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Deactivating effect of the pyridine n,π* states on the photoreactivity of 5-[2-(pyrid-*n*-yl)ethenyl]oxazole (*n* = 2, 3 and 4)

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ABSTRACT

This paper describes the results obtained in the study of the photobehaviour of heteroanalogs of stilbene bearing oxazole and pyridine rings at the opposite sides of the ethene moiety. The effect of the positional isomerism of the *n*-pyridyl group (*n* = 2, 3 and 4) on the competitive relaxation processes of the excited states (fluorescence, isomerization and cyclization) was investigated and compared with the behaviour previously reported for the 5-styryloxazole analogue.

The group in Zagreb prepared the compounds and followed their photochemistry in preparative conditions while the group in Perugia studied the spectral properties of the trans/cis isomers and the cyclization products and measured the quantum yields of the competitive processes in mild conditions with the main aim to clarify the mechanism of the primary stages after excitation. The photobehaviour revealed an important deactivation effect of the n,π* states introduced by the nitrogen atom. This effect reflects the one reported for styrylpyridines, the analogous compounds with a phenyl instead of an oxazolyl ring. Quantum-mechanical Hyperchem calculations proved to be useful to describe the conformational equilibria and the role of conformers on photoreactivity while more refined DFT calculations on the Z isomers allowed the structure dependent competition between their isomerization/cyclization processes and the possible role of intramolecular H-bonds on the deactivation pathways to be explained. For the compound with *n* = 4, side processes of hydrogen shift in the primary dihydrophenanthrene-like intermediate and of solvent addition accompanying the photocyclization process were evidenced.

1. Introduction

Recently our long-term interest on the photobehaviour of stilbene-like molecules was addressed to the trans (E) and cis (Z) isomers of *n*-styryloxazoles (***n*-StOx**, with *n* = 2, 4 and 5) [1–3]. The collaboration between the two laboratories in Zagreb and Perugia allowed the study of the competitive photoreactions (isomerization/cyclization) of the three positional isomers in two different experimental conditions, namely in preparative conditions (high intensity lamp, long irradiation times, high concentration and addition of iodine as efficient oxidant) to follow the overall photoreaction kinetics and to obtain the chemical yields, and in mild condition to measure the quantum yields of the competitive processes in the first stages of irradiation [1–3]. The measured quantum yields concerned fluorescence (ϕ_F), E → Z and Z → E photoisomerization ($\phi_{E\rightarrow Z}$ and $\phi_{Z\rightarrow E}$, respectively) and cyclization to a dihydrophenantrene-like (DHP) intermediate ($\phi_{Z\rightarrow DHP}$). In the presence of oxidants the latter was thermally dehydrogenated to the final phenanthrene-like (P) polycyclic product. Information on the isomerization and cyclization mechanisms of ***n*-StOx** are reported in the previous papers [2,3] where the photoreactivity was compared with that of stilbene whose quantum yields of the emissive and reactive relaxation processes reported in the literature in non-polar solvents at room temperature are 0.05, for fluorescence, and 0.50, 0.35 and 0.10 for the E → Z, Z → E and Z → DHP photoreactions, respectively [4–6]. Further detailed information on the photoreaction mechanisms of *E*- and *Z*-stilbene can be found in refs [7–17].

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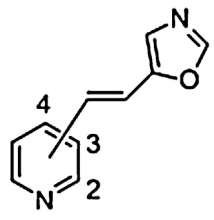
The quantum yields of *n*-styryloxazoles were found rather similar to those of stilbene for the trans (E) isomers with $n = 4$ and 5 (high yield of E ⇆ Z photoisomerization, accompanied by very weak fluorescence) while the reactivity of the Z isomers was found to be reduced with respect to stilbene for both isomerization and cyclization. On the contrary, the compound with $n = 2$ showed a reduced reactivity of E and an increased reactivity of Z in the Z → E direction but no cyclization at all. Apart from the effects of the position of the styryl group at the oxazole ring, it was found that the relative abundance of the various conformers (due to rotation of the aryl groups around the quasi-single bond with the ethenic bridge) [18,19], and the possible formation of intramolecular H-bonds on the deactivation pathways play an important role, particularly on the cyclization process. Quantum-mechanical Hyperchem calculations proved to be useful to describe the conformational equilibria and the role of conformers on photoreactivity while more refined DFT calculations on the Z isomers allowed the explanation of the structure dependent competition between their isomerization/cyclization processes [2,3]. The effect of a *para*-methoxy substituent at the phenyl ring [2] and the replacement of the phenyl ring with a second heteroaromatic group, 5-[(2-(furan-2-yl)ethenyl)]oxazole [3] were also investigated. The yields measured for the latter were $\phi_{E\rightarrow Z} = 0.38$ and $\phi_{Z\rightarrow E} = 0.24$ but no cyclization was detected in the first stages of irradiation. In fact, the Z conformer able to cyclize was predicted by calculations to be practically absent in the conformational equilibrium thus explaining the absence of cyclization in the first stages of irradiation. Interestingly, the experiments on preparative scale, using iodine as oxidant and performed in benzene at ~40 °C until full conversion of the starting reagents (~24 h of irradiation), showed a high chemical yield also for this compound [1].

