The Photoluminescence of Some β-Nitrostyrenes. Excited State Energies in Unsaturated Nitro-compounds

By **David J. Cowley,** School of Physical Sciences, New University of Ulster, Coleraine, Northern Ireland

The luminescences of various β-nitrostyrenes, $XC_6H_4CH=C(R)NO_2$, where X = H, Cl, OCH_3, or $N(CH_3)_2$ and R = H or CH_3, are reported. When X = H, Cl, or OCH_3 only phosphorescence is observed in glassy media at 77 K whereas when X = $N(CH_3)_2$ only a fluorescence, strongly dependent in intensity on solvent polarity and temperature, is detectable. An interpretation is given supported by PPP–SCF–MO–CI calculations. It is argued that the singlet and triplet n,π^* states are located around 2.95 and 2.50 eV respectively in every case and that the energy of the intramolecular charge-transfer π,π^* excited singlet state, which is sensitive to substituents and solvent polarity, determines the resulting photophysical behaviour.

THE luminescence characteristics of many aromatic nitro-compounds have been reported [1-4] from time to time. Most simple nitroaromatics exhibit only a weak to moderate phosphorescence but highly conjugated systems, *e.g.* 6-nitrochrysene,[5] or systems containing strong electron-donating substituents,[6,7] may show a good fluorescence. More recently,[8] attention has been focused on the dependence of the luminescences on the electronic structures of isomeric nitroanilines and their *N*-methylated derivatives and on the solvent media; in particular the complementarity of fluorescence and phosphorescence.

These features are manifest also in the data we report for a number of β-nitrostyrene derivatives, and can be utilised to determine the layout of the lower lying excited states in a range of nitro-compounds. From PPP–SCF–MO–CI calculations on the nature and energies of the excited states the roles played by both the intramolecular charge-transfer $(NO_2 \longleftarrow XAr)$ π,π^* state and the nitro-group localised n,π^* states are more readily seen. The results are relevant to the photochemistry of many nitroaromatics as yet unexplored in detail.

EXPERIMENTAL

Materials.—The *trans*-isomers of the β-nitrostyrenes were prepared by condensation of the appropriate aldehydes and nitroalkanes using published methods,[9] and purified by column chromatography and recrystallisation as required. Solvents were of spectroscopic or redistilled AnalaR grade and were non-emissive under excitation in the spectral regions used in this work.

Spectra.—U.v. absorption and uncorrected fluorescence spectra of 10^{-4}—10^{-5}M solutions were obtained as described in an earlier paper.[10] The fluorescence quantum yield ϕ_F of compound [IV; X = p-$N(CH_3)_2$] in benzene was determined relative to that of fluorescein in 0.1N aqueous sodium hydroxide (ϕ_F 0.90 assumed) for 460 nm excitation. The yields for all other systems were measured with respect to that of compound [IV; X = p-$N(CH_3)_2$] in benzene for 420—450 nm excitation.

---

[1] S. P. McGlynn, T. Azumi, and M. Kinoshita, 'Molecular Spectroscopy of the Triplet State,' Prentice–Hall, New Jersey, 1969, ch. 6.

[2] Landolt-Börnstein, New Series, Group II, vol. 3, 'Luminescence of Organic Substances,' Springer–Verlag, Berlin, 1967.

[3] E. Lippert, *Z. phys. Chem.* (*Frankfurt*), 1954, **2**, 328.

[4] E. Lippert, *Z. Electrochem.*, 1957, **61**, 962.

[5] O. S. Khahil, H. G. Bach, and S. P. McGlynn, *J. Mol. Spectroscopy*, 1970, **35**, 455.

[6] A. V. Aristov and E. N. Viktorova, *Optics and Spectroscopy*, 1967, **22**, 506.

[7] D. Gegiou, K. A. Muskat, and E. Fischer, *J. Amer. Chem. Soc.*, 1968, **90**, 3907.

[8] O. S. Khahil, C. J. Seliskar, and S. P. McGlynn, *J. Chem. Phys.*, 1973, **58**, 1607.

[9] O. Schales and H. A. Graefe, *J. Amer. Chem. Soc.*, 1952, **74**, 4486.

[10] D. J. Cowley, *J.C.S. Perkin II*, 1975, 287.

