Influence of Solvent on the Electronic Absorption and Fluorescence Spectra of *trans*-1-(4-*NN*-Dimethylaminophenyl)-2-nitroethylene

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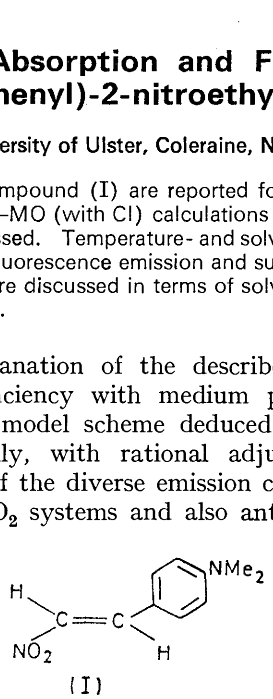
The electronic absorption and fluorescence spectra of the title compound (I) are reported for a wide range of solvents. Spectral assignments are made with the aid of PPP–SCF–MO (with CI) calculations and the nature of the lowest energy, intramolecular, charge-transfer transition is discussed. Temperature- and solvent-induced shifts of the fluorescence band of (I) are interpreted. The induction of fluorescence emission and subsequent quenching on addition of polar solvents to cyclohexane solutions of (I) are discussed in terms of solvent effects on the juxtaposition of the n–π^* and π–π^* singlet and triplet energy levels.

THE class of substituted dipolar molecules of structure D–Ar–A (where D is an electron donor group, Ar is a conjugated π electron system wholly or in part aromatic, and A is an electron acceptor group) is characterised by highly polar excited electronic states of low energy (2·5—4·0 eV). The lowest energy electronic absorption band of such D–Ar–A systems is normally intense (oscillator strength f 0·1—1·0), shows large shifts with change in solvent polarity, and is ascribed to an intramolecular charge-transfer (ICT) excitation. Various SCF–MO (with CI) calculations by ourselves and other workers [1,2] give quantitative support to the qualitative interpretation [3] of the electronic properties of D–Ar–A systems put forward by Suppan. The electronic absorption spectra, and to a lesser extent the fluorescence spectra, of a number of D–Ar–A compounds including those [4-6] where A = NO_2 have been reported but detailed studies and interpretations of electronic states are few. It has been noted that the fluorescence efficiency can be markedly solvent dependent.

We report spectral observations for the nitrostyrene (I) together with the predictions of PPP–SCF–MO (with CI) calculations. Using this evidence of the energies and nature of the lower lying molecular excited states, an explanation of the described variation in fluorescence efficiency with medium polarity is constructed. The model scheme deduced for (I) can be applied fruitfully, with rational adjustment to the interpretation of the diverse emission characteristics of many D–Ar–NO_2 systems and also anticipates solvent effects on certain photochemical reactions of nitroaromatics as yet unexplored. Some insight into the occurrence of distinctive short fluorescence decay times for some D–Ar–A compounds,[7] including (I), is also given.



(I)

Finally, controversy has been generated over the role of the solvent in determining the form of the luminescence from some electron-donor, substituted aromatic nitriles.[8,9] We report briefly for comparison on the molecular association of polar solvents with (I), a similar, highly dipolar D–Ar–A compound.

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[1] A. E. Lutskii, *Optical Spectroscopy*, 1973, **34**, 624.

[2] H. Labhart and G. Wagnière, *Helv. Chim. Acta*, 1963, **46**, 1314.

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

[4] E. Lippert, *Z. Phys. Chem.* (*Frankfurt*), 1954, **2**, 328.

[5] E. Lippert and F. Moll, *Z. Electrochem.*, 1954, **58**, 718.

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

[7] N. Mataga and T. Kubota, 'Molecular Interactions and Electronic Spectra,' Marcel Dekker, New York, 1970, p. 404.

[8] O. S. Khalil, R. H. Hofeldt, and S. P. McGlynn, *Chem. Phys. Letters*, 1972, **17**, 479.

[9] K. Rotkiewicz, K. H. Grellmann, and Z. R. Grabowskii, *Chem. Phys. Letters*, 1973, **19**, 315.

EXPERIMENTAL

The nitrostyrene (I) was prepared by the method of Drain and Wilson.[10] All solvents were of analytical reagent or spectroscopic grade, distilled before use, and non-emissive in the required wavelength region for this work. Poly(methyl methacrylate) (PMMA) samples were obtained by thermal polymerisation (70°; 6 h; in the dark) of freshly distilled methyl methacrylate solutions containing (I), with a trace of AZDN (αα′-azobis-2-methylpropionitrile) initiator.