The present paper aims to examine the effect of the replacement of the phenyl ring of **5-StOx** with a second heteroaromatic group of weak acceptor character (pyridyl) on the photobehaviour and the role of the positional isomerism (varying the attachment position of the pyridine moiety to the ethene bridge). These effects will be described for the three analogues of **5-StOx**, namely the 5-[2-(pyrid-*n*-yl)ethenyl]oxazole (***n*-PyEt-5Ox**, where $n = 2$, 3 and 4) (Scheme 1).

The paper also aims to compare the results with those obtained for the analogous compounds bearing only one heteroaryl group, oxazole (see above) or pyridine. In the Perugia laboratory the photobehaviour of compounds bearing the pyridyl group, namely the three positional isomers of *n*-styrylpyridine (***n*-StPy**, $n = 2$, 3 and 4), has been deeply investigated in previous works [20–24]. It was shown that isomerization to Z is the main deactivation pathway of the E isomers, that ISC is practically negligible for these compounds and that the proximity effect (presence of n,π* states nearby located to the π,π* states, whose coupling may favour return to the ground state by internal conversion, IC) plays an important role on fluorescence and photoreaction. In that case the quantum yields were similar to those of stilbene for $n = 3$ only, due to its much less efficient IC (experimental and computed), because the nitrogen atom at the *meta* position is located at a quasi-node of the M.O. (thus reducing the proximity effect) [20]. For the other two positional isomers with $n = 2$ and 4, both the reactive and emissive yields were rather smaller than those of stilbene because the vibronic coupling between the two lowest excited states induced IC in the relaxation of these compounds, as also confirmed by theoretical calculations [23,24]. Smaller changes with respect to stilbene were found for Z → E isomerization, probably owing to lack of planarity of the Z form which hinders the transmission of the perturbative effect of the heteroatom to the ethene double bond [20]. The cyclization yield was again similar to that of stilbene for **3-StPy** but almost one order of magnitude smaller for the other two positional isomers [21]. The new results on the three pyridyl derivatives of **5-StOx** investigated will be particularly compared with those available for ***n*-StPy** [20–24].



***E*-*n*-PyEt-5Ox**

Scheme 1. E isomers of the compounds with two heteroaryl groups: 5-[2-(pyrid-*n*-yl)ethenyl]oxazole (***n*-PyEt-5Ox**, $n = 2$, 3 and 4).

2. Experimental

2.1. Synthesis and irradiation of *n*-PyEt-5Ox

The investigated compounds (Scheme 1) were prepared by Van Leusen reaction from the (*E*)-3-(pyrid-*n*-yl)acrylaldehydes (n = 2, 3) and TosMIC as described for the synthesis of (*E*)-5-[2-(pyrid-4-yl)ethenyl]oxazole [1]. The new *E*-2- and *E*-3-pyridyl derivatives were characterized by spectroscopic methods (see Supporting information). To obtain the Z-isomers the benzene solution of all three *E*-***n*-PyEt-5Ox** ($c = 3.5 \times 10^{-3}$ mol/dm^3) purged with argon was irradiated in a Rayonet at 350 nm for 15 min (2-PyEt-5Ox), 30 min (3-PyEt-5Ox) and 40 min (4-PyEt-5Ox) and transformed to a mixture of E and Z-isomers ($E/Z \approx 1:1$). The Z-isomers were separated from the mixtures by repeated column chromatography combined with thin layer chromatography (petroleum ether/ether variable ratio).