Phosphorescence spectra (uncorrected) and phosphorescence lifetimes were obtained, using the rotating-can accessory of the Perkin-Elmer MPF-2A fluorimeter, for clear glasses formed on cooling 10^{-3}—10^{-4}M solutions, previously nitrogen-flushed, to 77 K in sealed 2 mm internal diameter Spectrosil tubes. Phosphorescence yields ϕ_P at 77 K were determined using benzophenone in ethanol as reference (ϕ_P 0.74 assumed; measured lifetime 6.0 ms) assuming that the ratios of the optical densities at the excitation wavelength at 77 K correspond to those of the 293 K absorption spectra. The absolute values may be in error by ±50% but we attach more confidence (±15% error) to the relative yields for the nitrostyrenes.

TABLE 1

Lowest-energy CT absorption band maxima $\bar{\nu}_A$ of 4′-substituted β-nitrostyrenes at 293 K

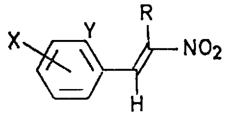
	$\bar{\nu}_A$/kK	
Compound	Cyclohexane	Ethanol
(I)	33.33	32.47
(II)	32.68	31.95
(III; X = *p*-OCH_3)	29.85	28.82
[IV; X = *p*-$N(CH_3)_2$]	25.00	23.15
(V)	25.25	23.87

Pariser–Pople–Parr–SCF–MO–CI Calculations.—A published computer program,[11] modified slightly to utilise repulsion integrals derived from a simple Mataga expression, was used. Some details[12] of the conventional parametrisation adopted here have appeared. Effective ionisation potentials I_X' for Cl, OCH_3, and $N(CH_3)_2$ substituents, regarded as single atomic centres of Z 2, were set in a coarse fashion at 31.16, 27.18, and 23.16 eV respectively. These values gave reasonable correspondence of theoretical and experimental u.v. absorption band maxima and ground-state dipole moments for substituted nitrobenzenes and nitrostyrenes. The two-electron repulsion integrals γ_{XX} were set at 16.5 eV and β_{CX} fixed at −2.00 eV.

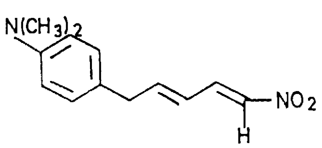
Further refinement of the parameters is not warranted by the resulting improvement in results with respect to the context of this work. Excited-state energies *etc.* were obtained after inclusion of at least 25 singly-excited configurations in the CI calculations.

RESULTS

The nitrostyrenes (I)—(VIII) and the nitrobutadiene (IX) were investigated.



(I) X = Y = R = H
(II) X = *p*-Cl, Y = R = H
(III) X = OCH_3, Y = R = H
(IV) X = $N(CH_3)_2$, Y = R = H
(V) X = *p*-$N(CH_3)_2$, Y = H, R = CH_3
(VI) X = *o*-OCH_3, Y = H, R = CH_3
(VII) X = *p*-Cl, Y = H, R = CH_3
(VIII) X = *p*-$N(CH_3)_2$, Y = Cl, R = H



(IX)

(a) *U.v. Absorption Spectra*.—Table 1 gives the energies of the lowest energy, intramolecular charge-transfer, π*,π absorption band maxima for a select set of *para*-substituted nitrostyrenes in which the substituent group X varies in π-electron donor ability (H) < Cl < $^-OCH_3$ < $^-N(CH_3)_2$. The shift of $\bar{\nu}_A$ to lower energy and the increasing influence of solvent polarity on the band position with increase in the substituent X donor ability is wholly expected and reflects the increasing charge migration on absorption of light.

TABLE 2

Fluorescence and phosphorescence characteristics of some β-nitrostyrenes

	Fluorescence at 293 K			
	$\bar{\nu}_F$/kK		ϕ_F	
Compound	Cyclohexane	Benzene	Benzene	Anisole
(V)	None	20.08		0.007
(VIII)	None	20.33	0.02	0.28
[IV; X = *p*-$N(CH_3)_2$]	None	20.08	0.13	0.17
(IX)	20.08	18.28	0.12	
[IV; X = *o*-$N(CH_3)_2$]	18.45	18.32	0.10 *	

	Phosphorescence at 77 K			
	$\bar{\nu}_P$/kK		$10^4\phi_P$	τ_P(ms)
Compound	Diethyl ether	Ethanol	Ethanol	Ethanol
(I)	19.12	19.08	6	7
(II)	18.87	18.94	13	5
(III; X = *o*-OCH_3)	19.23	19.19	20	12
(III; X = *m*-OCH_3)	18.73	18.66	15	9
(III; X = *p*-OCH_3)	18.45	18.38	44	32
(VI)		19.23	<1	

Estimated error in ϕ_F values ±15%.

