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Evidence for Electron Transfer of Excited Indigo Dyes with both Electron-Acceptors and Electron-Donors

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SUMMARY

N,N'-Disubstituted indigo derivatives undergo a very efficient electron transfer reaction in their excited singlet state due to a low reduction potential (ca. −0·6 V). The rate constant of the reaction is of the same order as that of a diffusion-controlled reaction, when the electron-donating molecules have an oxidation potential lower than 1·0 V.

Surprisingly, the same dyes undergo a quenching of their singlet excited state by tetracyanoquinodimethane, a strong electron-accepting molecule. This unusual behaviour has been rationalized on the basis of their voltammetric curves. The effect of this phenomenon on the stability of these dyes is discussed on the basis of a self-quenching process.

1. INTRODUCTION

The influence of electron transfer between dyes and electron-donors or electron-acceptors is known to accelerate the fading of the dyes in polymers. In the case of *trans*-indigo, the stability of the dye has been attributed to hydrogen bonding[1] in the ground state, as established from crystallographic data.[2] However, this explanation does not provide a wholly satisfactory explanation for the photostability of indigo as the energy of the singlet excited state, 200 kJ/mol, is greater than the energy

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needed to break two typical hydrogen bonds. Another explanation which has been put forward[3] is a rapid intramolecular proton transfer between the amino and the carbonyl groups; this phenomenon is in good agreement with the well-established enhanced (10^6-fold) acidity of the aromatic amino groups in the excited state as compared to the ground state and, similarly, the increase of the basicity of carbonyl groups.[4]

When indigo is substituted on the two nitrogen atoms by an alkyl or an acyl group, then a *trans–cis* isomerization occurs under illumination,[5-7] a typical photochemical reaction for substituted olefins.[8,9]

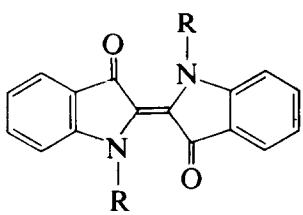
Indigo and thioindigo derivatives interact in their excited state with hydroxyl compounds such as phenols[10] and alcohols;[11] on the other hand, there was yet no evidence that *N,N'*-disubstituted indigos interact with electron-donors or electron-acceptors. Usually, molecules in their excited state behave as either acceptors or donors in encounter complexes.

The voltammetric curves of the *trans* isomers of *N,N'*-diacetyl (**I**), *N,N'*-dibenzoyl (**II**) and *N,N'*-di-*p*-chlorobenzoyl (**III**) indigos show reversible oxidation and reduction waves separated by less than 1·5 V (Fig. 1). Such a small difference between these two waves has prompted an investigation of their photochemical behaviour in electron acceptor–donor reactions.

2. EXPERIMENTAL

2.1. Materials

The *trans* isomers of the *N,N'*-disubstituted indigos were prepared according to the Blanc and Ross procedure[12] for the *N,N'*-diacetyl (**I**) derivative, and to Posner's method[13] for the *N,N'*-dibenzoyl (**II**) and *N,N'*-di-*p*-chlorobenzoyl (**III**) derivatives.



I R = CH_3CO—
II R = C_6H_5CO—
III R = *p*-Cl—C_6H_5CO—

The purity of the compounds has been verified by thin-layer chromatography on silica gel (elution with 80:20 (v/v) benzene/ethyl acetate).

Solvents for absorption and emission measurements were of spectrograde (Merck) quality and were used without further purification.

2.2. Voltamperometric curves

Redox potentials were obtained by cyclic voltammetry using a P.A.R. model 173 potentiostat monitored by a P.A.R. model 175 programmer coupled to a TGM *X–Y* Sefram recorder. The electrochemical measurements were performed in acetonitrile solution using 0·1M tetrabutylammonium perchlorate as supporting electrolyte. The reference electrode was a calomel electrode saturated with KCl. The working electrode was a platinum gauze and the counter electrode was a 1 cm × 1 cm platinum surface.

