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# The pH Control of the Decolouration Rate of Spironaphthoxazine Derivatives

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The thermal stability of the coloured open form of 5-methoxy- (**7**) and 5′-piperidinomethyl-1,3,3-trimethylspiro(indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine) (**6**) is strongly dependent on pH.

Organic photochromic compounds have attracted wide interest, because of their reversible changes not only of colour but also of molecular structure upon irradiation with light.[1] Spironaphthoxazine derivatives, which are among the most popular of these compounds, undergo a photochromic reversible cleavage of the C(spiro)–O bond. They have been applied to light shielding materials, *etc.*, because they are satisfactorily photodurable and exhibit rapid colour changes.

There have been recent reports of attempts to thermally stabilize the coloured open form of spironaphthoxazines

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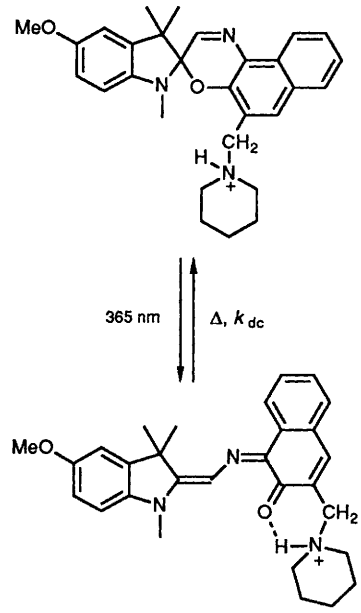
without losing their normal photochromic properties. These involved substitution of long alkyl chains into the indolinyl nitrogen atom,[2] chelation with divalent metals,[3] and deposition onto cellulose polymers.[4] We herein describe a novel type of thermal stabilization for the coloured open form of spironaphthoxazines, based on intramolecular hydrogen bond formation between the quinoidal oxygen and the nearby protonated amino group.

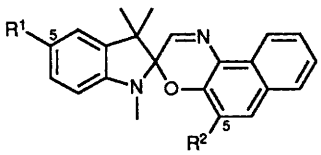
The spironaphthoxazine derivatives (**1**)—(**7**) were prepared by ordinary procedures and identified by NMR spectroscopy. The photocolouration was carried out by using a 500 W high pressure Hg lamp with a 7-51 Corning glass filter. The absorption spectra and thermal decolouration rates were measured by a diode-array spectrophotometer (Hewlett-Packard HP8452A).

In Table 1 are listed the absorption maxima of the coloured open form in the visible region, $\lambda_{max.}$, the absorbance at $\lambda_{max.}$ immediately after UV irradiation, $OD_{max.}$, and the thermal decolouration rate, $k_{dc}$, in acetone and water/acetone [1 : 1 (v/v)].

The value of $k_{dc}$ decreases with increasing electron donating ability of the substituent at C-5 of the indolinyl ring in the order Cl < H < MeO with concomitant small red shifts of $\lambda_{max.}$. For all the spironaphthoxazines employed, the values of both $\lambda_{max.}$ and $OD_{max.}$ are larger in water/acetone than those in pure acetone. Moreover, the values of $k_{dc}$ are smaller in the former, indicating that the coloured open form is more stabilized in the polar solvent. These effects of added water almost levelled off when the water content reached 1 : 1 (v/v)




**Scheme 1**




(**1**)—(**7**)

