

PHOTOCHEMICAL BEHAVIOUR OF DIPYRROLES

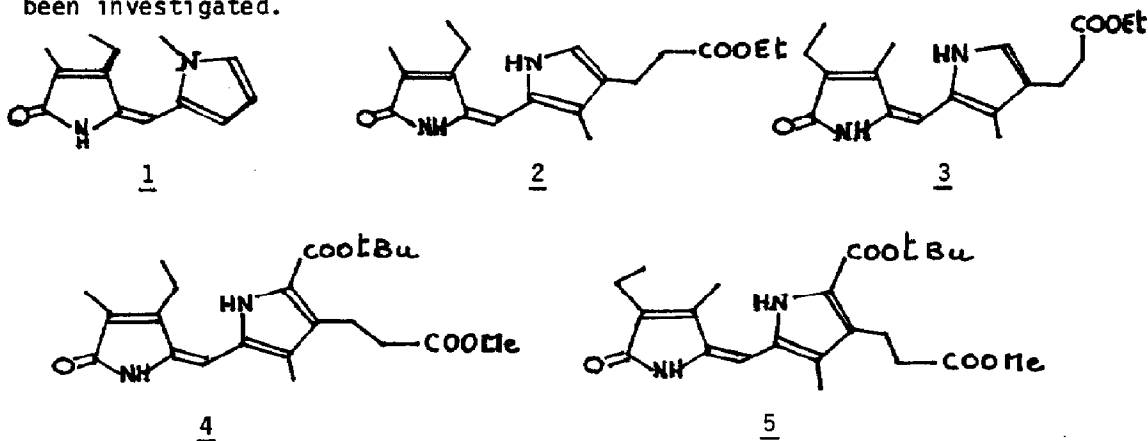
J. Kossanyi and S. Sabbah

Laboratoire de Chimie Structurale et Photochimie, ERA 557, Université Pierre et Marie Curie, 4 Place Jussieu, 75230 Paris Cedex 05 (France)

A. Queguiner and J. Duflos

Laboratoire de Chimie Organique, Institut Supérieur de Chimie Industrielle de Rouen, 76130 Mont-Saint-Aignan (France)

The photochemical behaviour of dipyrroles has received little attention. Several articles have reported the E-Z isomerisation of such molecules induced by daylight during the preparation or the purification of these compounds¹⁻⁴. Since tetrapyrrolic products constitute pigments⁵ and are involved also in the plant photoreceptor phytochrome⁶ we have been interested in the emission and the photoisomerisation of dipyrroles as a start for the understanding of more complex molecules. Compounds 1 to 5 have been investigated.



All these compounds, designed as E isomers by opposition to their Z isomers in which the two nitrogen atoms face each other, show a broad absorption with a maximum of $\epsilon = 29,000$ to $32,000 \text{ l.mole}^{-1} \text{ cm}^{-1}$ around 390 nm and very unefficient non-structured fluorescence at room temperature. At 77 K no phosphorescence has been detected but the fluorescence increases by almost 3 order of magnitude for 1, 2 and 3 (see table). The lifetime has

been measured at 77 K by single photon counting technique for compounds 2 and 3. Its value is too short to be measured at room temperature and is of the order of 2 ns at 77 K. This result in addition to the variation of the fluorescence efficiency with the temperature is indicative of a very rapid

Table. Absorption, fluorescence and singlet lifetime of compounds 1-5.

		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Absorption	λ_{\max} (nm)	387	390	390	386	386
	ϵ (l.mole ⁻¹ cm ⁻¹)	27,000	30,000	29,000	32,000	32,000
fluorescence	λ_{\max} (nm)	445	440	440	450	450
	ϕ_f (25°C)	7×10^{-4}	8×10^{-4}	8×10^{-4}	2×10^{-4}	4×10^{-4}
	ϕ_f (77 K)	0.60	0.98	0.80	0.36	0.40
	$k_f \times 10^8$		4.9	3.8		
	τ_s (ns)		2.0	2.1		

nonradiative deactivation of the singlet state probably by E-Z isomerisation. At room temperature the efficiency of this process is higher than 0.1.

Quenching of the singlet excited state by CBr₄ (as followed by inhibition of the fluorescence) gives a straight Stern-Volmer plot with a slope which varies from 33 to 90 l.mole⁻¹ depending on the compound. This quenching cannot involve singlet energy transfer between the two molecules but rather either a reaction between the two encounters or an increase of the efficiency of the singlet to triplet intersystem crossing of the molecule. The rate constant of this process would be of the order of $3 \times 10^{10} \text{ s}^{-1}$. More details will be given.

References

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