2.3. Fluorescence emission

All three *trans* isomers, **I**, **II** and **III**, do fluoresce when excited in their long wavelength charge-transfer absorption band (560 nm for **I** and 575 nm for **II** and **III**). No phosphorescence emission could be detected for these compounds.

Ultraviolet–visible absorption spectra were recorded on a Varian Cary 219 model spectrometer; emission spectra were performed using a Perkin-Elmer MPF 44-B spectrofluorimeter equipped with a DCS 2U correction unit.

2.4. Singlet lifetimes

The fluorescence decay of the *trans* isomers **I**, **II** and **III** has been measured with a frequency-doubled YAG laser (30 ps pulse) from Quantel.[14] The light emitted by the sample in chloroform solution is received at right angles by the photocathode of a high speed S11-type photodiode and the signal transmitted to a Tektronix 7104 oscilloscope. The light beam was split before passing through the cell and one part was focused on a Gen Tec pyroelectric detector; the signal obtained was proportional to the energy of the excitation light.

2.5. Fluorescence quenching

The quenching of the fluorescence of indigo derivatives **I**, **II** and **III** has been carried out in acetonitrile solution at 20 °C. The concentration was adjusted to about 0·1 optical density at the excitation wavelength, which was chosen at the maximum of the visible absorption band. The apparent rate constant k_q for the quenching of the fluorescence by the electron-donor or the electron-acceptor was deduced from the slope $k_q\tau_s$ of the well-known Stern–Volmer plot.[15] The process was repeated for all the electron-donor molecules. The quenching rate constant k_q can be evaluated since the lifetime of the singlet excited state has been measured independently.

3. RESULTS AND DISCUSSION

3.1. Voltammetry

Voltamperometric curves of the *trans* isomers **I**, **II** and **III** show two distinct reduction waves and at least one oxidation wave. Depending on the compound, the reduction waves are reversible or not. For instance (Fig. 1) compound **II** shows three waves at $-0{\cdot}58$ V (reversible), $-1{\cdot}18$ V and $+0{\cdot}64$ V (not reversible) in acetonitrile solution. The potential difference between the oxidation wave and the reduction wave is of the order of 1·2 V. Since the energy of the lowest singlet excited state (as determined from the intercept between the absorption and fluorescence spectra) is 2·1 eV, it corresponds to a 0·9 eV excess of energy as compared with the energy associated with the 1·20 V potential difference.

Consequently, one would expect electron donors with an oxidation potential lower than 1·5 V to be able to reduce efficiently the singlet excited state of the *N,N'*-disubstituted indigo derivatives **I**, **II** and **III**. For this reason the quenching of the fluorescence of these three compounds by a series of electron-donor molecules in polar solvents has been investigated.

3.2. Fluorescence quenching

The selective irradiation of the indigo derivatives In°, in the presence of an electron-donating molecule, yields first the lowest excited singlet state ^{1}In* which can undergo several deactivation processes: fluorescence (with the rate constant k_f), non-radiative decay (k_{nrs}), intersystem crossing to