Absorption spectra of 10^{-4}—10^{-5}M solutions in silica cells (10 mm) were recorded on Unicam SP 800 or Perkin-Elmer 402 instruments with holmium glass calibration of wavelength. Uncorrected fluorescence spectra were obtained using a Perkin-Elmer MPF-2A spectrofluorimeter for solutions $<0{\cdot}05$ in optical density per 10 mm path length at the excitation wavelength.

Relative yields of fluorescence for 420 nm excitation wavelength were determined (to ±10%) with respect to solutions of (I) in benzene at room temperature; corrections were made for differences in solvent refractive index and solution optical density at 420 nm, but not for the small variation of detector response over the range 480—550 nm. Low temperature fluorescence measurements were made on solutions sealed in silica tubes (4 mm inside diameter) inserted in a cylindrical gas-cooled Dewar (13 mm inside diameter); temperatures were monitored to ±1° by thermocouple. For measurements at 77 K, sample tubes were immersed directly in liquid nitrogen coolant. The presence of dissolved oxygen in the samples did not affect the fluorescence yields recorded as determined by control experiments.

Parametrisation for the PPP–SCF–MO–CI calculations, which was conventional,[2] is reported elsewhere.[11]

RESULTS AND DISCUSSION

Absorption Spectra.—(i) *Assignment of absorption bands*. Table 1 gives the observed spectral bands of (I) in cyclohexane and ethanol in the visible and near-u.v. regions. $\pi^* \longleftarrow \pi$ Transition energies and the excitation characters, calculated within the PPP–SCF–MO approximation including configurational interaction of 25 singly excited configurations, are given for comparison. The SCF–MO atomic orbital coefficients appear in Table 2(*a*) and excited state charge densities and dipole moments in Table 2(*b*).

TABLE 1

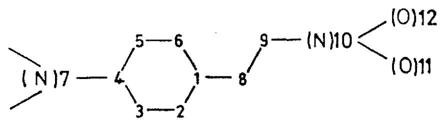
Observed and calculated electronic transitions of (I)

Solvent	$\lambda_{\max.}$/nm	Energy/eV	ε_M/l mol^{-1} cm^{-1}	$f_{\text{obs.}}$	Energy/eV	$f_{\text{calc.}}$	Excited state composition (after CI)
Cyclohexane	400	3·09	27,000	0·47	2·987	0·435 ^{y}	$\psi_1 = 0{\cdot}946\chi_{78} - 0{\cdot}294\chi_{58}$
Ethanol	434	2·87					
Cyclohexane	326	3·80	2400	0·04	3·854	0·041 ^{x}	$\psi_2 = 0{\cdot}923\chi_{710} + 0{\cdot}290\chi_{69} + 0{\cdot}199\chi_{68}$
Ethanol	333	3·73					
Cyclohexane	257	4·82	11,800	0·25	4·322	0·461 ^{y}	$\psi_3 = 0{\cdot}971\chi_{79} + 0{\cdot}104\chi_{58} - 0{\cdot}119\chi_{610} - 0{\cdot}108\chi_{59}$
Ethanol	270	4·62					

f = Oscillator strength. y and x: transitions polarised mainly along and perpendicular to the long axis of the molecule, respectively. χ_{nm} = electronic configuration after one-electron excitation from molecular orbital n to molecular orbital m (see Table 2).

TABLE 2

(*a*) SCF Molecular orbitals and atomic orbital coefficients for (I)



MO designation	MO energy/eV	Atomic orbital coefficients × 10^3 1	2	3	4	5	6	7	8	9	10	11	12
ψ_1	−18·66	10	1	1	1	1	2	0	42	108	724	481	480
ψ_2	−13·99	444	356	338	390	338	357	172	312	196	−11	−38	−30
ψ_3	−12·90	7	−2	−11	−18	−11	−3	−10	21	17	2	−710	703
ψ_4	−12·58	−307	−25	255	474	251	−32	294	−511	−439	2	46	100
ψ_5	−10·64	−345	−379	−74	322	25	−274	435	314	499	31	−84	−91
ψ_6	−10·47	32	−463	−494	−31	504	529	−45	−37	−51	−3	8	10
ψ_7	−8·21	353	62	−332	−136	−326	63	751	−13	−245	−41	55	56
ψ_8	−3·07	44	−139	6	131	9	−141	−107	296	−126	−621	469	469
ψ_9	−1·50	343	−290	−105	385	−83	−308	−237	328	−489	277	−169	−171
ψ_{10}	−0·90	13	−507	494	11	−503	495	−6	0	−9	3	−1	−1
ψ_{11}	+0·40	−326	6	304	−475	295	17	216	511	−407	97	−45	−47
ψ_{12}	+2·42	−489	387	−336	329	−339	391	−116	288	−159	25	−9	−10

