EXCITED STATES OF 6-NITRO-8-METHOXY-2*H*-CHROMENE STUDIED BY EMISSION AND ABSORPTION SPECTROSCOPY: CORRELATION WITH PHOTOCHROMISM OF SPIROPYRANS

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Summary

We have studied the variation of absorption spectrum (at 20 °C) and the luminescence characteristics (at 77 K) of the 6-nitro-8-methoxy-2*H*-chromene, with the nature of solvent. A relative order of lowest energy $n\pi^*$ and $\pi\pi^*$ singlet and triplet states is checked. This order is linked to the photochromic behaviour of heterocyclic spiropyrans compounds likely substituted on the benzopyran part of the described chromene.

Introduction

The general process involved in photochromism of heterocyclic spiropyrans may be described by the following scheme:
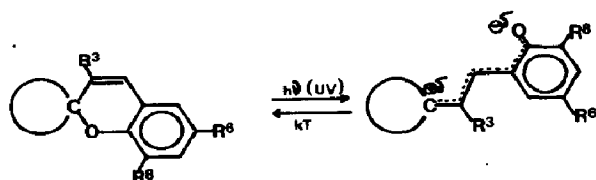
Spiropyrannic molecule may be considered as constituted by two parts: a "left" heterocyclic part and a "right" benzopyrannic one or -2*H*-chromene. The chromene part absorbs u.v. excitation and through the cleavage of C–O bond, there is formation of a photomerocyanine, the thermal stability of which depends on the nature of substituents on the benzopyran part and on the structure of the "left" heterocyclic part. This reaction is reversible, particularly by the thermal effect. Recently, the 6-nitro-8-methoxy-2*H*-chromene (1) has been synthesized [1],
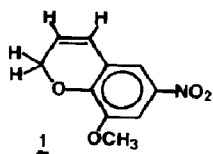
This compound is the exact model for the "right" part of spiropyrans having generally the best photochromic properties (R_6 = NO_2, R_8 = OCH_3).

The chromene part of spiropyrans has an important role in the mechanism of photocoloration; we have considered it interesting to classify the relative order of lowest energy $n\pi*$ and $\pi\pi*$ singlet and triplet levels of the molecule 1.

This disposition must be very significant in the ability of photocoloration.

Experimental

The u.v. spectra were measured either on a Leres Spila spectrophotometer or on a Beckmann Acta V one. The phosphorescence excitation and emission spectra were carried out on a Perkin Elmer/Hitachi MPF-3 L spectrophotometer. These spectra are not corrected. The phosphorescence lifetimes were determined from decay curves on a Tektronix 5103 N oscilloscope. The solvents used were of Merck spectroscopic quality.

Results and Discussion

The u.v. spectrum of 6-nitro-8-methoxy-2H-chromene in cyclohexane, ethanol and EPA (ether–isopentane–ethanol 5:5:2) is described in Table 1, and we shall compare it later with phosphorescence excitation spectrum. Moreover, the position of lowest energy transition has been studied in low polarity solvents and in Fig. 1 the variation of λ_{max} with solvent dielectric constant is plotted ($\Delta\lambda_{max}$ = ±2 nm).

Considering the high value of molar extinction coefficient of this transition and the bathochromic shift produced by increasing the solvent polarity, we can assign it to a $S_0 \rightarrow {}^1(\pi\pi*)$ transition. Besides, the molecule 1 being little polar, we must use solvents of weak dielectric constant to note an increasing variation in λ_{max} values.