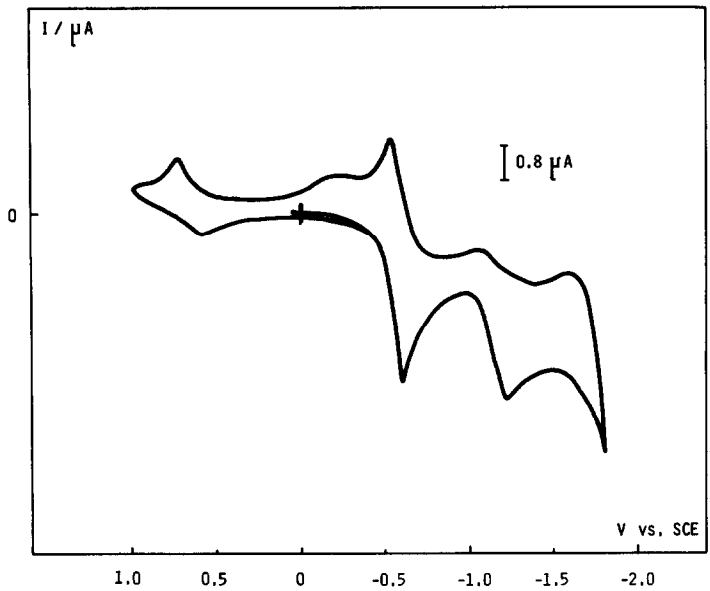


Fig. 1. Cyclic voltammetry of a CH_3CN solution containing 0·1 M $TBAClO_4$ and $6{\cdot}5 \times 10^{-4}$ M *N,N'*-dibenzoylindigo (**II**) at a Pt electrode. Scan rate 20 mV s^{-1}.

the triplet state (k_{isc}) or formation of an excited complex with the electron-donor D (k_q); usually, the exciplex formed from a singlet excited state reverts subsequently to the starting ground state materials. An additional reaction, which must be taken into account, is the formation of a twisted singlet excited state In_t^* by a 90° rotation around the central double bond. This twisted form is the expected intermediate in the *trans–cis* isomerization of the starting molecule.

Since no triplet excited state could be detected for the three indigo derivatives studied here, the discussion may be limited to the deactivation processes from the singlet state. The reactions can be depicted as follows:

$$^1In^* \xrightarrow{k_f} In^\circ + h\nu' \quad (1)$$

$$^1In^* \xrightarrow{k_{isc}} {}^3In^* \quad (2)$$

$$^1In^* \xrightarrow{k_{nrs}} In^\circ + \Delta \quad (3)$$

$$D + {}^1In^* \xrightarrow{k_q} {}^1(In \cdots D)^* \quad (4)$$

$$^1(In \cdots D)^* \longrightarrow In^\circ + D \quad (5)$$

$$^1In^* \xrightarrow{k_t} In_t^* \quad (6)$$

As both the fluorescence and intersystem crossing processes are inefficient ones, the formation of the twisted form must be the principal deactivation process of the excited singlet state.

The addition of the electron-donating molecules to the solution of the indigo derivatives **I, II** and **III** does not change the shape of the absorption spectra, nor that of the fluorescence spectra nor the fluorescence excitation spectra. All that is observed is a decrease of the intensity of the emission and, particularly, no long wavelength fluorescence band. This has been characterized in several cases as the emission of an exciplex.

Inhibition of the fluorescence by the electron-donor D follows the Stern–Volmer equation (7):

$$\frac{\Phi_f^\circ}{\Phi_f} = 1 + k_q \tau_s [D] \tag{7}$$

where k_q is the rate constant for the quenching process and formation of the exciplex (relation (4)) and τ_s the singlet lifetime in the absence of the quencher. This lifetime has been measured directly from the fluorescence decay after excitation with a frequency-doubled YAG laser. The following values have been obtained: 2·06 ns for **I**, 2·74 ns for **II** and 1·76 ns for **III**.[14] They represent the reciprocal of the sum of the rate constants of the processes which deactivate the singlet excited state, i.e.:

$$\frac{1}{\tau} = k_f + k_{isc} + k_i \tag{8}$$

Figure 2 shows the different plots obtained for the fluorescence inhibition of compound **II** by a series of electron-donors.

In each case, a straight line is obtained by plotting Φ_f°/Φ_f versus the concentration of the quencher D, thus verifying that the interaction occurs well at the level of the singlet excited state. Usually, such a quenching of the singlet state, by an electron-donor–acceptor exchange process, forms no detectable separate ions, in contrast to the ion-pairs involved in a process originating from a triplet excited state; thus, it shows an expected spin-selection rule.[16]

3.3. Influence of the oxidation potential of the quencher

The oxidation potential of the electron donors used as quenchers varies from 0·35 to 1·60 V versus SCE.

