Univ. Coll. Ann. Rev.
Vol 17 (1992).

FLUORESCENCE QUENCHING OF FLUORENE AND AZAFLUORENE COMPOUNDS BY SOME PYRIDINE AND QUINOLINE N-OXIDE DERIVATIVES

By

M. M. ABO ALY

Chemistry Department, Faculty of Science,

Ain Shams University, Cairo, Egypt

ABSTRACT

The electronic absorption spectra of 4 - nitropyridine N-oxide (4-NO_2 PYNO), 4-chloropyridine N-oxide (4-Cl PYNO), quinoline N-oxide (QuNO), 4-chloroquinoline N-oxide (4-Cl QUNO) and 4-nitroquinoline N-oxide (4-NO_2 QuNO) have been recorded in different organic solvents in the U.V. and visible regions. Pyridine and quinoline N-oxide oompounds are found to be strong quenchers for some organic fluorescent molecules such as fluorene and azafluorene. From the fluorescence measurements, stern-volmer quenching constants (Ksv) are determined. Quenching mechanism is explained in terms of electronic charge transfer and energy transfer processes.

INTRODUCTION

Though much work has been done on the solvent influences on the electronic spectra of pyridine and quinoline derivatives, less work has been done on similar studies on pyridine

and quinoline N-oxide derivatives. We have previously reported a vibrational study concerning the laser Raman and infra-red spectra of (4-Cl PYNO) and (4-NO_2 PYNO) [1]. The present investigation is devoted to attribute the electronic transition, to observed absorption bands of the studied compounds. The solvent effect on these electronic transitions especially those of intramolecular charge transfer, has been interpreted. We have likewise recorded the fluorescence spectra of the two compounds fluorene and azafluorene. A quenching study of these two compounds by the pyridine and quinoline-N-oxide derivatives are analysed and explained.

Experimental

Measurements:

Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 3ß double beam spectrophotometers in the wavelength range 450-200 nm using 1 cm quartz cells. Fluorescence spectra were recorded on Shimadzu RF 500 instrument using ethanol as solvent.

Materials:

The pyridine and quinoline N-oxides were prepared as described by E. Ochiai [2]. Pure fluorene and azafluorene were purchased from L. light & Co. Ltd. England and Aldrich respectively and used as received.

RESULTS AND DISCUSSION

Electronic spectra of some pyridine and quinoline N-oxides:

The observed spectral data concerning the absorption bands with their assignments are summarized in Table 1. Generally the spectra of all studied pyridine and quinoline N-oxides exhibit two bands, in the wavelength range 200-255 nm, and 259-380 nm. The first peak is a strong solvent independant band and attributed to an electronic transition of π-π^* type [3,4]. The higher wavelength band (259-380 nm) is assigned to an intramolecular charge transfer band (ICT) within the whole molecule. In such systems ICT acquires a lower excitation energy (higher wavelengths) as the electron withdrawing power of the substituent is increased [5,6], therefore, the largest λ max is in case of (4-NO_2 PYNO) and (4-NO_2 QUNO). One notes also that λ max (ICT) in water solvent follows the following trend:

λmax (4-Cl PYNO) < λmax (4-NO_2 PYNO) $\approx \lambda max$ (QUNO) < λmax (4-NO_2 QUNO)

Moreover, in case of hydrogen bonding solvents, protonation of the negative charge on the oxygen atom decreases the electron density available for this atom as shown by CNDO calculation [1,5,7], thus more energy is required to cause excitation and λ max is observed at lower values. This blue shift has been observed in analogous compounds [5,6].

Emission spectra of fluorene and azafluorene. Quenching by some PYNO and QUNO derivatives:

The spectra of fluorene and azafluorene quenching have been recorded in ethanol (Figs. 1 and 2). Fluorene absorbs at λAbs. = 296 nm and fluoresce at λF = 313 nm. Azafluorene absorbs at λAbs. = 345 nm and fluoresce at λF = 377 nm. A drastic inhibition in the fluorescence emission of the two compounds is observed when a dilute solution of the quenchers are added. The quenching process follows the Stern-Volmer equation Fo/F = 1 + Ksv [Q] where F and Fo are the relative fluorescence intensities in presence and in absence of the quencher of concentration [Q]. Ksv is the Stern-Volmer constant. Kav values are determined from the slope of the Fo/F vs [Q] lines. The obtained Ksv values in ethanol are given in Table 2.