No $n\pi*$ transition at longer wavelengths has been seen by absorption, so the chromene (1) has a $S_1(\pi\pi*)$ level. Balny and coworkers [2] have assigned to the indolinic spiropyran (2) having the same substitution on benzopyran
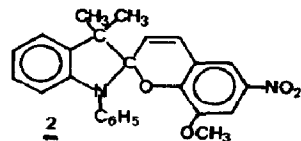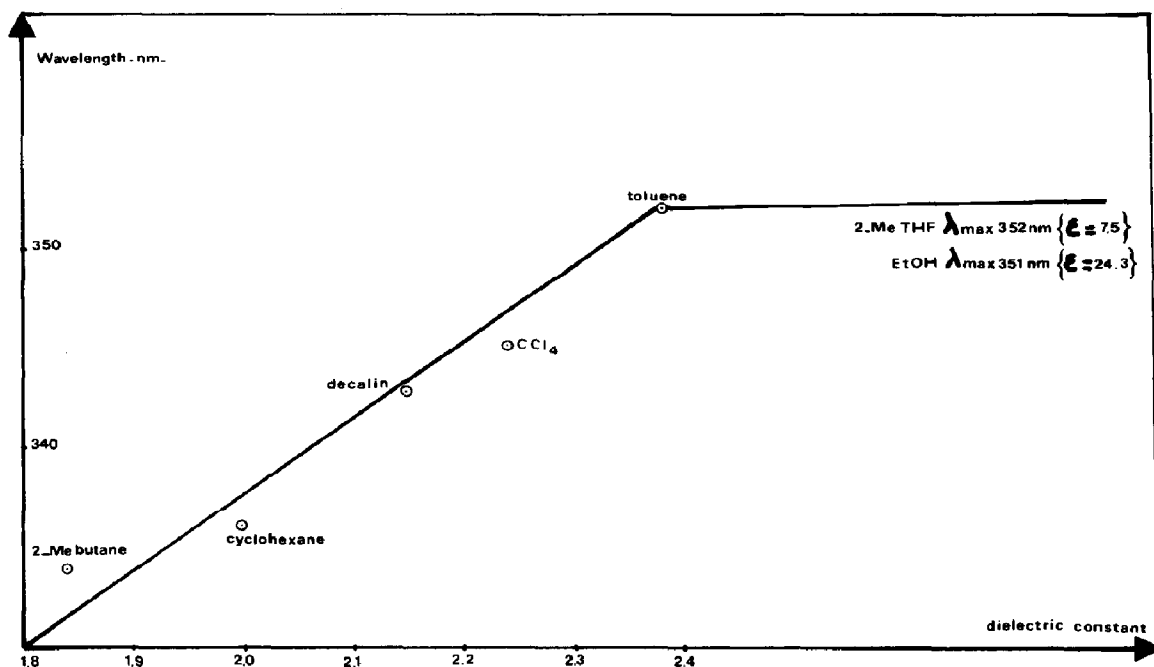
TABLE 1

U.v. absorption of 6-nitro-8-methoxy-2*H*-chromene.

Solvent		The concentration is about $10^{-5}\ M$							
Cyclohexane	λ (nm)	216	(244)	249	(255)	(275)	282	(289)	336
	log ε	(4.20)	(4.18)	(4.20)	(4.09)	(3.89)	(3.94)	(3.84)	(3.79)
Ethanol	λ (nm)	215	(244) .	250	(257)		283		351
	log ε	(4.12)	(4.12)	(4.16)	(4.04)		(3.81)		(3.72)
EPA	λ (nm)	216	(244)	248	(255)		282		338
	log ε	(4.18)	(4.18)	(4.20)	(4.11)		(3.90)		(3.86)

(λ) = shoulder.

Fig. 1. Variation of absorption λ_{max} with solvent dielectric constant.

part as chromene (1), a S_1 ($n\pi^*$) level and that by considering the variation of λ_{max} phosphorescence excitation spectrum with solvent polarity. As Table 2 and Fig. 2 show, the phosphorescence excitation spectrum of 6-nitro-8-methoxy-2*H*-chromene varies widely for high concentrations and gets steady for low concentrations. This variation could be explained by the formation of excimers when the concentration gets high enough. But in a solvent such as ethanol, the indolinic spiropyran (2) is little soluble and it seems possible that the hypsochromic shift observed [2] by changing isopentane for ethanol is due to the difference of concentration. As for us, we have studied at a con-

TABLE 2

Variation of phosphorescence excitation spectrum of chromene (1) with concentration in EPA (λ_{em} = 520 nm).