The reduction potential of an excited state E_{red}^* can be calculated from

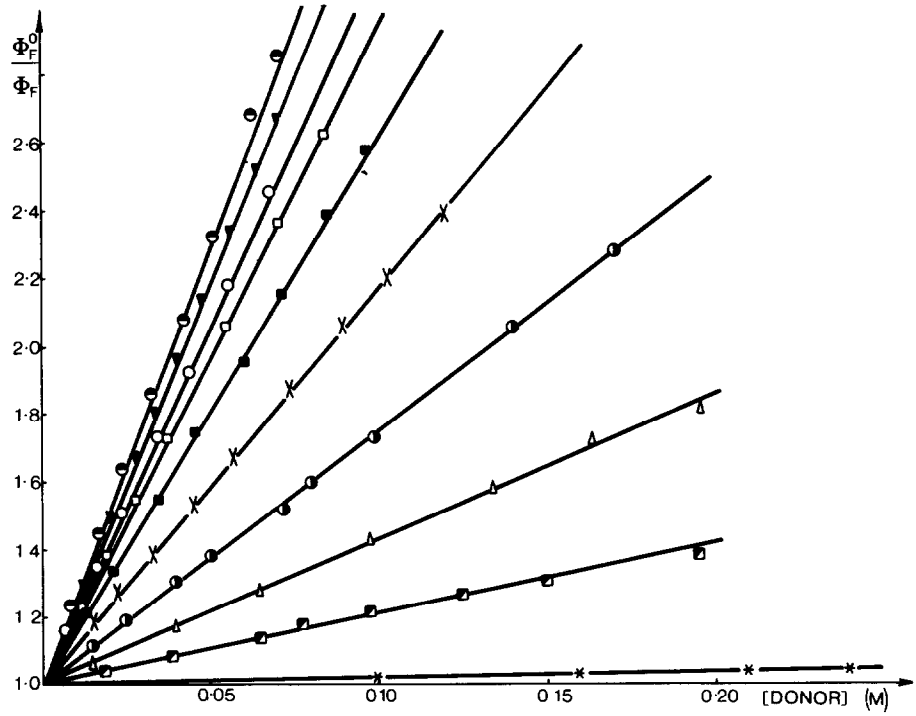


Fig. 2. Stern–Volmer plot of the fluorescence quenching of *N,N'*-dibenzoylindigo (**II**) by a series of electron-donors (see Table 1) in acetonitrile solution. E_{ox}^{D}: ◓, 0·35 V; ▼, 0·53 V; ○, 0·76 V; □, 0·86 V; ■, 1·03 V; ×, 1·28 V; ◑, 1·34 V; △, 1·45 V; ◩, 1·49 V; ★, 1·60 V.

the reduction potential of the ground state E_{red} of the same molecule, by using[17,18] relation (9):

$$E_{red}^{*}(In^{*}/In^{-}) = E_{red}(In/In^{-}) + \Delta E_s \tag{9}$$

where ΔE_s is the energy of the singlet excited state. The reduction potential of the *N,N'*-disubstituted indigo derivatives lies around −0·6 V and the energy of the singlet excited state is 2·1 eV; consequently, the reduction potential of the excited singlet state $E_{red}^{*}(In^{*}/In^{-})$, as deduced from the relation (9), is 1·5 V.

The free energy ΔG of the electron transfer reaction can be calculated in a first approximation from the general equation (10):

$$\Delta G = E_{ox}^{D} - E_{red}^{A} - \Delta E_s \tag{10}$$

if one neglects the coulombic work required to form the encounter

TABLE 1

Oxidation Potentials[a] of the Electron-Donor Molecules, Reduction Potentials[a] of the Electron-Accepting Indigo Derivatives **I**, **II** and **III**, and Logarithms of the Quenching Rate Constant $\log k_q$ for the Different Values of the Free Energy Change ΔG of the Charge-Transfer Complex Formation

