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# Interaction between naphthyl-indolyl-ethenes and aliphatic amines Effects on fluorescence and *trans*→*cis* photoisomerization

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## Abstract

The fluorescence of two *trans* naphthyl-indolyl-ethenes in solvents of different polarity and H-bonding ability is quenched by aliphatic amines. The H-bonded complexes formed both in the ground- and in the first excited singlet state are responsible for the quenching in non-hydroxylated media. In methanol the interaction, which occurs only in the excited state, leads to the deprotonation of the indolyl-moiety. The consequences of the quenching on the *trans*→*cis* photoisomerization yield are reported. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Naphthyl-indolyl-ethenes; Aliphatic amines; Fluorescence; *Trans*→*cis* photoisomerization

## 1. Introduction

The photochemical behaviour of styrylpyridines [1,2], styrylquinolines [3] and naphthyl-pyridyl-ethenes [4,5], the aza-analogues of stilbene and styrylnaphthalenes, has been extensively studied. These studies showed that *trans*→*cis* photoisomerization and fluorescence are the main deactivation paths for the electronically excited stilbene aza-analogues and that the relative importance of these processes strongly depends on the position of the nitrogen atom. This follows the mixing of the $\pi,\pi^*$-states with the $n,\pi^*$-states introduced by the lone pair of the pyridine nitrogen. Some of these compounds have a wavelength-dependence of the photochemical processes which is due to the coexistence of nearly isoenergetic conformational isomers arising from the rotation of the aryl groups around the single bond linking them to the ethenic carbons [[6,7] and references therein].

In solution, the photochemistry of a molecule of the above classes is affected by the presence of species which act as electron donors, such as alkali halides [8,9] and aromatic amines [10–12], or electron acceptors, such as cyano-aromatics [13] and $Ag^+$ [14]. Moreover, the pyridinic or the quinolinic nitrogen of the above molecules becomes a much stronger basic center upon light excitation and, in aqueous medium, the prototropic equilibration in the excited state perturbs the photochemistry [4,15].

We are interested in the photochemistry of ethene derivatives containing a pyrrole or an indole ring. At variance with the compounds containing pyridine or quinoline residues, the lone pair of the pyrrolic ring is conjugated with the $\pi$-electrons of the aromatic system [16] so that no $n,\pi^*$-states which could favour the radiationless deactivation of the excited molecule are present. The main deactivation channel of the electronically excited *trans* 2-styrylpyrrole, 3-styrylindole and two isomeric naphthyl-indolyl-ethenes is the geometrical isomerization about the ethylenic double bond ($\Phi_c = 0.5–0.6$), which is not affected by the characteristics of the solvent (polarity and/or hydrogen bonding ability); the fluorescence yields are very low ($\Phi_f \approx 0.005$) [17]. As a consequence of the delocalization of the lone pair on the aromatic system, the pyrrolic nitrogen is not basic and its hydrogen has acidic characteristics. The absence of *cis*→*trans* photoisomerization for *cis* 2-(2-(2-pyridyl)ethenyl)indole was attributed to intramolecular H-bonding between the indole >N-H and the lone pair of the pyridinic nitrogen [18,19].

In this paper we report on the interactions of two *trans* naphthyl-indolyl-ethenes (NIE) with aliphatic amines in solvents of different polarity and H-bonding ability and on the ensuing modifications of the photochemical properties of NIEs. The results underline the influence of the

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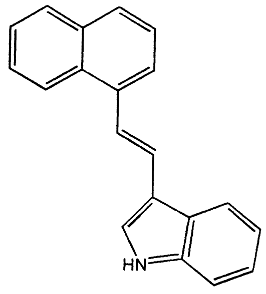
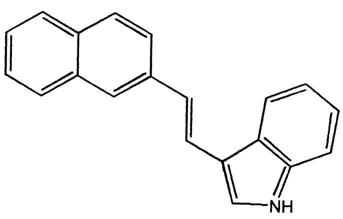
medium on the fate of the chemical species resulting from the interaction



1,3-NIE



2,3-NIE

## 2. Experimental

The synthesis of the examined compounds was described previously [17]. The solvents, Carlo Erba RS grade, were used as received. The amines, Carlo Erba or Aldrich, were distilled over NaOH immediately before use.