(*b*) Calculated excited state dipole moments and charge distributions (π electron only) net atomic charge density * × 10^3

State	μ/D	1	2	3	4	5	6	7	8	9	10	11	12
ψ_0	8·45	−70	22	−78	0	−76	25	255	79	−108	946	−499	−496
ψ_1	36	50	20	20	7	19	16	765	3	−49	569	−711	−708
ψ_2	17	26	−174	−162	4	−170	−154	731	69	−78	926	−507	−504
ψ_3	23	−62	−54	25	−122	25	−60	736	−21	−275	879	−521	−518

* A negative sign indicates an excess over the formal nuclear charge. Atomic numbering corresponds to that in Table 2(*a*).

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[10] D. J. Drain and W. Wilson, *J. Chem. Soc.*, 1949, 767.

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

The lowest energy $\pi^* \longleftarrow \pi$ excitation is indisputably the highly allowed ICT from the ring system to the nitro-group along the long axis of the molecule. The other major band, observed at *ca.* 260 nm, corresponds well to the calculated third excited configuration, and possesses some ICT character in which X_{79} plays a major part. The ICT character is reflected in the appreciable bathochromic shifts of the two major bands with increasing solvent polarity.

The two weaker bands observed at *ca.* 312 and 326 nm show only nominal and equal red shifts in changing from cyclohexane to ethanol and must arise from transitions to a state of dipole moment only slightly greater than that of the ground state; the MO calculations predict the existence of only one state in this region, that resulting largely from the electron excitation $\psi_7 \longrightarrow \psi_{10}$ with no charge transfer to the nitro-group. These weak bands may be vibrational components, separation *ca.* 1300 cm^{-1}, akin to that of the main, long wavelength, band. Alternative explanations are conceivable. Spurious absorption caused by, for example, *cis*-isomer impurity is not an explanation in view of the known high purity of the compound (I), and the absence of appreciable thermal or photoisomerisation, verified experimentally.

Since compounds such as nitrobenzene and nitroethylene[12] are reported to have $\pi^* \longleftarrow n$ absorption bands in the visible–near-u.v. region of the spectrum and knowing from the PPP calculations that the lowest vacant π^* orbital is predicted to be the same (namely the nitro antibonding MO) for a wide range of unsaturated nitro-systems, it is possible that one of the weak bands arises from a $\pi^* \longleftarrow n$ transition. If this is the case it implies appreciable intensity borrowing from a $\pi^* \longleftarrow \pi$ transition.

(ii) *Solvent shifts.* Absorption and fluorescence band maxima for (I) in many solvents are given in Table 3.

The substantial bathochromic shift of the major ICT absorption band with increasing solvent polarity is indicative of a substantial increase in dipole moment of the compound on excitation. The ground state dipole moment[13,14] of (I) is 7·7 D and a value of 18 D has been reported[15] for the first excited state dipole moment on the basis of electric-field fluorescence polarisation studies. The PPP calculations [Table 2(b)] grossly overemphasise the extent of charge transfer (mainly from the NMe$_2$ group) but predict reasonably the relative changes on excitation. Variation in the effective ionisation potential for the amino-nitrogen atom affects markedly the extent of charge release but only slightly the form and order of the molecular orbitals and the excited state compositions after CI. Figure 1 shows the shape of the longest wavelength absorption band of (I) in cyclohexane, benzene, and chloroform typifying the progressive alteration in appearance as solvent polarity is increased.

Strong electrostatic interaction of polar solvents with a dipolar solute, *e.g.* (I), is to be expected and hence the existence of discrete solute–solvent complexes must be considered in any spectral data interpretation.