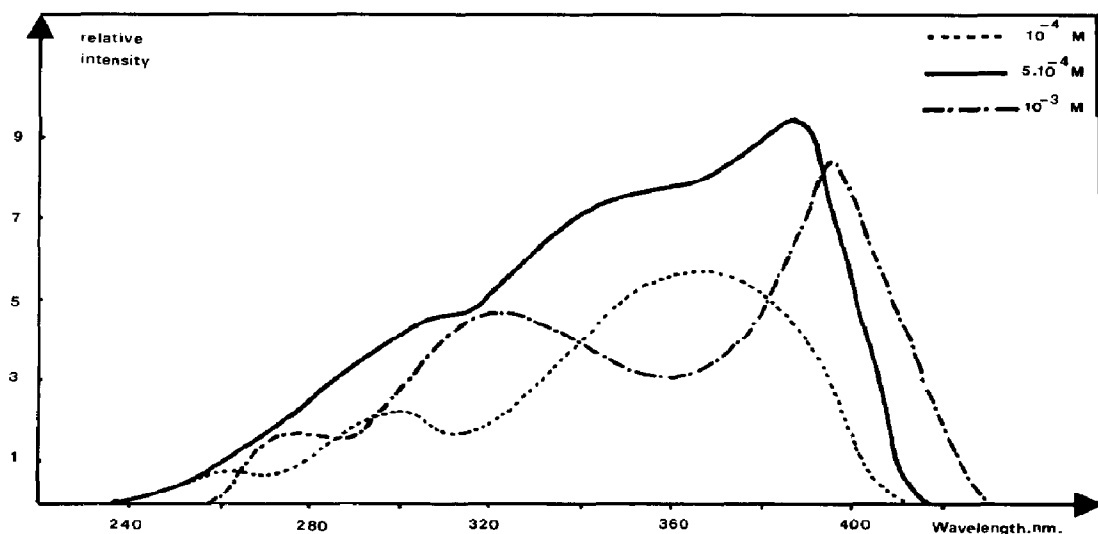| Concentration	$10^{-5}\,M$	$10^{-4}\,M$	$5 \times 10^{-4}\,M$	$10^{-3}\,M$
λ (nm)	263, 300, 365	263, 300, 365	307, 360, 387	275, 320, 395

Fig. 2. Plot of phosphorescence excitation spectrum of 6-nitro-8-methoxy-2H-chromene in EPA as a function of concentration.

centration of $10^{-4}\,M$, the variation of phosphorescence characteristics of 6-nitro-8-methoxy-2H-chromene with solvent polarity. The experimental data are summarized in Table 3 and the phosphorescence emission spectrum in EPA is given in Fig. 3.

First, by raising solvent polarity, a bathochromic shift of upper band of phosphorescence excitation spectrum occurred. That observation is in connection with results obtained in absorption: the lowest energy singlet is $\pi\pi^*$ type indeed. The difference of 27 nm noted on $S_0 \rightarrow {}^1(\pi\pi^*)$ band, between absorption spectrum and phosphorescence excitation spectrum in EPA (cf. Tables 1 and 3), must be considered as a result of temperature effect. Similarly, Becker [3] has found a shift in absorption spectra by comparative study of indolino–spiropyrans as room temperature and at 77 K.

We note too a bathochromic shift of (0 - 0) phosphorescence band, always by increasing solvent polarity which seems to prove that the triplet responsible for emission is also of $\pi\pi^*$ type.

TABLE 3

Phosphorescence characteristics of 6-nitro-8-methoxy-2H-chromene in different solvents (concentration 10^{-4} M)