The absorption spectra were recorded with Varian DMS 80 or Perkin Elmer 320 spectrophotometers and the fluorescence spectra with a Perkin Elmer MPF 44 spectrofluorimeter equipped with an accessory for spectral correction. The fluorescence quantum yields were determined with reference to quinine sulphate in 0.1 M $H_2SO_4$ ($\Phi_f = 0.55$). The photoisomerization quantum yields were measured spectrophotometrically as described in [17].

The fluorescence lifetimes were measured by a time correlated single photon counting system (IBH Consultants). The nanosecond flash-lamp was filled with hydrogen, the instrumental response function has a full width at half maximum of 2.5 ns. Fluorescence decays described by two-exponential components were extracted from the observed emission signals by deconvolution of the instrumental response function via a non-linear fitting procedure using the least squares method. The software package was provided by IBH Consultants.

## 3. Results and discussion

### 3.1. Absorption spectra

Fig. 1 shows the absorption spectrum of the *trans* isomers of 1-(1-naphthyl)- and 1-(2-naphthyl)-2-(3-indolyl)ethene (1,3-NIE and 2,3-NIE, respectively) in *n*-hexane/$CH_2Cl_2$ (9/1, v/v, the mixed solvent was used to overcome the solubility problems of NIEs) and in *n*-hexane/$CH_2Cl_2$ containing 0.6 M diethyl-amine (DEA). The bathochromic shift, ~8 nm for both the compounds, induced by the amine presence is attributed to the formation of a complex between NIE and DEA. A similar shift was observed in presence of 0.6 M ethyl- (EA), triethyl-amine (TEA) and other amines used in this study. A bathochromic shift was observed also in other aprotic solvents ($CH_2Cl_2$, acetonitrile and dimethylsulphoxide) but the extent of the shift steadily decreases with the increasing polarity of the solvent. In aprotic, low polarity solvents which act as H-bonding acceptor (ethyl ether, tetrahydrofuran and dioxane), the shift was just detectable. No shift was observed in protic solvents.

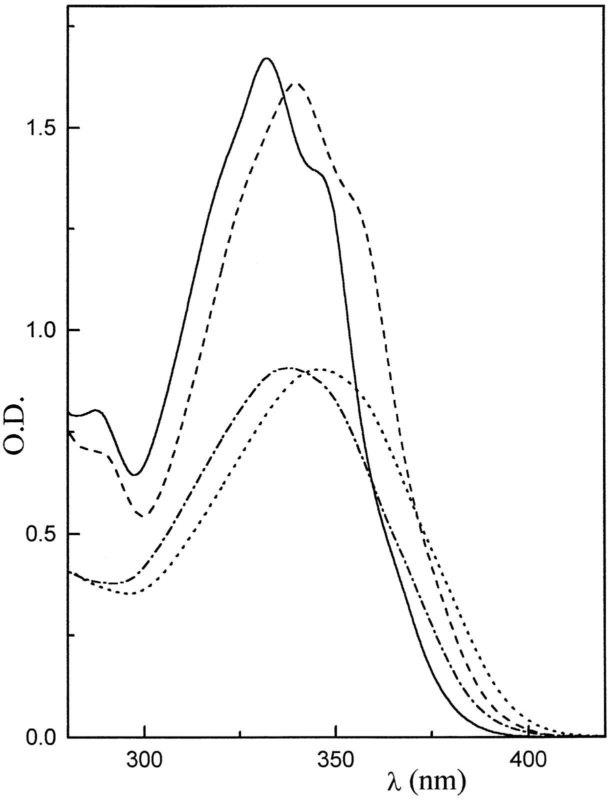


Fig. 1. Absorption spectra (4.3 × $10^{-5}$ M, cells 1 cm path) of 1,3-NIE (– · –) and 2,3-NIE (———) in *n*-hexane/$CH_2Cl_2$ (9/1, v/v) and 1,3-NIE (. . .) and 2,3-NIE (- - -) in *n*-hexane/$CH_2Cl_2$ (9/1, v/v) 0.6 M diethylamine.