Electron-donor	E_{ox}^{D} (*V*)	**I** $E_{red}^{A} = -0{\cdot}58\,V$		**II** $E_{red}^{A} = -0{\cdot}60\,V$		**III** $E_{red}^{A} = -0{\cdot}55\,V$	
		ΔG (*eV*)	$\log k_q$	ΔG (*eV*)	$\log k_q$	ΔG (*eV*)	$\log k_q$
N,N'-Diphenyl-*p*-phenylenediamine	0·35	−1·21	10·22	−1·13	9·97	−1·23	10·05
Phenothiazine	0·53	−1·03	10·01	—	—	—	—
N,N'-Dimethyl-*p*-toluidine	0·65	−0·91	10·05	−0·83	9·93	−0·93	9·94
N,N-Diethylaniline	0·76	−0·80	10·05	−0·72	9·88	−0·82	9·92
Triphenylamine	0·86	−0·70	10·03	−0·62	9·85	−0·72	9·87
N-Methylaniline	1·03	−0·53	10·00	−0·45	9·77	−0·55	9·84
Aniline	1·28	−0·28	9·87	−0·20	9·62	−0·30	9·68
1,4-Dimethoxybenzene	1·34	−0·22	9·61	−0·14	9·44	−0·24	9·47
1,2-Dimethoxybenzene	1·45	−0·11	9·44	−0·03	9·19	−0·13	9·24
1,3,5-Trimethoxy-benzene	1·49	−0·07	9·27	+0·01	8·88	−0·09	8·86
Naphthalene	1·60	+0·04	7·80	+0·12	7·89	+0·02	7·99

[a] Versus SCE.

complex; E_{ox}^{D} is the oxidation potential of the donor and E_{red}^{A} the reduction potential of the acceptor; under the present circumstances E_{red}^{A} represents $E_{red}(\mathrm{In/In}^{\cdot-})$. By combining relations (9) and (10), one obtains for the indigo derivatives **I**, **II** and **III**:

$$\Delta G = E_{ox}^{D} - E_{red}^{*}(\mathrm{In}^{*}/\mathrm{In}^{\cdot-}) \tag{11}$$

According to Rehm and Weller,[17] the overall free energy change of the electron-transfer reaction can be related to the quenching rate constant of the excited state by the electron-donating or electron-accepting counterpart. By assuming that the electron transfer process occurs according to an outer-sphere mechanism, the rate constants can be expressed by a relation such as

$$k_q = A \exp(-\Delta G^{\ddagger}/RT)$$

The logarithms of the values of k_q, the rate constant of the quenching of

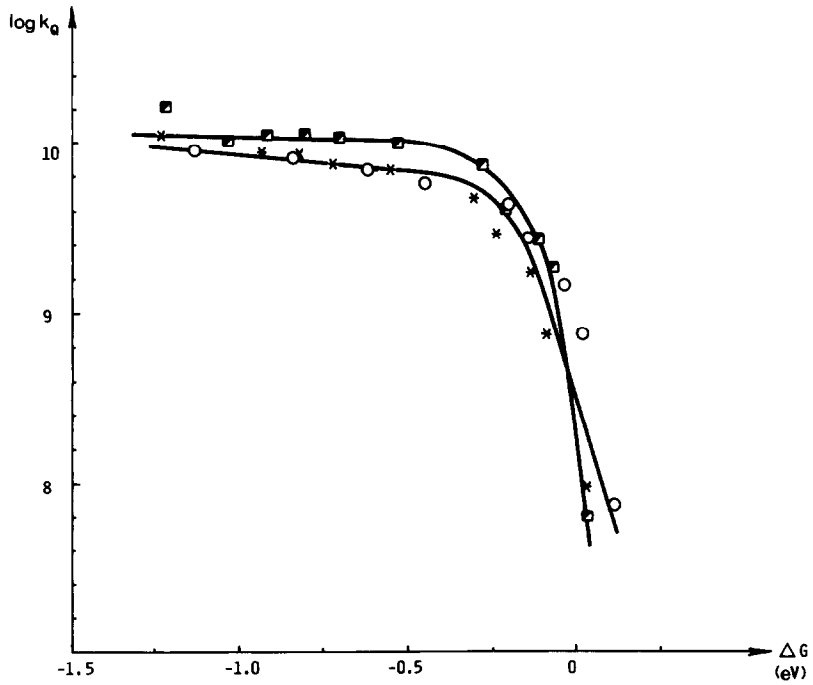


Fig. 3. Plot of the logarithm of the quenching rate constant versus ΔG for *N,N'*-diacetylindigo (◩), *N,N'*-dibenzoylindigo (○), and *N,N'*-di-*p*-chlorobenzoylindigo (★).