Quenching Mechanism:

Over the last few years considerable interest has been devoted to study the fluorescence quenching of aromatic hydrocarbons by various types of inorganic and organic quenchers [8,9,10]. Anthracence fluorescence for example is quenched by pyridinium ion in both inter and intramolecular processes [8] and the quenching rate constants depend upon the electron affinity of the acceptor. Concerning our results, we have not observed any charge transfer band between (4-NO_2

PYNO), (4-Cl PYNO) as donors and iodine as acceptor which indicates that these two derivatives have weak electron donating character. Likewise, in all studied solutions of fluorene and azafluorene, neither the absorption wavelengths nor the emission ones are practically changed by quencher addition, excluding the possible formation of a ground or excited state complexes.

By examining the results of Table 2, we observe the following:

i. In case of azafluorene, the highest Ksv value is obtained for (4-NO_2 QUNO). Also (4-NO_2 PYNO) strongly quenches azafluorene, whereas no quenching occurs when using (4-Cl and 3-OH PYNO) as quenchers (Table 2). These observations suggest that quenching may occurred through electron or charge transfer mechanisms.

ii. The trend observed from Ksv values for fluorene is similar to that of azafluorene when PYNO derivatives have been used as quenchers. However (4-NO_2 QUNO) weakly quenches fluorene in particular when compared with (QUNO) (Table 2) which indicates that an electron transfer mechanism is not the sole only the factor determining the quenching process.

The other mechanism which can be operative is the energy transfer (ET) one. ET quenching pathway is more efficient by

increasing the spectral overlap between the fluoreacence band of the donor and the absorption band of the acceptor. It was found, that the ET rate incrcases by increasing the overlap integral between the emission spectra of benzene as a donor and the absorption spectrum of some aromatic hydrocarbons (chrysene, phenanthrene and naphthalene) as acceptors [11]. Our results (Table 2) show that Ksv values increase by increasing the overlap mentioned above. In case of azafluorene the highest two Ksv values are obtained for the two quenchers (4-NO_2 QUNO) and (4-NO_2 PYNO). For fluorene, the highest Ksv values are obtained for (4-NO_2 PYNO) and (QUNO). It is very interesting to note that the Ksv values for the last two quenchers have been inverted when azafluorene is changed into fluorene. This last observation strongly confirms the important contribution of (ET) process as a quenching route.

ACKNOWLEDGEMENT

We thank Prof. Dr. M.S.A. Abdel Mottaleb of the same department for his help and encouragement. Thanks also to Mrs S. Morsi for her kind experimental assistance.

REFERENCES

1. M.M. Abo Aly and S. Morsi, Spectrochim. Acta, 48A, 615 (1992).

2. E. Ochiai, J. Org. Chem., 18, 534 (1953).

3. T. Kubota, J. Am. Chem. Soc. 87, 453 (1965).

4. H. Miyazaki, T. Kubota and M. Yamakawa. Bull. Chem. Soc. Jpn. 45, 780 (1972).

5. M.S.A. Abd El-Mottaleb, Z. Naturforsch, 37a, 1353 (1982).

6. M.R. Mahmoud, A.M. Awad and A.M. Shaker. Spectrochim. Acta 41A, 1177 (1985).

7. M.S.A. Abd El-Mottaleb, M.M. Abo Aly. Unpublished results.

8. G.M. Michael Blackburn, G. Lockwood and V. Solan, J.C.S. Perkin II, 1452 (1976)

9. T. Moriya, Bull. Chem. Soc. Jpn, 57, 1723 (1984).

10. V. Wintgen, J. Pouliquen, M. Simalty and J. Kossanyi, J. Photochem. 26, 131 (1984).

11. P.S. Engel and C. Steel, Acc. Chem. Res. 6, 275 (1973).

Table 1: The electronic spectra of some pyridine and quinoline N-oxide derivatives.

a) Compound	b) CCl_4 λmax	log E	C_2H_5OH λmax	log E	CH_3OH λmax	log E	H_2O λmax	log E	Assignment
4-NO_2 Py N-O	250		233		231		227		$\pi - \pi^*$
	337	4.270	322	4.30	338	4.276	310	4.088	(ICT)
4-Cl Py N-O	248		207		223		209		$\pi - \pi^*$
	278	4.188	267	4.152	277	4.170	259	4.203	(ICT)
Qu N-O	257		229		229		229		$\pi - \pi^*$
	330	3.66	315	3.720	315	3.685	312	3.680	(ICT)
4-NO_2 Qu N-O	255		256		253		249		$\pi - \pi^*$
	380	4.176	376	4.026	376	4.160	365	3.840	(ICT)
4-Cl Qu N-O	252		220		218		222		$\pi - \pi^*$
	355	3.960	330		328	3.920	320	3.900	(ICT)

a) See text for the name of the compound

b) λmax: absorption maximum wavelength in nm

c) ICT= intramolecular charge transfer

Table 2: Quenching of fluorene and azafluorene fluorescence by some pyridine and quinoline N-oxide derivatives[a].