The spectral variations in *n*-hexane/$CH_2Cl_2$, handled by the Benesi–Hildebrand equation [20], gave the equilibrium constants at 20°C, $K_g$, collected in Table 1 together with the

Table 1
Association constants ($K_g$ in $M^{-1}$) at 20°C in *n*-hexane/$CH_2Cl_2$ (9/1, v/v)

| | $K_g$ 1,3-NIE | $K_g$ 2,3-NIE | Hydrogen affinity[a] | Ionisation potential* |
|---|---|---|---|---|
| Ethylamine | 10.6 | 8.4 | 528 | 914 |
| Diethylamine | 11.8 | 11.5 | 480 | 833 |
| Triethylamine | 8.8 | 6.4 | 453 | 779 |
| Propylamine | 14.5 | 16.9 | 527 | 907 |
| Dipropylamine | 8.6 | 12.8 | 480 | 824 |
| Tripropylamine | 1.8 | 3.5 | 446 | 764 |
| Piperidine | 18 | 19 | 485 | 836 |
| *N*-Methyl-piperidine | 16.5 | 14.8 | 464 | 800 |
| Pyrrolidine | 16 | 19.2 | 490 | 846 |
| *N*-Methyl-pyrrolidine | 14 | 17 | 471 | 811 |
| Pyridine | 7.45 | 8.95 | – | – |

[a] Data in kJ $mol^{-1}$, from Ref. [21].

ionisation potentials and the hydrogen affinities of the amines [21]. For both the NIE, the $K_g$ values of the alicyclic amines are higher than those of the aliphatic amines. Moreover primary and secondary aliphatic amines are stronger complexants than the corresponding tertiary amines. A similar behaviour was found for the ground-state interaction between carbazole and the same amines [22]. In Ref. [22], the observed regular increase of the $K_g$ value with increasing ionisation potential and hydrogen affinity of the amines allowed us to establish a H-bonding nature of the interaction, in which the hydrogen donor is the >N–H group of the carbazole. In the case of NIE–amine system, the correlation of $K_g$ with the hydrogen affinity of the amines is not univocal. Anyway, the absence of any detectable variation in the absorption spectrum when the amines are added to an alcoholic solution of NIE and the very low interaction observed in aprotic H-bonding acceptor solvents, underline that the >N–H group of NIEs plays an important role in the formation of the complex.

### 3.2. Fluorescence spectra

The studied *trans* naphthyl-indolyl-ethenes have small fluorescence quantum yield, which are scarcely affected by the solvent ($\Phi_f \approx 0.005$ and $\approx 0.02$ for 1,3- and 2,3-NIE, respectively). The fluorescence quantum yields depend weakly on the excitation wavelength, due to the presence in solution of conformational isomers with slightly different absorption spectra [17]. Dual exponential fluorescence decays confirmed the presence of at least two conformers for both the NIEs. At the emission $\lambda_{max}$, the fluorescence lifetimes (in parenthesis the relative abundances) of the two emitting species present in *n*-hexane/$CH_2Cl_2$ solutions excited at the absorption maximum are $\tau \sim 0.2$ ns (92%), 3.5 ns (8%) for 1,3-NIE and ~0.2 (97%), 2.3 ns (3%) for 2,3-NIE.

The fluorescence behaviour of 1,3- and 2,3-NIE in all the experiments that will be described is similar; from now, the pertinent figures will refer to 2,3-NIE because its higher $\Phi_f$ allowed us to obtain a less noisy signal.

The fluorescence spectrum of 2,3-NIE in *n*-hexane is shown in Fig. 2 together with the spectra of the solutions containing different concentrations of piperidine: all the spectra were obtained by exciting at the wavelength of the isosbestic point. The presence of piperidine, or of any amine of Table 1, caused a quenching of the emission of both the NIEs and a modification of its spectral distribution: this suggests that the quenching of the NIEs fluorescence occurs with the concomitant formation of a new emission. This is confirmed by the shape of the Stern–Volmer (SV) plots, $\Phi_f^0/\Phi_f$ and $I_f^0/I_f$, reported in Fig. 3. For both the NIEs, the $\Phi_f^0/\Phi_f$ plots curve downward more than the corresponding $I_f^0/I_f$ plots indicating that a new red-shifted emission increases with the increasing [piperidine]. An approximate value for the fluorescence quenching Stern–Volmer constants ($K_{sv}$), obtained from the slope of the $I_f^0/I_f$ curves at low amine concentrations, are collected in Table 2. One can see that $K_{sv} \leq K_g$: this is in agreement with the formation of a ground state fluorescing complex as result of the interaction of NIEs with the amines. With the calculated $K_{sv}$ values, we calculated the residual emission of the free NIE and hence the difference spectra reported in the inset of Fig. 2. The curves in the inset are the emission spectra of the species arising from the ground-state interaction of NIEs with piperidine: similar spectra were obtained with all the other amines reported in Table 2.