* Neat cyclohexane solution.

(b) ***Phosphorescence Data***.—When X = H, Cl, or OCH_3 only phosphorescence was observed. No phosphorescence was detectable when X = $N(CH_3)_2$.

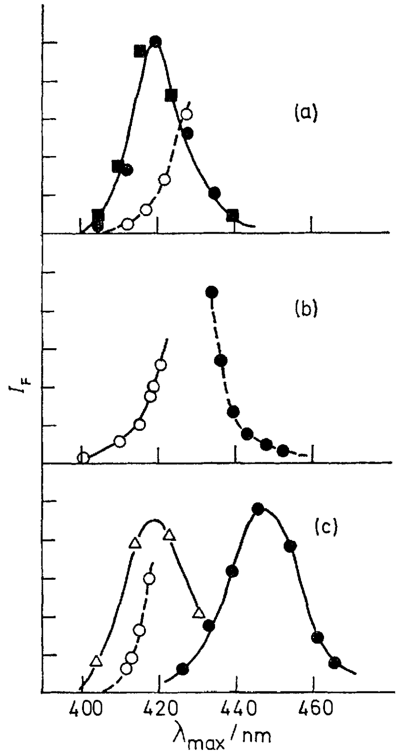
---

[11] N. N. Greenwood, 'Computing Methods in Quantum Organic Chemistry,' Wiley, New York, 1972.

[12] T. S. Cameron, D. J Cowley, and J. E. Thompson, *J.C.S. Perkin II*, 1974, 774.

The phosphorescence emission spectra consisted in each case of two or three fairly well resolved vibrational components with separation 1 300 ± 100 cm^{-1} independent of solvent or substituent X (NO_2 group symmetric stretch). The first component, which was normally about three times more intense than the second with the third component very weak indeed, was taken to be the 0,0 band.

The low phosphorescence yields approximately parallel the measured lifetimes (Table 2). Of the three methoxynitrostyrenes, the *para*-isomer (III; X = *p*-OMe) exhibits the highest ϕ_P, the longest lifetime τ_P, and the lowest emission energy, a situation with parallel in the nitroanilines.[8]



(a) Compound [IV; X = *p*-$N(CH_3)_2$] dissolved in cyclohexane containing chloroform (■), piperidine (●), and benzene (○). (b) Compound [IV; X = *o*-$N(CH_3)_2$] dissolved in benzene–cyclohexane mixtures (●), and compound (V) dissolved in various ethers and methyl benzenes (○). (c) Compound (IX) dissolved in chloroform–cyclohexane mixtures (●), and compound (VIII) dissolved in methylbenzenes (○) and chloroform–cyclohexane mixtures (△). I_f is the fluorescence intensity (arbitrary units)

The phosphorescence yield is lowered significantly by β-methyl substitution, *cf.* (VII) with (II), (VI) with (III; X = *o*-OCH_3).

Compound (VII) showed neither fluorescence nor phosphorescence under a variety of conditions.

(c) *Fluorescence Data.*—Measurements of fluorescence were made both at 77 and 293 K in many solvents for each compound but only a few examples are recorded in Table 2 (but see also the Figure). While the absorption band maxima shift considerably with change in solvent polarity the fluorescence band maxima are insensitive to such a change, as discussed elsewhere.[10]

The Figure depicts the variation of fluorescence yields for a few compounds with solvent polarity; the latter is represented empirically by the position of the π^*,π charge-transfer absorption band maxima of the particular compound in the solvent media. For a given compound the reported fluorescence intensities in various solvent mixtures may be compared quantitatively, *i.e.* they are relative quantum yields, but not so between compounds. For all compounds included in the Figure, but excluding (V), the maximum fluorescence yields in solution at room temperature were moderate (*ca.* 0.1). The yield for (V) was only 0.007 under these conditions. The fluorescence yields of all compounds increased on cooling solutions to 77 K (yields up to *ca.* 0.3). Full results on *inter alia* the effect of temperature on the fluorescence of the representative compound [IV; X = *p*-$N(CH_3)_2$] have been published.[10]

(d) *PPP-SCF-MO Calculations.*—Table 3 gives energies of the lower-lying singlet and triplet π,π^* excited states obtained from PPP calculations on some key and representative nitroaromatic systems. Experimental data are included for comparison.

