patent No. 1184496, 1967.
3. Gray, R., Walton, D., Bickerton, J., Richards, P. and Heptinstall, J., *Dyes and Pigments*, 1996, **30**, 321.
4. Metzger, J., Larive, H., Dennilauler, R., Baralle, R. and Gaurat, C., *Bull. Soc. Chim. France*, 1964, **11**, 2868.

5. Strekowski, L., Lipowska, M. and Patonay, G., *Synth. Comm.*, 1992, **22**, 2539.
6. Griffiths, J., *Colour and Constitution of Organic Molecules.* Academic Press, New York, 1976.
7. Dewar, M., *The PMO Theory of Organic Chemistry.* Plenum Press, New York, 1975.
8. Zuguang, Y. and Chin, J., *App. Chem*, 1991, **8**, 82.
9. Tyfuyultov, N. and Fabian, J., *Polymethine Dyes.* St Kliment Chridski University Press, Bulgaria, 1991.
10. Ishchenko, A., Bricks, Y., Kuchkovski, A. and Tolmachev, A., *Dyes and Pigments*, 1987, **8**, 353.
11. Zhu, Z., Zhang, J. and Chen, L., *Dyes and Pigments*, 1994, **25**, 49.
12. Brooker, L., White, F., Heseltine, D., Deyes, G., Dent, S. and Van Lare, E., *J. Phot. Sci.*, 1953, **1**, 173.