the fluorescence of indigo derivatives **I**, **II** and **III** by a series of electron-donating molecules of known oxidation potential, are given in Table 1. Also shown is the free energy change ΔG for the charge-transfer complex formation, calculated with the aid of eqn (11). The oxidation potentials of the electron-donors are taken from a paper by Balzani *et al.*[19] As can be seen, for low oxidation potentials of the donors, k_q reaches a maximum value (Fig. 3) close to the diffusion rate constant, $2{\cdot}7 \times 10^{10}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ in acetonitrile solution,[20] whatever ΔG may be. With increasing oxidation potential of the donor, $\log k_q$ decreases linearly as depicted in Fig. 3 for the three *N,N'*-disubstituted indigo derivatives studied. In the ideal case, the plot of $\log k_q$ versus ΔG should consist of a plateau region (when ΔG is rather negative) connected by a small smooth region with a linear Arrhenius-type section, the slope of which is $-1/2{\cdot}3RT = -0{\cdot}74\,\mathrm{mol\ kcal}^{-1}$ at 297 K. Usually, the intermediate region, centered around $\Delta G = 0$, shows a net curvature, as observed in Fig. 3. The slope of the apparent-Arrhenius straight part of the curve is $-0{\cdot}63\,\mathrm{mol\ kcal}^{-1}$ for **I**, a

value which is 85 % of that of the ideal case. For the benzoyl derivatives **II** and **III**, it reaches only 50 % of the theoretical value. The modification of the slope has been attributed to a deviation of the intrinsic barrier of the electron transfer reaction.[21] Only a weak modification is found when the barrier is lower than 5 kcal mol^{-1}.

No detectable quenching of the fluorescence was observed when weak reducing agents such as thiophene (+1·91 V) or toluene (+1·98 V) are used.

There are some differences between the three indigo dyes studied, as can be seen from Fig. 3. These can be attributed to two main causes. First, the lifetime of the dyes has been measured in chloroform solution whilst the quenching processes have been carried out in acetonitrile solution. It is known that the polarity of the solvent has an influence on the excited states and this is specially true when the dipole moment of the excited state differs considerably from that of the ground state. This is probably the case here and, consequently, the reason why the quenching rate constant (*ca.* $1 \times 10^{10}\,M^{-1}\,s^{-1}$) by strongly reducing products is slightly lower than that expected for a diffusion-controlled process ($2{\cdot}7 \times 10^{10}\,M^{-1}\,s^{-1}$). Second, the difference in curvature can be attributed to the variation of the intrinsic barrier of the electron transfer reaction between the *N,N'*-diacetyl derivative and the *N,N'*-dibenzoylated ones. Such a variation has been observed already for substituted anthraquinones.[22]

3.4. Influence of electron-accepting molecules

This influence has been examined after it was noted (*vide supra*) that there was only a small difference between the first reduction wave and the oxidation wave on the voltamperometric curves of the indigo derivatives **I**, **II** and **III**. Tetracyanoquinodimethane (TCNQ) has been taken as electron-acceptor since this compound is known to form efficiently electron-donor–acceptor complexes with good electron-donors such as tetrathiofulvalene (TTF).[23] Acetonitrile was used as solvent because of the weak solubility of TCNQ in non-polar solvents.