Transitions (from S_0) to S_2 and S_3 are invariably weak, with calculated and experimental oscillator strengths of ≤ 0.01, while transitions to S_1 and S_4 are strong; for example, for the *para*-substituted nitrostyrenes the experimental and theoretical oscillator strengths are in the range 0.3—0.5.

The experimental singlet manifold is reproduced quite closely in the calculations and also, perhaps surprisingly well, the $S_1 - T_1$ energy differences and the T_1 energies. From the meagre published data on triplet–triplet absorption spectra of aromatic nitro-compounds[13] the computed T_2 energy levels appear to be grossly underestimated (by as much as 1 eV).

In our calculations the $S_1(\pi,\pi^*)$ state is dominated by the charge-transfer excitation χ_{CT} from the highest filled molecular orbital of the X–Ar system into the lowest vacant antibonding molecular orbital (see Table 3). The latter orbital is located almost exclusively on the acceptor nitro-group for a very wide range of compounds. The specific results support quantitatively the descriptive arguments given by Suppan[14] for D–Ar–A systems.

The extent of actual electron migration in χ_{CT} depends, as expected, on the ability of the donor group X to release charge *i.e.* on the effective ionisation potential I_P'. Thus the S_1 state molecular dipole moment (π-electron) is large and increases rapidly for X = H < Cl < OCH_3 ⋘ $N(CH_3)_2$, this trend being confirmed, in the absorption spectral data (Table 1).

The lowest π,π^* triplet state, T_1, is described mainly in terms of an intra-X–Ar excitation in the calculations. Experimentally, there is an absence of any marked dependence of $\bar{\nu}_P(0,0)$ on solvent polarity (Table 1) or on the electron-donor ability of substituent X. The minor contribution of $^3\chi_{CT}$ to T_1 may be reflected in the order of T_1 energies for compounds (III; X = *o*-OCH_3), (III; X = *m*-OCH_3), and (III; X = *p*-OCH_3) which is the reverse of that for the S_1 levels. The latter order is explicable on a simple electrostatic model.[15]

Using our PPP parameters or similar conventional

---

[13] J. J. Mikula, R. W. Anderson, jun., and L. E. Harris, *Adv. Mol. Relaxation Processes*, 1973, **5**, 193.

[14] P. Suppan, *J. Mol. Spectroscopy*, 1969, **30**, 17.

[15] See for example, A. E. Lutskii, *Optics and Spectroscopy*, 1973, **34**, 624.

values,[16] the lowest π,π^* triplet level is computed to lie at *ca.* 1.7—2.0 eV and arises from a highly localised excitation on the nitro-group, from the non-π-bonding molecular orbital located solely on the oxygen atoms into the anti-bonding molecular orbital on NO_2. The corresponding singlet state lies above 6 eV. The triplet energy is very sensitive * to the values adopted for β_{NO}, γ_{NN}, γ_{OO}, *etc.* These parameters are important in determining the charge distribution internal to the nitro-group but have minor effects on the relationship of the nitro-group to the rest of the unsaturated system.