TABLE 3

Absorption and fluoresence band maxima of compound (I) at 20 °C

Solvent	$\bar{\nu}_A$/kK	$\bar{\nu}_F$/kK
Cyclohexane	25·00	[20·70]
Carbon tetrachloride	24·51	
Mesitylene	23·92	20·70
p-Xylene	23·81	20·58
Toluene	23·70	
Benzene	23·36	20·08
Diethyl ether	23·81	19·88
Tetrahydropyran	23·53	18·42
Pyridine	22·37	18·45
Piperidine	22·30	18·48
Bromobenzene	22·68	18·94
Anisole	22·68	18·87
Chloroform	22·62	18·69
1,1,2,2-Tetrachloroethane	22·03	18·69
Acetonitrile	22·75	
Acetone	22·94	18·80
Ethanol	23·15	
t-Butyl alcohol	23·15	18·90
Ethylene glycol	21·88	18·69
Dimethylformamide	22·24	18·66
Dimethyl sulphoxide	21·90	
Water (10% ethanol)	21·28	

[ ] By extrapolation from solvent mixtures; $\bar{\nu}_A$ = wavenumber of absorption band maxima; $\bar{\nu}_F$ = wavenumber of fluorescence band maxima.

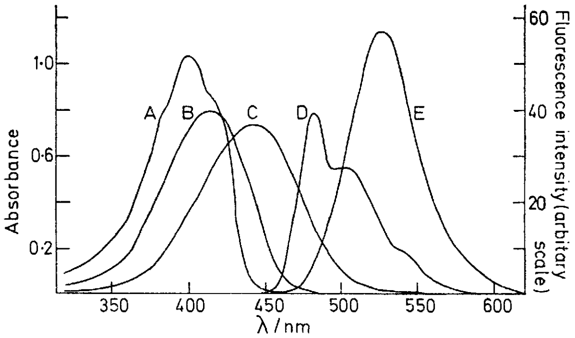

FIGURE 1 Typical absorption and fluorescence curves of (I): A, absorption spectrum in cyclohexane (293 K); B, absorption spectrum in benzene (293 K); C, absorption spectrum in chloroform (293 K); D, fluorescence spectrum in 6% v/v diethyl ether–methylcyclohexane (77 K); E, fluorescence spectrum in anisole (293 K). Absorbance and fluorescence intensity scales are arbitrary

Beer's law is strictly obeyed, at several wavelengths examined, for 10^{-6}—2×10^{-4}M solutions of (I) in cyclohexane, benzene, and ethanol at room temperature. Thus, aggregation of the dipolar molecules in non-polar media and formation of solvated monomers in more polar media is not thought to be a likely explanation of the changes in band shape under the experimental conditions reported above.

Absorption band shifts for binary solvent mixtures of cyclohexane and various solvents are given in Figure 4. Isosbestic points in the absorption curves on addition of

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

[13] R. J. Dolter and C. Curran, *J. Amer. Chem. Soc.*, 1960, **82**, 4153.

[14] V. N. Vasil'eva, V. V. Perekalin, and V. G. Vasil'ev, *Doklady Akad. Nauk S.S.S.R.*, 1961, **141**, 620.

[15] J. Czekalla, W. Liptay, and K.-O. Meyer, *Ber. Bunsengesellschaft Phys. Chem.*, 1963, 465.

polar solvents to cyclohexane solutions of (I) were not observed, solely a monotonic red shift of the absorption band.[16] The data were analysed according to the solvent lattice-site model[17] of Mazurenko. There are considered to be N_m solvent sites around the solute, populated dynamically by polar and non-polar solvent molecules in a statistical manner as governed by the interaction energies of the solvents with the solute in a Boltzmann fashion. The polar solvent is considered to differ from the non-polar solvent only in a contribution to the free energy of solvation arising from dipolar orientation. F_{or}/N_m Is defined as the minimum mean value of the orientational free energy per polar solvent molecule. All other interactions are assumed to be isotropic and equivalent for all solvent molecules in the cage around the solute.

If x is the mole fraction of polar solvent p, $(1 - x)$ the mole fraction of non-polar solvent n, and $\theta = (\bar{\nu}_n - \bar{\nu})/(\bar{\nu}_n - \bar{\nu}_p)$ where $\bar{\nu}_n$, $\bar{\nu}_p$, and $\bar{\nu}$ are the wavenumbers of the absorption (or fluorescence) maxima of the solute in non-polar, polar, and mixed solvent respectively, then plots of $\log[\theta/(1 - \theta)]$ against $\log[x/(1 - x)]$ should be linear and have a slope G of unity if the model is applicable. The intercept on the ordinate axis, γ, equals $-F_{or}/N_m kT$. Graphical treatment of our data in this way yielded good linear plots from which the values of F_{or}/N_m given in Table 4 were obtained.