Inhibition of the fluorescence of **I**, **II** and **III** by TCNQ gives linear Stern–Volmer plots with a unity intercept. The slopes of these curves differ from each other (Fig. 4) due to the fact that the three compounds have different singlet lifetimes (see Section 3.2). The rate constants of the quenching process calculated from these curves are $1.3 \times 10^{10}\,M^{-1}\,s^{-1}$

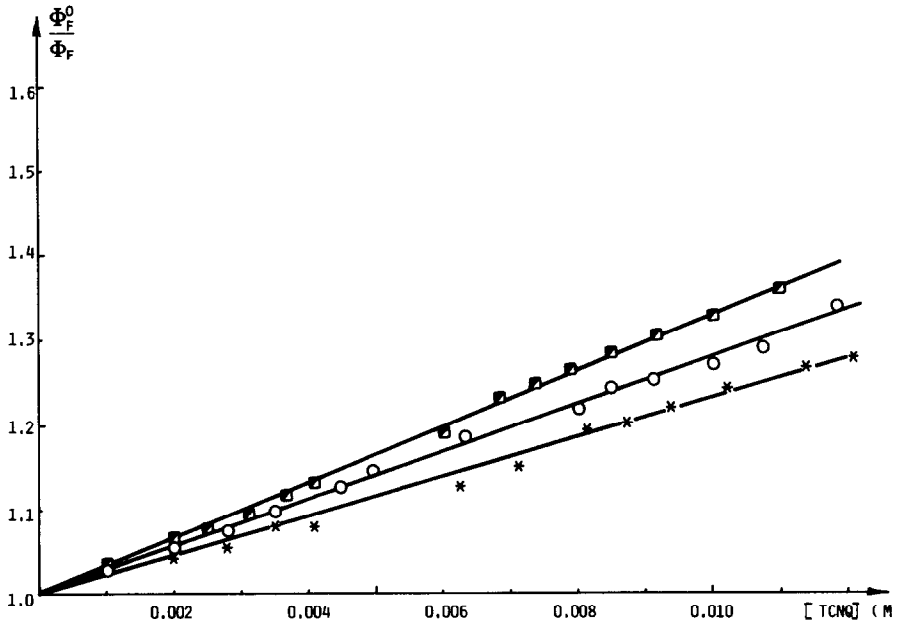


Fig. 4. Stern–Volmer plot of the fluorescence quenching of indigo derivatives **I** (▨), **II** (○) and **III**(★) by tetracyanoquinodimethane in acetonitrile solution.

for compounds **I** and **III** and $1 \times 10^{10}\,M^{-1}\,s^{-1}$ for compound **II**. These values are almost identical to those obtained for the fluorescence quenching of the same products by electron-donors (see Section 3.3) having high reducing properties.

Although this behaviour is not unexpected, it is not very often that the same dyes show strong affinities towards both electron-donors and electron-acceptors.

3.5. Influence of the redox reactions upon the stability of the dyes

The photochromic properties of the indigo derivatives, based on their *trans–cis* isomerization, is well established.[8] Their lightfastness, as taken from the Colour Index, is found to be 7–8 on wool, about 6 on silk and about 4 on cotton. There is a substituent effect for thioindigos on silk, the lightfastness being reduced by ethoxy groups on the aromatic ring. A photoreduction mechanism has been put forward for this.[24] The easy formation of an electron-donor–acceptor complex between indigo dyes, which behave as good electron-acceptors and electron-donors is consistent with such a mechanism.

Similarly, the photodegradation of indigo on cotton fabric[25] has been attributed to a self-sensitized photo-oxidation mechanism, according to which indigo in its triplet state sensitizes oxygen to form singlet oxygen which, in turn, can react with the dye[26] and form isatin. As we have shown (*vide supra*), indigo derivatives also can behave as electron-donating molecules to form a charge-transfer complex with strong electron-withdrawing molecules. Such an oxidation process can be explained also by the formation of an intermediate radical-cation as the result of the charge-transfer reaction. Then this radical-cation reacts easily with oxygen to form a hydroperoxide leading subsequently to isatin.

Another explanation which has been put forward[24] is that 'fading occurs by an oxidation pathway on cotton and by a reduction pathway on protein fibres'; this is in complete agreement with the double electron-acceptor and electron-donor characters demonstrated here.