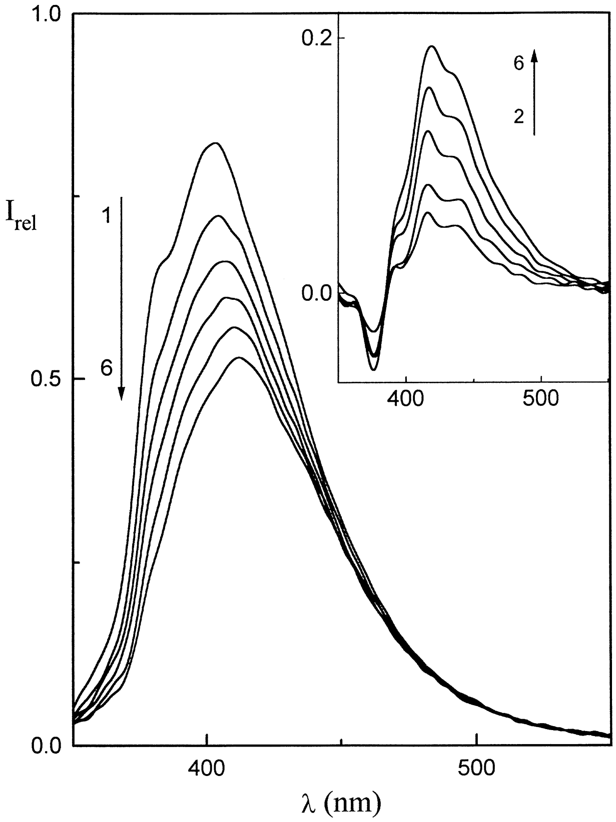


Fig. 2. Fluorescence emission spectra of 2,3-NIE ($4.3 \times 10^{-6}$ M) in *n*-hexane/$CH_2Cl_2$ (9/1, v/v) in presence of different piperidine concentrations. [piperidine]: 0, 0.03, 0.06, 0.1, 0.2 and 0.4 M. Inset: difference fluorescence spectra.

In solvents of increasing polarity, the addition of the amines scarcely affects the absorption spectrum of the NIEs. By contrast, large variations were observed in the fluorescence: the quenching of the NIEs emission occurred with formation of a new, red-shifted fluorescence (henceforth called *red*-fluorescence). Fig. 4 reports the emission spectra of 2,3-NIE in different solvents containing 0.8 M EA.

The *red*-florescence has been examined in detail in acetonitrile (ACN) in which it is well separated from the original emission of NIE. The quenching of the NIEs emission by all the amines occurred with an efficiency generally lower than that observed in *n*-hexane and the $I_f^0/I_f$ SV plots have a good linearity, in agreement with the clear-cut separation of the two emissions. The $K_{SV}$ for various amines, collected in Table 2, depends on the degree of substitution at the nitrogen