TABLE 4

Lattice-site model analysis of u.v. absorption data for (I) dissolved in solvent–cyclohexane mixtures

Solvent	Gradient G *	(F_{or}/N_m) */ kJ mol^{-1}
Carbon tetrachloride	1·00	0·0
Benzene	1·00	0·0
Diethyl ether	0·87	2·6
Acetone	0·95	3·2
Pyridine	0·96	1·8
Piperidine	0·93	2·2
Chloroform	0·91	1·9
Ethanol	0·98	1·9

* See text for definition.

The dipolar orientational interaction of most of the polar solvents examined in the study is comparable in magnitude to kT at room temperature (*ca.* 2·4 kJ mol^{-1}) but insufficiently large to suppose that only simple well-defined 1 : 1, or 1 : 2, solute–polar solvent complexes exist as opposed to a statistical distribution of 1 : 1 to 1 : N_m species (where N_m may be as large as 6). Obviously the solvation shell around (I) is populated preferentially by polar solvent.[16]

Fluorescence Spectra.—(i) *Band structure.* The vibrational structure, spacing *ca.* 1100 cm^{-1}, is best resolved in spectra of (I) in slightly polar media, *e.g.* diethyl ether–methylcyclohexane, at 77 K (Figure 1) but is seen in all spectra obtained at 77 K. Increase in solvent polarity results in a general red shift of all the band components and a shift of intensity within the emission envelope into transitions corresponding to higher levels of vibrational excitation in the electronic ground state. We do not find any evidence for solute–solvent exciplexes or conformational isomers.

(ii) *Solvent shifts of fluorescence band maxima.* The fluorescence emission undergoes appreciable red shift with gross increase in solvent polarity (Table 3) but the wavenumber difference $(\bar{\nu}_A - \bar{\nu}_F)$ does not vary greatly with change in solvent polarity. Hence one must conclude *either* that μ(excited) $\sim$ μ(ground) *or* that solvent orientational relaxation around the solute excited state is progressively more incomplete as the solvent polarity is increased thus countering the potentially greater dipolar stabilisation. The former situation does not hold in view of independent experimental evidence of the dipole moments and the close analogy of compound (I) to other D–Ar–A systems which behave ' normally.' From the quantum yield of fluorescence of (I) in benzene (*ca.* 0·1) and the integrated intensity of the lowest-energy absorption band, the fluorescence lifetime of (I) in benzene is estimated to be *ca.* 0·5 ns; experimentally we have shown it to be certainly less than 2 ns. Thus, for high concentrations of polar solvents when fluorescence of (I) is quenched appreciably the lifetime of the fluorescent state must be comparable to solvent rotational correlation times and incomplete orientational relaxation of solvent *before* excited solute emission is to be expected.[18]

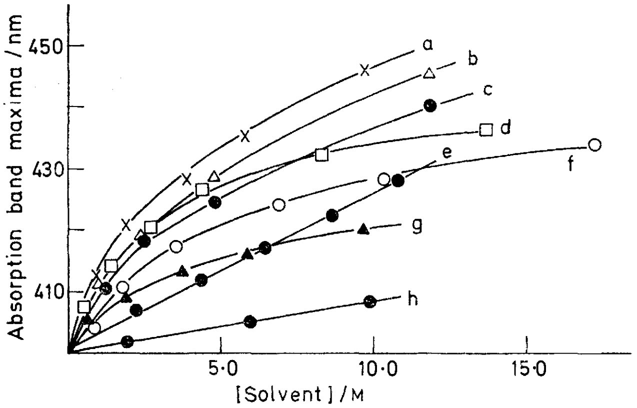

FIGURE 2 Absorption band maxima of (I) in various solvent–cyclohexane mixtures at 298 K: a, piperidine; b, pyridine; c, chloroform; d, acetone; e, benzene; f, ethanol; g, diethyl ether; h, carbon tetrachloride

This view is substantiated by the results for solutions of (I) in benzene–acetonitrile mixtures (Table 5). Addition of small quantities (0—2% v/v) of acetonitrile to benzene solutions of (I) produces a slight rise in fluorescence yield followed by a slow drop. Hence the fluorescence lifetime is not drastically altered in this range of polar solvent concentration and it is found that a Lippert plot[6] of $(\bar{\nu}_A - \bar{\nu}_F)$ *versus* solvent polarity function f(D,n) is tolerably linear; the slope yields a value of 14 D for the solute excited state dipole moment (*cf.* 18 D obtained from electric dichroism studies[15]).

