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Variation of the Bleaching Rate of some Photochromic Compounds Under Irradiation in Toluene

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VARIATION OF THE BLEACHING RATE OF SOME PHOTOCHROMIC COMPOUNDS UNDER IRRADIATION IN TOLUENE

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Abstract

The modification of the bleaching rate of a wide range of spiroheterocyclic photochromic compounds (27) has been studied under irradiation in solution of toluene

Introduction

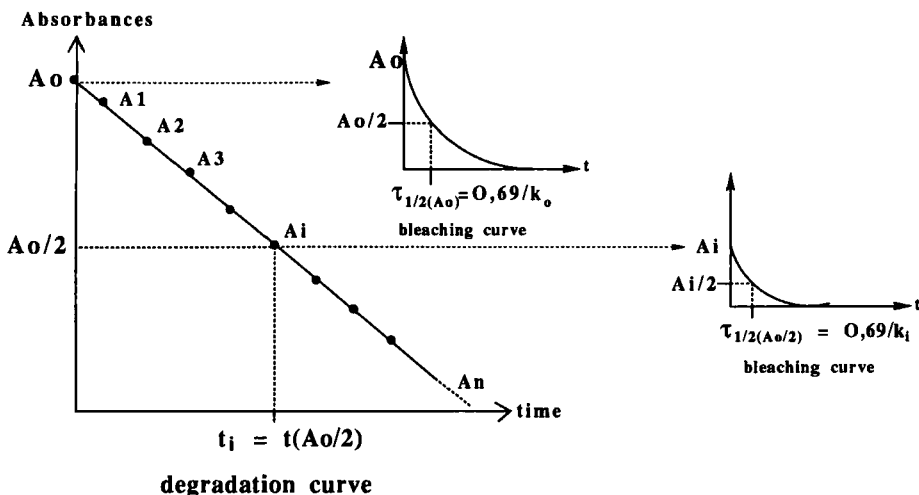
The compounds studied are some substituted in various ways spiro[indoline-naphthoxazines], spiro[indoline-benzoxazines], spiro[indoline-heterobenzoxazines] and nitro derivatives of spiro[indoline-naphthopyrans] and spiro[indoline-naphthoxazines]^[1] (figure 1).

This study has been performed with an experimental spectrophotometric apparatus called "Degraphot"^[2] allowing to estimate the fatigue resistance and also the fading rate at the half degradation time of the photochromic compounds ($A_0/2$).

In order to assess the way of these kinetic modifications, we can define some practical values:

$$t=0, A=A_0 \rightarrow \tau_{1/2}(A_0)$$

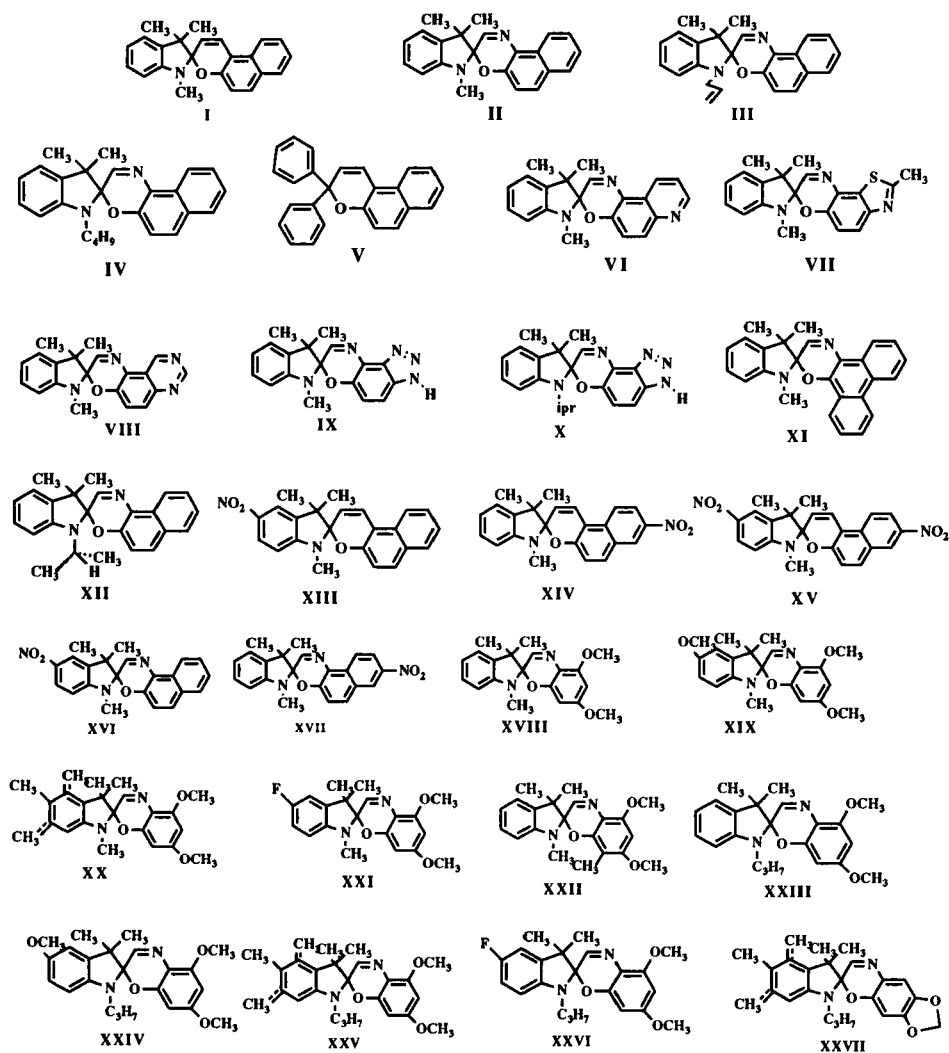
$$t=i, A_i=A_0/2 \rightarrow \tau_{1/2}(A_0/2)$$



so, the variation of the photomerocyanine halflifetime during irradiation can be expressed by:

$$\Delta\tau_{1/2}(\%) = \frac{\tau_{1/2}(\frac{A_0}{2}) - \tau_{1/2}(A_0)}{\tau_{1/2}(A_0)} * 100$$