Fluorescer[b]	Quencher	λmax (quencher) nm	log Ksv (l mol^{-1})
Fluorene	Qu N-O	313	4.143
	4-NO_2 Qu N-O	370	3.944
	4-Cl Qu N-O	330	3.736
	4-NO_2 PY N-O	322	4.477
	4-Cl PY N-O	267	3.845
	3-OH PY N-O	297	3.670
Azafluorene	4-NO_2 Qu N-O	370	4.470
	4-Cl Qu N-O	330	4.158
	Qu N-O	313	3.803
	4-NO_2 PY N-O	322	4.342
	3-OH PY N-O	297	
	4-Cl PY N-O	267	No quenching

a) Measurements are taken in ethanol as a solvent. Maximum absorption of fluorene and azafluorene are 296 and 345 nm respectively.

b) Maximum of the fluorenscence peaks of fluorene and azafluorene are 313 and 376 nm respectively.

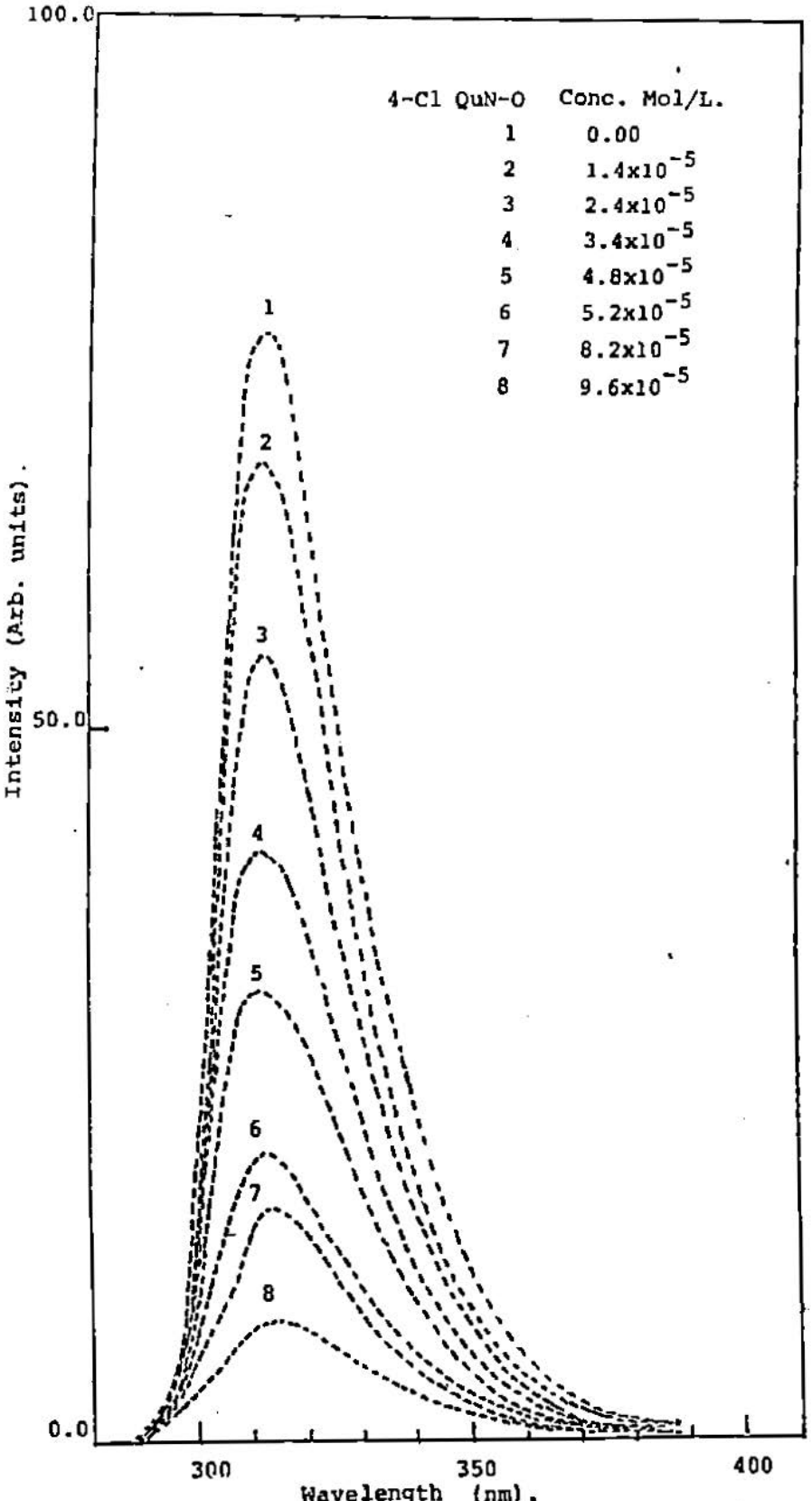

Fig. 2 : Fluorescence quenching spectra of fluorene in EtOH by 4-chloroquinoline N-oxide.