On further addition of acetonitrile the absorption

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[16] J. Midwinter and P. Suppan, *Spectrochim. Acta*, 1969, **25A**, 953.

[17] Yu. T. Mazurenko, *Optical Spectroscopy*, 1971, **31**, 583.

[18] E. Lippert, W. Lüder, and F. Moll, *Spectrochim. Acta*, 1959, **10**, 858.

maxima shows a continued monotonic red shift, whereas ($\bar{\nu}_A - \bar{\nu}_F$) quickly attains a steady value; concurrently the fluorescence yield diminishes rapidly.

(iii) *Temperature effects on fluorescence wavelength.* Data for (I) in PMMA, ethanol (A), and diethyl ether (DE) are given in Table 6 for the temperature range 77—300 K.

TABLE 5

Absorption $\bar{\nu}_A$ and fluorescence $\bar{\nu}_F$ maxima, and relative fluorescence yields I_F, of (I) in benzene–acetonitrile mixtures

[MeCN]/ mol l^{-1}	$\bar{\nu}_A$/ cm^{-1}	$\bar{\nu}_F$/ cm^{-1}	$\bar{\nu}_A - \bar{\nu}_F$/ cm^{-1}	I_f [a]	Δf [b]
0	23150	19840	3310	100	0·0045
0·095	23150	19720	3430	120	0·0293
0·19	23120	19490	3630	116	0·0526
0·38	23090	19230	3860	95	0·0856
0·76	23040	19050	3990	52	0·1290
1·14	22990	18900	4090	29	0·1570
1·52	22940	18830	4110	19	0·1762
1·90	22880	18800	4080	12	0·1907

[a] Corrected to equal optical density at the excitation wavelength 420 nm. [b] $\Delta f = \left[\frac{(D-1)}{(2D+1)} - \frac{(n^2-1)}{(2n^2+1)}\right]$ = solvent polarity function where D, the medium dielectric constant and n, the medium refractive index were assumed to depend linearly on the mole fraction of acetonitrile in the benzene solution.

TABLE 6

Variation with temperature of fluorescence maxima of (I)

PMMA		Diethyl ether		Ethanol	
T/K	λ_F/nm	T/K	λ_F/nm	T/K	λ_F/nm
77	508	77	495	77	513
165	513	151	527	145	523
170	513	154	528	152	524
195	513	167	524	160	523
215	513	179	520	167	525
238	513	197	516	183	525
252	513	208	513	298	510
273	513	220	508		
		236	503		
		256	500		
		297	496		

Matrix adjustment in PMMA appears to be incomplete at all temperatures as deduced from the constancy of the fluorescence emission maximum and the band positions of (I) at room temperature in liquid methyl methacrylate and PMMA of 527 and 513 nm respectively.

The variation with temperature of the emission maxima for A and DE solutions can be explained by the competition of the excited solute emission process with solvent orientational relaxation around the excited solute, with the disruptive influence of thermal agitation on optimum dipolar alignments becoming increasingly important at the higher temperatures.[18] The band position 'turnover point' occurs at a lower temperature for DE solution compared with A solution (in accordance with the lower rotational correlation time τ_R, related to the solution viscosity, of DE compared with A at all temperatures). The increase in fluorescence quenching, *i.e.* fluorescence lifetime τ_F decrease, in A relative to that in DE with increasing temperature (see below) also postpones the attainment of the condition $\tau_R \leqslant \tau_F$ until much higher temperatures for A than for DE solutions. A further consequence is that the blue shift in fluorescence wavelength maxima after the 'turnover point' is not as great for A as for DE solutions.

(iv) *Excitation spectra.* For compound (I) in binary cyclohexane–polar solvent mixtures the excitation spectra at room temperature, with maxima centred at *ca.* 440 nm depend on the solvent composition but are independent of the emission wavelength of observation. Increase of medium polarity increases the excitation spectrum bandwidth *via* an extension of the long wavelength side of the band to the red. This we attribute to the increasing statistical occupation of solvation sites around the solute (I) by polar solvent molecules in good accord with the Mazurenko model.