Figure 1: Structure of the photochromic compounds studied:



Discussion

It can be seen with a lot of compounds that there is a good correlation between the initial $\tau_{1/2}$ value of the photomerocyanine and the way of variation ($\Delta\tau_{1/2}$) after irradiation (figure 2) :

→The faster the initial ring closure time from the opened form is, the more its fading rate tends to increase during irradiation.

→The slower the initial bleaching rate of the compounds is, the more it tends to decrease during irradiation.

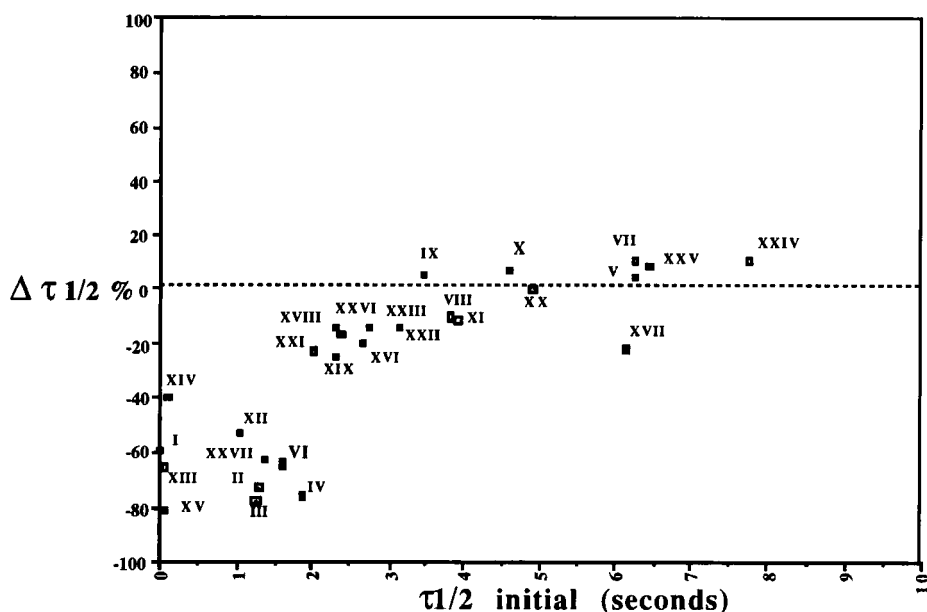


Figure 2: Modification of the photomerocyanine halflifetime ($\Delta\tau_{1/2}$) during irradiation versus its initial half lifetime ($\tau_{1/2}$)

Conclusion

Preliminary investigations show that the identified photoproducts^[3] of the photochromic compound itself do not induce the modification of the ring closure rate during irradiation. It seems that the photoproducts of the solvent can promote this phenomenon. Indeed, irradiated pure toluene induce a modification of the bleaching kinetic, when added to a fresh solution of photochromic derivatives. The benzaldehyde which is one of the toluene photodegradation products has been tested in order to assess this observation (figure 3):

It can be seen that an increase in the benzaldehyde concentration in toluene provoke (without irradiation) a decrease of the photomerocyanine lifetime of II and, on the other hand, an increase of the photomerocyanine lifetime of XXIV.

At this time, we cannot explain this process by a modification of the medium polarity because the benzaldehyde is effective since 10^{-5} - 10^{-4} M.l⁻¹. So, this phenomenon keep still unclear and more investigations are needed in order to explain these observations. It will be also interesting to study if this phenomenon occurs in polymer matrices.

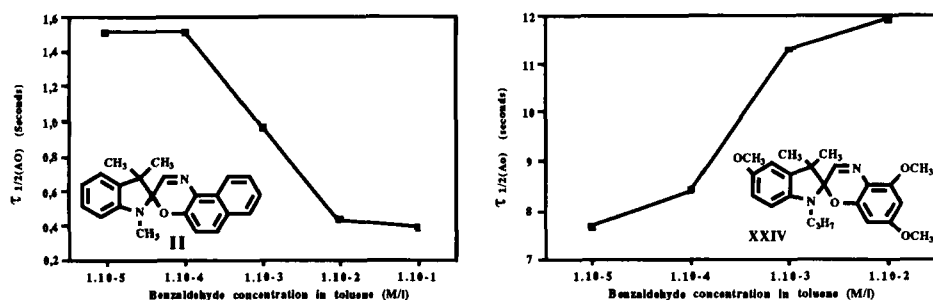


Figure 3: Effect of the benzaldehyde concentration in toluene on the photomerocyanine half lifetime ($\tau_{1/2}$) of II and XXIV (C [photochrome]= 5.10^{-6} M/l, 25°C).

Acknowledgment

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