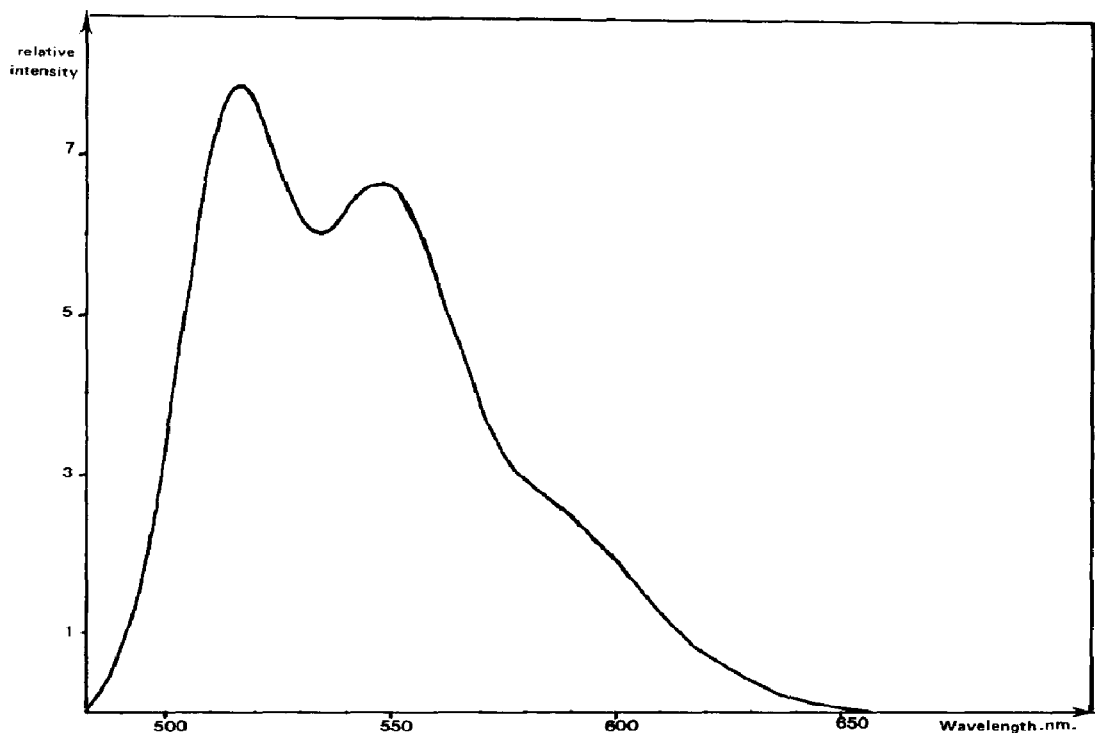|	Solvent											
	Methyl-cyclohexane			EPA			MeTHF			Ethanol		
$\lambda_{excitation}$ (nm)	283	307	360	263	300	365	282	324	377	265	302	368
$\lambda_{emission}$ (nm)	502	535	568	517	548	580	523	556	587	517	548	584
energy (cm^{-1})	19920	18692	17606	19342	18248	17241	19120	17986	17036	19342	18248	17123
$\Delta\bar{\nu} = \bar{\nu}_1 - \bar{\nu}_2$ (cm^{-1})	1228			1094			1134			1094		
$\tau_{phosphorescence}$ (ms)	100 ± 30			190 ± 30			220 ± 30			190 ± 30		

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Fig. 3. Plot of phosphorescence emission spectrum of 6-nitro-8-methoxy-2H-chromene in EPA at 77 K (concentration 10^{-4} M).

Other arguments will enhance this suggestion. If we suppose, for a moment, that the emitting triplet is a $n\pi^*$ type, it involves that triplet $(\pi\pi^*)$ should be higher, but as we have seen before, the first singlet being of $\pi\pi^*$ type, the energy gap between singlet and triplet states would be wider for $n\pi^*$ than for $\pi\pi^*$ levels, that being contrary to the general estimation about $n\pi^*$ and $\pi\pi^*$ levels [4].

Furthermore, if we consider vibrational structure phosphorescence emission spectrum, the first two transitions which are the most important ones, are separated in EPA by nearly 1100 cm^{-1} (Table 3). This vibrational spacing does not fit the symmetric O−N−O stretching frequency as mentioned by Becker [5] for the case of 6-nitro-substituted indolinic spiropyrans, and to which a $n\pi^*$ emission was assigned. This vibrational energy gap must be linked to a benzopyran nucleus vibration.

At last, when a non-polar solvent (methylcyclohexane) is used instead of a polar solvent (ethanol or MeTHF) the two $n\pi^*$ and $\pi\pi^*$ triplet levels are getting nearer when their relative position is so considered. That should bring at the same time a decrease of lifetime, since $\tau^3(n\pi^*) < \tau^3(\pi\pi^*)$, and an increase of vibrational energy gap. These two effects observed here enhance the hypothesis of the $\pi\pi^*$ character of emitting triplet. This $\pi\pi^*$ character is less

striking as experiments are undertaken in non-polar solvents (see following scheme).

polar solvent   non-polar solvent

——————————— $^3(n\pi^*)$ ——————————— $^3(n\pi^*)$

——————————— $^3(\pi\pi^*)$ ——————————— $^3(\pi\pi^*)$
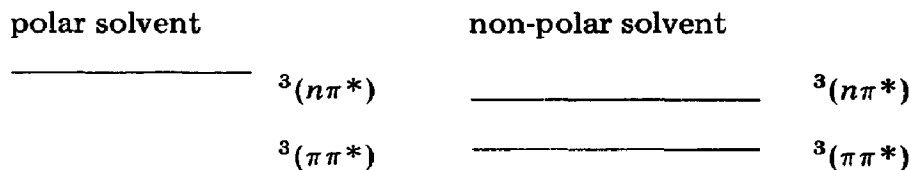
Now we have to consider the position of $n\pi^*$ triplet level compared to $\pi\pi^*$ singlet level. The absence of fluorescence measurable at room temperature as well as 77 K, makes us set the $^3(n\pi^*)$ level below $^1(\pi\pi^*)$ level. Our results are in agreement with Lippert's conclusions [6, 7] about luminescence of nitro-aromatic compounds in the biphenyl and stilbene series or with Russian researchers [8] about luminescence of nitro aryl-pyrazolines.