'niv. Coll. Ann. Rev.
'ol 17 (1992).

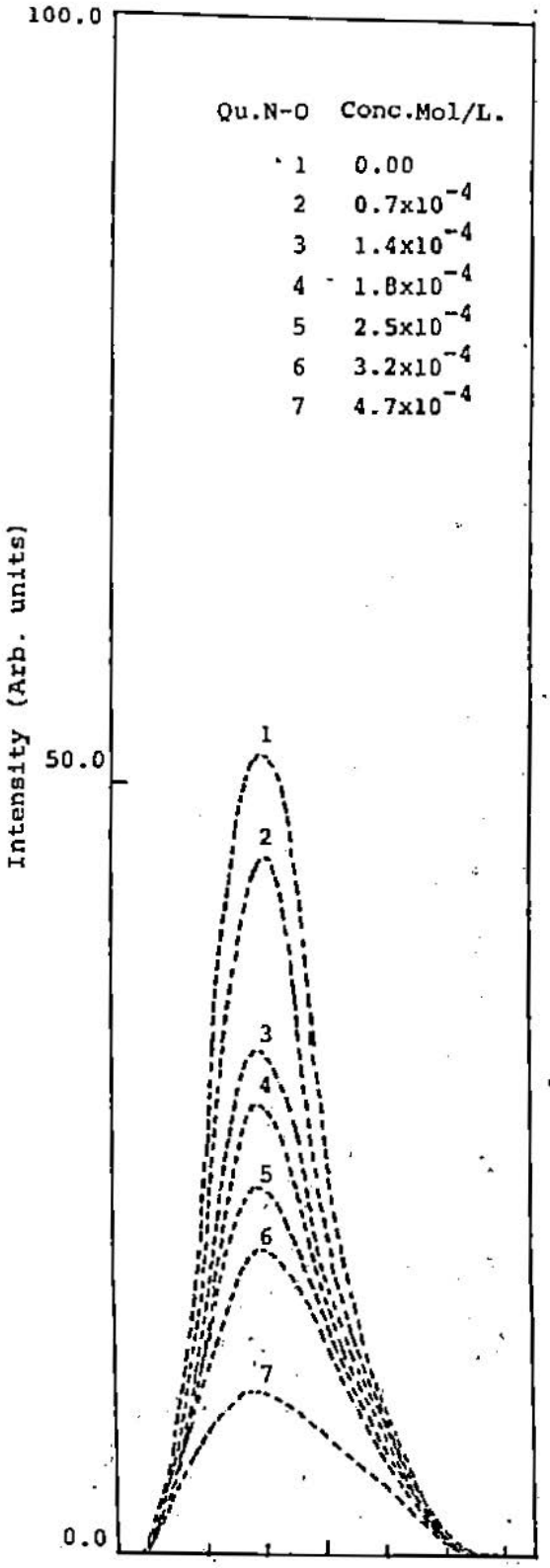

Fig. 1 : Fluorescence quenching spectra of azafluorene in EtOH by quinoline N-oxide.

Univ. Coll. Ann. Rev.
Vol 17 (1992).

ملخص البحث

أطياف الإمتصاص الإلكترونى لبعض مشتقات
البريدين والكينولين - ان - أكسيد. التأثير
التثبيطى لهذه المشتقات على الفلوريسنس
الناتج من الفلورين والآزافلورين

تم فى هذا البحث دراسة أطياف الإمتصاص الإليكترونى لخمسة مشتقات من البريدين - ان أوكسيد والكينولين - ان - أكسيد فى مذيبات عضوية مختلفه فى منطقتى الأشعة فوق البنفسجيه والمرئيه . وقد تم تحديد نوع الحزم الضوئية الناتجة لهذه المركبات . فى الجزئ الثانى من هذا البحث تمت دراسة التأثير التثبيطى لمشتقات البريدين والكينولين - ان - أكسيد على الفلوريسينس الناتج من الفلورين والآزافلورين . بإستخدام معادلة شترن - فولمر أمكن حساب معدل التثبيط وقد وجد أن ميكانيكيه التأثير التثبيطى يمكن أن تعزى الى إنتقال الطاقه بنسبه أكبر عن إنتقال الشحنه.