2.1.1. E-5-[2-(Pyrid-2-yl)ethenyl]oxazole (*E*-2-PyEt-5Ox)

(0.82 g, 96%), colourless crystals: mp 88–89 °C; UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 289 (Sh 15424), 308 (25585), 313 (26383); IR ($CHCl_3$/film), ν_{max}/cm^{-1}: 3109, 3091, 2923, 1556, 1432, 953, 843, 774; ^{1}H NMR NMR ($CDCl_3$; 600 MHz) δ/ppm: 8,61 (ddd, 1H, $J_{1,4} = 0.90$ Hz, $J_{1,3} = 1.74$ Hz, $J_{1,2} = 4.74$ Hz, H-1), 7.87 (s, 1H, H-10), 7.67 (td, 1H, $J_{1,3} = 1.74$ Hz, $J_{2,3} = J_{3,4} = 7.68$ Hz, H-3), 7.52 (d, 1H, $J_{6,7} = 15.87$ Hz H-6/7), 7.32 (ddd, 1H, $J_{1,4} = 0.90$ Hz, $J_{2,4} = 1.00$ Hz, $J_{3,4} = 7.68$ Hz, H-4), 7.17 (ddd, 1H, $J_{2,4} = 1.00$ Hz, Hz, $J_{1,2} = 4.74$ Hz, $J_{2,3} = 7.68$ Hz, H-2), 7.16 (s, 1H, H-9), 7.13 (d, 1H, $J_{6,7} = 15.87$ Hz, H-6/7); ^{1}H NMR (C_6D_6; 600 MHz) δ/ppm: 8.46 (ddd, 1H, $J_{1,4} = 0.92$ Hz, $J_{1,3} = 1.78$ Hz, $J_{1,2} = 4.68$ Hz, H-1), 7.65 (d, 1H, $J_{6,7} = 15.72$ Hz H-6/7), 7.18 (s, 1H, H-10), 7.05 (d, 1H, $J_{6,7} = 15.72$ Hz, H-6/7), 6.99 (td, 1H, $J_{1,3} = 1.78$ Hz, $J_{2,3} = J_{3,4} = 7.72$ Hz, H-3), 6.82 (s, 1H, H-9), 6.72 (ddd, 1H, $J_{1,4} = 0.92$ Hz, $J_{2,4} = 1.00$ Hz, $J_{3,4} = 7.72$ Hz, H-4), 6.56 (ddd, 1H, $J_{2,4} = 1.00$ Hz, Hz, $J_{1,2} = 4.68$ Hz, $J_{2,3} = 7.72$ Hz, H-2); ^{13}C NMR ($CDCl_3$; 150 MHz) δ/ppm: 154.39 (s, C-5), 150.93 (d, C-10), 150.20 (s, C-8), 149.90 (d, C-1), 136.78 (d, C-3), 129.05 (d, C-6/7), 126.00 (d, C-9), 122.98 (d,C-4), 122.75 (d, C-2), 116.75 (d, C-6/7); HRMS (MALDI-TOF/TOF) for $C_{10}H_8N_2O$: $(M+H)^+_{calcd} = 173.0709$, $(M+H)^+_{measured} = 173.0709$; MS *m*/*z* (%, fragment): 173 100, $(M+H)^+$.

2.1.2. Z-5-[2-(Pyrid-2-yl)ethenyl]oxazole (*Z*-2-PyEt-5Ox)

UV (EtOH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 272 (7857), 301 (9493), 311 (9378), 322 (Sh 6217); ^{1}H NMR ($CDCl_3$; 600 MHz) δ/ppm: 8.71(ddd, 1H, $J_{1,4} = 0.72$ Hz, $J_{1,3} = 1.80$ Hz, $J_{1,2} = 4.83$ Hz, H-1), 8.00 (s, 1H, H-9), 7.83 (s, 1H, H-10), 7.69 (td, 1H, $J_{1,3} = 1.80$ Hz, $J_{2,3} = J_{3,4} = 7.74$ Hz, H-3), 7.37 (ddd, 1H, $J_{1,4} = 0.72$ Hz, $J_{2,4} = 1.10$ Hz, $J_{3,4} = 7.74$ Hz, H-4), 7.21 (ddd, 1H, $J_{2,4} = 1.10$ Hz, Hz, $J_{1,2} = 4.83$ Hz, $J_{2,3} = 7.74$ Hz, H-2), 6.63 (d, 1H, $J_{6,7} = 13.02$ Hz H-6/7), 6.58 (d, 1H, $J_{6,7} = 13.02$ Hz, H-6/7); ^{1}H NMR (C_6D_6; 600 MHz) δ/ppm: 9.53 (s,