4. CONCLUSIONS

This dual behaviour of the excited state of the indigo derivatives as electron-acceptors and electron-donors is noteworthy. It indicates that a ground state molecule can behave as an electron-donor towards the excited singlet state of another molecule of the same species, and form an electron-donor–acceptor complex. This is a typical self-quenching case which should increase with the concentration of the dye in solution.[27] It would explain the decrease of the stability of the derivatives with the concentration. The phenomenon itself is totally understandable when one compares the redox potentials of the ground and excited states: since the oxidation potential of the ground state is found at *ca.* +0·6 V and the reduction potential of the singlet excited state is calculated to be at *ca.* +1·5 V, one expects the reduction of an excited indigo dye by the ground state of another molecule to be very effective.

REFERENCES

1. W. R. Brode, E. G. Pearson and G. M. Wyman, *J. Amer. Chem. Soc.*, **76**, 1034 (1954).
2. H. Eller, *Bull. Soc. Chim. France*, 1444 (1955).
3. G. M. Wyman, *Chem. Commun.*, 1332 (1971).
4. See for instance A. Weller, *Discuss. Faraday Soc.*, 183 (1965).

5. J. Weinstein and G. M. Wyman, *J. Amer. Chem. Soc.*, **78**, 4007 (1956).
6. C. R. Giuliano, L. D. Hess and J. D. Margerum, *J. Amer. Chem. Soc.*, **90**, 587 (1968).
7. G. M. Wyman and A. F. Zenhaeusern, *J. Org. Chem.*, **30**, 2348 (1956).
8. D. L. Ross and J. Blanc, *Techniques of chemistry*, Vol. III, Photochromism, ed. G. H. Brown, Wiley–Interscience, New York, 1971, p. 471.
9. J. Saltiel, D. W. L. Chang, E. D. Megarity, A. D. Rousseau, P. T. Shannon, B. Thomas and A. K. Uriarte, *Pure Appl. Chem.*, **41**, 559 (1975).
10. G. M. Wyman and B. M. Zarnegar, *J. Phys. Chem.*, **77**, 1204 (1973).
11. T. Karstens, *Ber. Bunsenges. Phys. Chem.*, **86**, 311 (1982).
12. J. Blanc and D. L. Ross, *J. Phys. Chem.*, **72**, 2818 (1968).
13. T. Posner, *Ber. Dtsch. Chem. Ges.*, **59**, 1977 (1926).
14. P. Valat, Institut Curie, Orsay, France. Personal communication.
15. N. J. Turro, *Modern molecular photochemistry*, Benjamin, Menlo Park, California, USA, 1978, p. 247.
16. D. Holten, M. Gouterman, W. W. Parson, N. W. Windsor and M. G. Rockley, *Photochem. Photobiol.*, **23**, 415 (1976).
17. D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 843 (1969); *Israel J. Chem.*, **8**, 259 (1970).
18. H. Beens and A. Weller, in *Organic molecular photophysics*, Vol. 2, ed. J. B. Birks, John Wiley, London, 1975, p. 159.
19. R. Ballardini, G. Varani, M. T. Indelli, F. Scandola and V. Balzani, *J. Amer. Chem. Soc.*, **100**, 7219 (1978).
20. S. Murov, *Handbook of photochemistry*, Marcel Dekker, New York, 1973, p. 55.
21. F. Scandola, V. Balzani and G. Schuster, *J. Amer. Chem. Soc.*, **103**, 2519 (1981).
22. I. Kawenoki, B. Keita, L. Nadjo and J. Kossanyi, *Nouveau J. Chim.*, **6**, 387 (1982).
23. J. H. Perlstein, *Angew. Chem. Int. Ed. Engl.*, **16**, 519 (1977).
24. N. A. Evans, in *Photochemistry of dyed and pigmented polymers*, ed. N. S. Allen and J. F. McKellar, Applied Science Publishers, London, 1980, pp. 132–3.
25. F. Scholefield, E. Hibbert and C. K. Patel, *J. Soc. Dyers Colourists*, **44**, 236 (1928).
26. N. Kuramoto and T. Kitao, *J. Soc. Dyers Colourists*, **95**, 257 (1979).
27. This study is in process of completion and will be published later.