In nitro-substituted molecules, for which the lowest energy singlet has a $\pi\pi^*$ character and is set in a range inferior to 500 nm, the excitation energy does not give any fluorescence emission by intersystem crossing $^1(\pi\pi^*) \rightarrow {}^3(n\pi^*)$ of the nitro group.
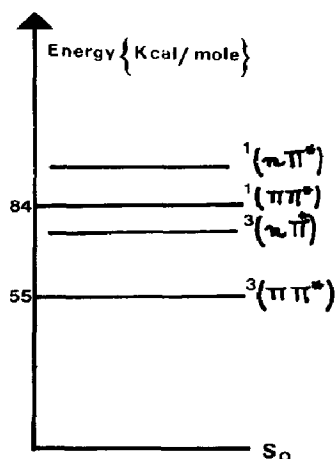

Fig. 4. Relative order of lowest $\pi\pi^*$ and $n\pi^*$ singlet and triplet energy levels in 6-nitro-8-methoxy-2H-chromene.

Finally, we can suggest the following relative order for the different excited states in Fig. 4. If the experimental data discussed here do not fit exactly those of Balny [2] and Becker [5] relating to the energetic order of $(n\pi^*)$ and $(\pi\pi^*)$ configurations, we must, however, mention that we have got by now a properly appropriate model for the benzopyran part [1] and that moreover Russian workers [9] who have recently studied some indolino–spiropyrans have come to the same conclusions as ourselves.

Conclusion

Consequently we have proposed a classification of different $n\pi*$ and $\pi\pi*$ lowest energy singlet and triplet states for the 6-nitro-8-methoxy-2*H*-chromene, which is the best model for the "right" part of heterocyclic spiro-pyrans having generally the best photochromic properties.

In the ascribed relative order, the non-radiative deactivation of $^1(\pi\pi*)$ state is efficient by intersystem conversion $^1(\pi\pi*) \to {}^3(n\pi*)$. As a result, that assumes fluorescence inhibition and increases the lower $\pi\pi*$ triplet state population.

This relative energetic order should be also considered for spiropyrans having the same type of substitution on benzopyran ring as the chromene (1), (substituent H or Me in 3 position). This would explain that those compounds are more photocolorable than mainly 6-methoxy-8-nitro isomers, for which relative energetic order could be different. However, the photomerocyanine obtained by u.v. irradiation of chromene (1) presents a light absorption between 450 and 550 nm in toluene, but any kinetic measurement could be achieved at room temperature, because of the instability and the weak molar absorption of photoproduct. In the case of a 6-nitro-8-methoxy substitution, intervention of a triplet state would occur preferentially in photocoloration of spiropyrans. Intermolecular sensitization and quenching experiments of this reaction are on by now and should allow us to suggest an efficient mechanism [10].

Acknowledgements

References

1 P. Appriou, J. Brelivet, C. Trebaul, F. Garnier and R. Guglielmetti, Bull. Soc. Chim. Fr., in press.
2 C. Balny, M. Mosse, C. Audic and A. Hinnen, J. Chim. Phys., 68 (1971) 1078.
3 N. W. Tyer Jr. and R. S. Becker, J. Am. Chem. Soc., 92 (1970) 1289.
4 J. W. Sidman, Chem. Rev., 58 (1958) 689.
5 N. W. Tyer Jr. and R. S. Becker, J. Am. Chem. Soc., 92 (1970) 1295.
6 E. Lippert, Z. Phys. Chem., 2 (1954) 328.
7 E. Lippert, Z. Elektrochem., 61 (1957) 962.
8 A. N. Nurmukhametov and V. G. Tishchetao, Opt. Spektrosk., 23 (1967) 83.
9 I. L. Belaits and T. D. Platonova, Opt. Spektrosk., 35 (1973) 218.
10 F. Garnier, J. Guillerez, P. Appriou and R. Guglielmetti, (undertaken work).