TABLE 3

Calculated and experimental singlet and triplet π,π^* state energies

Compound	State energies/eV						P_{CT} †	
	S_1	S_2	S_3	S_4	T_1	T_2	S_1	T_1
(I)	3.92 (4.15)	4.45	5.37	5.40 (5.48)	2.20 [2.36]	3.49	0.92	0.33
(II)	3.84 (4.06)	4.46	5.29 (5.38)	5.35	2.29 [2.34]	3.49	0.92	0.33
2-$O_2NC_{10}H_7$ (X)	3.59 (3.35)	4.20 (3.93)	4.53	4.72 (4.77)	2.02 [2.34] [a]	3.18	0.89	0.22
$H_2NC_5H_4NO_2$-*o* (XIa)	3.38 (3.20)	4.37 (4.60)	4.80 (5.04)	5.71 (5.53)	2.56	2.94	0.95	0.10
$H_2NC_6H_4NO_2$-*m* (XIb)	3.65 (3.56)	4.42 (4.63)	4.80 (5.04)	5.67 (5.49)	2.55	3.06	0.95	0.12
$H_2NC_6H_4NO_2$-*p* (XIc)	3.83 (3.87)	4.35	4.97	5.76 (5.49)	2.58 [2.41]	3.47	0.94	0.25
[III; X = *p*-OCH_3]	3.69 (3.68)	4.42	5.02	5.27 (5.08)	2.38 [2.27] [b]	3.49	0.90	0.25
[IV; X = *p*-$N(CH_3)_2$]	2.99 (3.09)	3.85 (3.81)	4.32	4.72 (4.73)	1.67	2.85	0.90	0.34
(IX)	2.96 (2.91)	3.83	3.96	4.37	1.61	2.47	0.84	0.27

( ) = Experimental absorption band maxima in non-polar solvent; [ ] = experimental phosphorescence (0,0) band in ethanol at 77 K.

† P_{CT} = Fractional contribution to the excited state after CI of the charge transfer excitation χ_{CT} (highest occupied molecular orbital on X–Ar system into nitro-group π^* orbital).

[a] Ref. 19. [b] Ref. 8.

We feel justified in ignoring this somewhat embarrassing level, as grossly underestimated in energy, for the purpose of the subsequent discussion. It lies above 3.5 eV probably.

DISCUSSION

Attention is drawn to two key features of our results, which are also implicit [3,4] or made explicit [6,8] in other reports of nitroaromatic luminescences.

First, the complementarity of phosphorescence and fluorescence emissions. The changeover from phosphorescence to fluorescence can be accomplished by increasing the ' size ' of the conjugated system Ar to which the nitro-group is joined, by increasing electron density in the Ar system *via* electron-donor substituents, and in certain cases by change in solvent polarity and matrix rigidity (*via* temperature) or by combinations of these factors. Secondly, the marked influence of solvent on fluorescence yields, which must be related to the large dipole moments of the first π,π^* excited singlet states and the magnitude of the relaxation term associated with solvent reorganisation about the excited solute.

The luminescence behaviour in the series of nitrostyrenes (with ready inclusion of other compounds) can be correlated empirically with the energy of the Franck–Condon S_1, π,π^*, state; the latter can be determined from the u.v. absorption band maxima after an allowance, reckoned to be *ca.* 0.15 eV, for the difference between the band maxima and the actual energy of the 0,0 transition. From our results (see Tables and Figure) and other published data,[4,6,7] the boundary line between phosphorescence–fluorescence emission occurs when the u.v. absorption band maxima is *ca.* 410 nm (3.10 eV), *i.e.* when S_1 is *ca.* (3.10—0.15) = 2.95 eV. We note that the intrinsic radiative lifetime of S_1, calculated to be *ca.* 5 ns, does not alter markedly across this boundary line as evidenced by the experimental u.v. absorption band intensities and the calculated oscillator strengths.

Thus, lack of fluorescence from S_1 when $S_1 > 2.95$ eV in energy must arise from a rapid, competitive, non-radiative decay route. Similarly, absence of any appreciable phosphorescence when $S_1 < 2.95$ eV implies inefficiency in intersystem crossing from S_1 or in internal conversion within the triplet manifold or both. The nature of $T_1(\pi,\pi^*)$, as judged by the experimental findings and by PPP calculations, and hence also the radiative transitions $S_0 \longleftarrow T_1$, does not alter substantially on crossing the boundary line.

The efficiencies of the luminescences in the nitrostyrenes will be strongly influenced by the non-radiative

---

* Thanks are due to Professor J. Michl for useful comments. Model calculations by us on the nitroethylene system confirm the sensitivity of the triplet energy to these parameters (E_T 1.0—4.0 eV for not unusual values of β_{NO}, *etc.*).

[16] K. R. Loos, U. P. Wild, and H. H. Gunthard, *Spectrochim. Acta*, 1969, **25A**, 275.

geometric isomerisation processes depleting the excited states. The low phosphorescence yields of the nitrostyrenes in this study relative to those of various nitroaromatic systems are indicative of this, as is also the effect thereon of β-methyl substitution.