The excitation spectrum of (I) at 77 K is mildly structured and the overall form is relatively independent of matrix polarity; the whole band system shifts to the red with polarity increase.

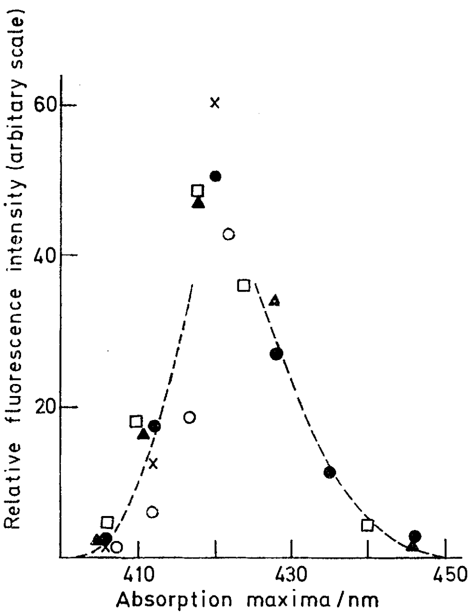

FIGURE 3 Relative fluorescence intensities of (I) in various solvent–cyclohexane mixtures at 298 K: ▲, pyridine; □, chloroform; ×, anisole; ○, benzene; ●, piperidine

(v) *Solvent effects on fluorescence intensity.* Incremental addition of other solvents to cyclohexane solutions of (I) leads invariably to the appearance of fluorescence emission of increasing intensity. In Figure 3 the abscissa has been chosen to be the position of the absorption band maxima in the media concerned as an empirical, and more accurate, measure of the polarity of the medium taking into account all forms of solvent–solute interaction. It is analogous to the use of Kosower Z values. For a reasonable range of 'polar' solvent types the onset of fluorescence occurs when the absorption band maximum reaches a wavelength greater than 405 nm. Significantly this is also true for many other D–Ar–NO_2 compounds under investigation by us at present.

Addition of fair amounts of even weakly polar solvent to cyclohexane solutions of (I) or fluorescent solutions of (I) in benzene lowers the fluorescence yield dramatically (Figure 3). In most pure polar solvents, *e.g.* ethanol, acetonitrile, chloroform, *etc.*, the fluorescence yield is very low.

(vi) *Temperature effects on fluorescence intensity.* In rigid PMMA media the fluorescence yield of (I) decreases slowly with increasing temperature; for ethanol (A) and diethyl ether (DE) solvents the decline in fluorescence is marked above 140 and 220 K respectively. Since A and DE have almost identical m.p.s and DE is *less* viscous than A at all temperatures, the difference in the temperatures at which quenching becomes evident must be related to the difference in the dipolar interaction of the two solvents with the solute (I), A interacting more strongly than DE, *i.e.* $F_{or}(A) > F_{or}(DE)$.

Plots of $\log_{10} I_F$ *versus* $1/T$ (Figure 4), where I_F is the fluorescence intensity and T the absolute temperature, yield apparent activation energies of quenching, E_a, of *ca.* 13 and 11 kJ mol^{-1} for DE and A solutions respectively, whereas the corresponding Arrhenius activation energies associated with the viscosity behaviour [19] are 7·2 and 12·8 kJ mol^{-1} respectively.

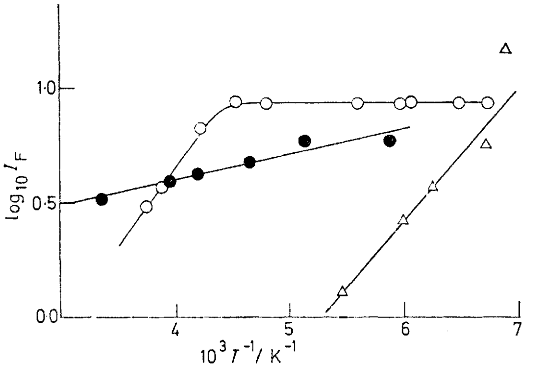

FIGURE 4 Variation of log (relative fluorescence intensity, I_F) with the reciprocal of the absolute temperature for (I) in PMMA (●), diethyl ether (○), and ethanol (△) glasses

Comments.—From the spectral evidence and the results of the MO calculations given in this paper it is clear that fluorescence emission in the title compound occurs from a single electronically-excited state which can be identified with the lowest lying, highly dipolar, π–π^* (ICT) state, hereafter designated S_1.