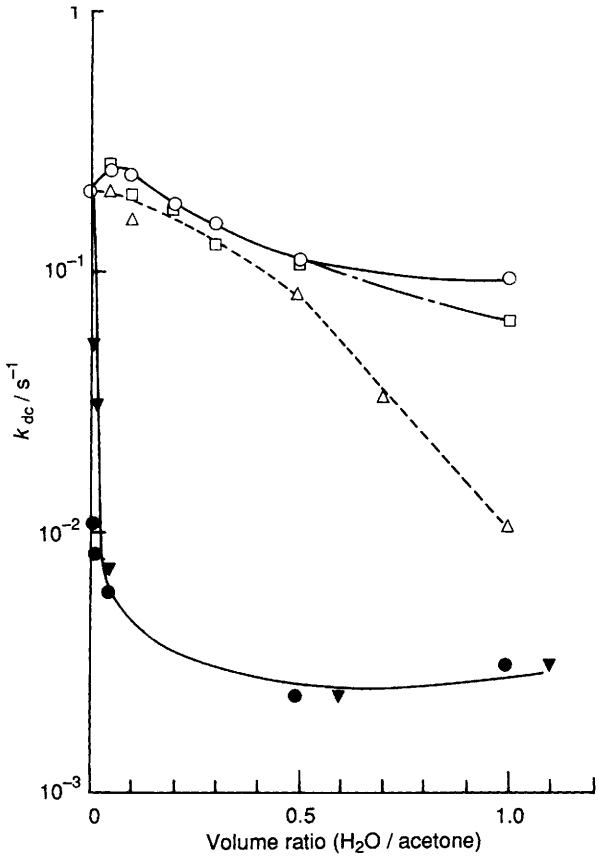



**Figure 1.** The pH dependence of $k_{dc}$ in the mixture of the buffer, water, and acetone at 20 °C: pH 9 (○), pH 8 (□), pH 7 (△), pH 6 (▼), pH 5 (●). The borate buffer was used for pH 8—9 and the McIlvaine buffer for pH 5—7.

**Table 1.** $\lambda_{max.}$, $k_{dc}$, and $OD_{max.}$ of spironaphthoxadines ($5 \times 10^{-5}$ mol dm$^{-3}$) in acetone and in water/acetone.

| | | | Acetone | | | Water/acetone [1 : 1 (v/v)] | | |
|---|---|---|---|---|---|---|---|---|
| Compound | $R^1$ | $R^2$ | $\lambda_{max.}$ /nm | $k_{dc}$[a] /s$^{-1}$ | $OD_{max.}$ | $\lambda_{max.}$ /nm | $k_{dc}$[a] /s$^{-1}$ | $OD_{max.}$ |
| (**1**) | Cl | H | 596 | 1.05 | 0.06 | 606 | 0.76 | 0.09 |
| (**2**) | H | H | 596 | 0.91 | 0.08 | 610 | 0.17 | 0.36 |
| (**3**) | H | MeO | 570 | 0.93 | 0.08 | 606 | 0.16 | 0.43 |
| (**4**) | MeO | H | 614 | 0.27 | 0.16 | 622 | 0.035 | 0.39 |
| (**5**) | MeO | MeO | 608 | 0.25 | 0.10 | 620 | 0.030 | 0.59 |
| (**6**) | H | PM[b] | 606 | 0.90 | 0.12 | 616 | 0.021 | 0.60 |
| (**7**) | MeO | PM[b] | 614 | 0.25 | 0.22 | 624 | 0.0032 | 1.25 |

[a] Measured at 20 °C. [b] Piperidinomethyl group.

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relative to acetone. The red shift of spectra due to addition of water suggests that the spironaphthoxazines have a neutral quinoidal structure in the open form, unlike spiropyran derivatives which have a zwitterionic form.[1]

It is noteworthy that the compounds (**6**) and (**7**), which have a piperidinomethyl substituent at C-5′, show extraordinary retardation in $k_{dc}$ in the presence of water ($k_{dc}$ in water/acetone: $k_{dc}$ in acetone 1/50 ~ 1/80 : 1). For 5′-methoxy substituted compounds (**3**) and (**5**), the added water has no such effect on $k_{dc}$. Since the p$K_b$ value of *N*-methylpiperidine is reported to be 3.9, it seems likely that the piperidinomethyl group is in the onium form preferentially in water/acetone. Therefore, it is possible that the protonated piperidinium nitrogen atom makes a six-membered ring with the quinoidal oxygen through the hydrogen bond (Scheme 1), resulting in stabilization of the coloured open form.

This stabilization effect was dependent on the solvent used. Dioxane was as good as acetone, but acetonitrile and pyridine were not. This may be interpreted in terms of the intermolecular interaction between these organic solvents and water.[5] The former two solvents are less subject to both hydration and hydrogen bond formation than the latter two, which are able to interrupt the intramolecular hydrogen bond of the solute.

Figure 1 shows the plots of $k_{dc}$ of (**7**) ($5 \times 10^{-5}$ mol dm$^{-3}$) *vs.* the content of buffer water at several pHs in acetone at 20 °C. The value of $\lambda_{max.}$ was unchanged in the range of pH used. While there appears only little decrease in $k_{dc}$ at pH >8, the addition of small amounts of slightly acidic water (pH 5—6) induces a significant decrease in $k_{dc}$. An identical pH effect was observed for (**6**), but not for (**3**) and (**5**). This suggests that the protonation of the piperidinomethyl group is important for the extraordinary retardation in $k_{dc}$. Organic acids such as acetic acid or benzoic acid gave rise to the related stabilization of the coloured open form. Satisfactory results were also obtained for polymer matrices such as a poly(methylmethacrylate) film containing (**7**) and benzoic acid.

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