That such isomerisation pathways are the prime factor in determining the fluorescence–phosphorescence complementarity is, however, doubtful in view of the following. (*a*) A parallel pattern of luminescence behaviour is observed in the nitroanilines.[8] (*b*) The pattern for the nitrostyrene series at low temperatures in rigid matrices, where isomerisation yields are negligible, is identical to that observed at room temperature where isomerisation does occur.[17] (*c*) The presence of phosphorescence does not correlate with the absence of geometric isomerisation (although the presence of fluorescence might appear to correlate thus).

We favour an explanation involving a familiar electronic state crossover of singlet and triplet π,π^* and n,π^* levels. The following evidence is offered as to the energies of such levels and their variation with structure and solvent.

From sensitisation and quenching studies on the photo-abstraction of hydrogen by nitrobenzene, the n,π^* triplet level is reckoned to lie at 2.65 eV (60.8 kcal mol^{-1}). Modified PPP calculations by Plotnikov [18] place $T_1(n,\pi^*)$ at 2.62 eV in nitrobenzene and indicate that the $S_1(n,\pi^*) - T_1(n,\pi^*)$ energy difference is $\lesssim 0.5$ eV. Lim and Stanilaus [19] make the tentative suggestion that a small shoulder at 378 mm (3.27 eV) in the phosphorescence excitation spectrum of 2-nitronaphthalene is due to π^*,n excitation.

Our MO calculations indicate that, for the series of nitrostyrenes studied and also for the compounds given in Table 3, the lowest vacant π^* orbital is located essentially on the nitro-group. Thus we deduce that the π^*,n excitation should be almost independent of the structure of the molecular residue X–Ar *i.e.* the n,π^* states are approximately constant in energy. Further since the π^*,n excitation is highly localised, the $^1(n,\pi^*)$ and $^3(n,\pi^*)$ state molecular dipole moments will be close to that of S_0, the ground electronic state. *Differential* shifts in state energies with change in solvent polarity will be very small, as for $T_1(\pi,\pi^*)$, but unlike those of $S_1(\pi,\pi^*)$. Solvent-induced fluorescence *e.g.* for compounds [IV; $X = p\text{-N(CH}_3)_2$], (V), (VIII), and (IX) is readily related to structure-induced fluorescence as a consequence of shifting $S_1(\pi,\pi^*)$ relative to other states in a continuous rather than in an abrupt fashion.

We propose that the absence of fluorescence when $S_1 > ca.$ 2.95 eV arises because of the rapid internal conversion process $S_1(\pi,\pi^*) \longrightarrow S_1(n,\pi^*)$. The observed phosphorescences of the nitrostyrenes, as for many phosphorescent nitroaromatics,[1] lie in the range 2.27—2.41 eV and appear to originate from predominantly π,π^* triplet states. The lifetimes of the nitrostyrenes perhaps indicate appreciable n,π^* character in the emitting states. Labelling states as nominally pure, on our model the above data requires $T_1(n,\pi^*)$ to lie above 2.4 eV.

Enhanced intersystem crossing ($S_1\ \pi,\pi^* \longrightarrow T_1\ n,\pi^*$) might, in accordance with the El Sayed rules,[20] be the origin of fluorescence quenching as the energy of $S_1(\pi,\pi^*)$ approaches *ca.* 2.85 (440 nm) $- 0.15 = 2.70$ eV (see Figure) as a result of changes in molecular structure and/or solvent polarity.

In summary, we assign energies to the singlet and triplet n,π^* levels of *ca.* 2.95 and 2.50 eV respectively and rationalise the luminescence characteristics of many nitroaromatics on the basis of the anticipated S_1 energy and its nature. The results are relevant to many, as yet unexplored or unrationalised, photochemical reactions of nitroaromatics and solvent effects thereon.

Thanks are extended to Dr. N. M. D. Brown for assistance with the MO calculations.

[5/177 *Received*, *27th January*, 1975]

---

[17] D. J. Cowley, unpublished data.

[18] V. G. Plotnikov, *Optics and Spectroscopy*, 1965, **19**, 217.

[19] E. C. Lim and J. Stanislaus, *Chem. Phys. Letters*, 1970, **6**, 195.

[20] M. A. El-Sayed, *Accounts Chem. Res.*, 1968, **1**, 8.