Two major features require explanation: first, the sudden appearance of fluorescence from S_1 with increase in solvent polarity and secondly, the subsequent quenching of this fluorescence on further increase in solvent polarity.

Discussion of the energies of the excited electronic states is complicated by the magnitude of the solvent effects thereon and the importance of solvent relaxation about the Frank–Condon excited solute. However since the lowest vacant π^* (antibonding) orbital in the nitrostyrene compounds is located mainly on the nitro-system [Table (2*a*)] the lowest singlet and triplet n–π^* states, designated S_1^n and T_1^n, resulting from localised excitations of the nitro-group, are expected thereby to be close to the electronic ground state S_0 in dipolar character. *Differential* solvent shifts of the energies of these states with respect to that of the ground state are expected to be small ($<$0·1 eV perhaps). On the other hand, the S_1(ICT) state suffers large shifts in energy relative to S_0 with solvent polarity change ($\leqslant$0·6 eV). The corresponding π–π^* triplet state by analogy with other systems is probably closer to S_0 in dipolar character. Thus S_1 is essentially the only state under consideration here, which may vary significantly in energy relative to S_0 with change in medium polarity. The observation of the marked solvent effects on the fluorescence emission characteristics of (I) is strongly related to this consideration.

While other arguable interpretations do exist, we suggest that the data are best accounted for by a familiar electronic state cross-over model. A second non-fluorescent, electronic state in the region of S_1 is postulated. The origin of its non-fluorescent character and possible photochemical properties, *e.g.* dissociation, *etc.*, are of little consequence to the main argument. The only serious candidates for the role appear to be the singlet and triplet n–π^* states, S_1^n and T_1^n. However, if T_1^n is invoked in this role then it is difficult to account satisfactorily for the subsequent quenching of fluorescence in highly polar media. Charge-transfer mechanisms of quenching are not a real possibility in view of the disparate electron donor characters of the polar solvents used in the study. Using the ability of the solvent to shift the absorption band as an index of dipolar interaction with the solute, the solvents are almost equally efficient in their quenching effect relative to their dipolar character, *i.e.* the quenching is a general phenomena.

The most plausible explanation in our view requires that S_1 lies above S_1^n in energy in non-polar media, that the process $S_1 \longrightarrow S_1^n$ is efficient, and that S_1^n is non-radiative in its major decay processes. Polar solvent may then be considered to induce fluorescence by lowering S_1 below S_1^n in energy, the critical point lying at *ca.* 3·1 eV on the basis of the most probable Frank–Condon state energy.

Molecular orbital calculations [20] and a wide range of experimental data suggest that S_1^n–T_1^n energy separations in general are small ($\leqslant$0·5 eV). Thus if S_1^n is located at *ca.* 3·1 eV then T_1^n should be at *ca.* 2·6 eV [†] and polar solvent may then stabilise S_1(ICT) sufficiently to bring it close in energy to T_1^n. In such circumstances, if $S_1 \longrightarrow T_1^n$ is moderately efficient, fluorescence quenching and a reduced lifetime would result. The absence of phosphorescence in compound (I) would also follow on this scheme if the lower-lying π–π^* (ICT)

[†] Since the lowest vacant π^* orbital in most nitroaromatic systems is located predominately on the nitro-group we anticipate the lowest (n,π^*) triplet states of such systems to be very similar in energy. The (n,π^*) triplet state of nitrobenzene lies at 2·65 eV as determined experimentally from sensitisation and quenching studies of the photochemical hydrogen abstraction reactions.

[19] 'Handbook of Chemistry and Physics,' 50th edn., Chemical Rubber Co., Cleveland, 1970, F-39.

[20] V. G. Plotnikov, *Optical Spectroscopy*, 1965, **19**, 217 and references therein.

triplet state was populated appreciably only *via* the n–π^* state S_1^n, a proposition for which good parallels exist.[21,22] When the S_1 energy lies above S_1^n then phosphorescence from π–π^* triplet states populated *via* S_1^n should be possible on this model. The nitroanilines appear to exemplify these conclusions in practice.[23]

We are at present engaged in attempting to distinguish unambiguously between various explanations by examination of a wide range of D–Ar–NO_2 systems and in the exploration of the photochemical reactions of such systems, especially solvent affects on the possible reaction modes.[24]

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