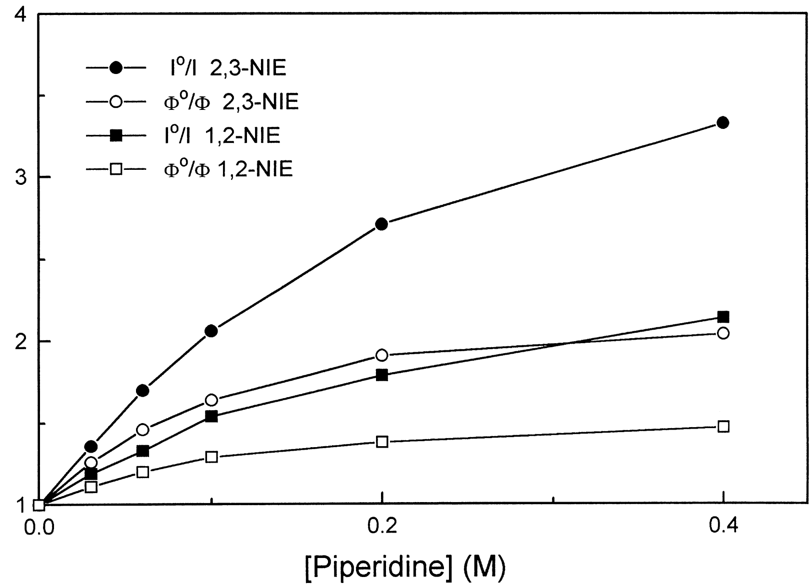


Fig. 3. Stern-Volmer plots for the fluorescence yields ($\Phi_f^0/\Phi_f$) and for the fluorescence intensity of the first vibronic band ($I_f^0/I_f$) of 1,3-NIE and of 2,3-NIE in $n$-hexane/CH$_2$Cl$_2$ (9/1, v/v).

atom: tertiary amines being the poorest quenchers. In ACN two emitting conformers are present and more than 90% of the emission is due to the conformer with lifetime ~0.2 ns (see data of Table 3). This allowed to calculate a maximum value for the quenching rate constant $k_q \approx 5 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, in the hypothesis that ground state complexation does not appreciably contribute to the fluorescence quenching. In fact, it was not possible to measure the ground state complexation constant, $K_g$, being too small the modifications of the absorption spectrum induced by the amine presence.

For both the NIEs, the wavelength of the *red*-fluorescence maximum regularly decreases with the decreasing ionisation potential of the amine and increases with the increasing concentration of the primary and secondary amines while remains unaltered with the increasing concentration of tertiary amines. For example, in solutions of 2,3-NIE, the maximum shifts from 546 nm at [EA] = 0.06 M, to 562 nm, at [EA] = 0.6 M. A ~ 7 nm shift was observed for the same range of DEA. Smaller shifts (~10 nm) were observed for 1,3-NIE.

The dependence of the $K_{SV}$ values and of the *red*-fluorescence $\lambda_{max}$ on the amine hydrogen affinity and the shift of the $\lambda_{max}$ of this fluorescence with the increasing [amine] suggest that more than one type of interaction is responsible for the quenching of NIEs fluorescence by the amines. One of these processes, the ground state complexation, can be easily evidenced in nitrile-type solvents by low-temperature emission experiments inspite of the tiny variations of the absorption spectrum at room temperature. Fig. 5 reports the emission spectra of 2,3-NIE in a butyronitrile matrix at 77 K in the absence and in the presence of 0.9 M EA, DEA and TEA; in the inset of the figure, the fluorescence excitation spectra in the absence and in the presence of EA are reported. For both the NIEs, the original emission was

Table 2
Stern–Volmer constants ($K_{SV}$, M$^{-1}$, accuracy within 10%) for the fluorescence quenching of 1,3-NIE and 2,3-NIE in $n$-hexane/CH$_2$Cl$_2$ (9/1, v/v) and in acetonitrile

| | 1,3-NIE | | 2,3-NIE | |
|---|---|---|---|---|
| | $n$-Hexane/CH$_2$Cl$_2$ | Acetonitrile | $n$-Hexane/CH$_2$Cl$_2$ | Acetonitrile |
| Ethylamine | 3.7 | 1.6 | 9.3 | 1.5 |
| Diethylamine | 3.6 | 0.8 | 9.3 | 1.6 |
| Triethylamine | 3.0 | 0.35 | 7.5 | 0.5 |
| Propylamine | 7 | – | 7.0 | – |
| Dipropylamine | 7 | – | 8.0 | – |
| Piperidine | 3.5 | 1.0 | 11.5 | 1.7 |
| *N*-Methyl-piperidine | 3.5 | 0.7 | 8.5 | 1 |
| Pyrrolidine | 23 | 1.0 | 15.5 | 1 |
| *N*-Methyl-pyrrolidine | 13 | 0.7 | 12.5 | 0.5 |
| Pyridine | 6 | – | 11.5 | – |
| Ethylenediamine | – | 1.2 | – | 1.6 |

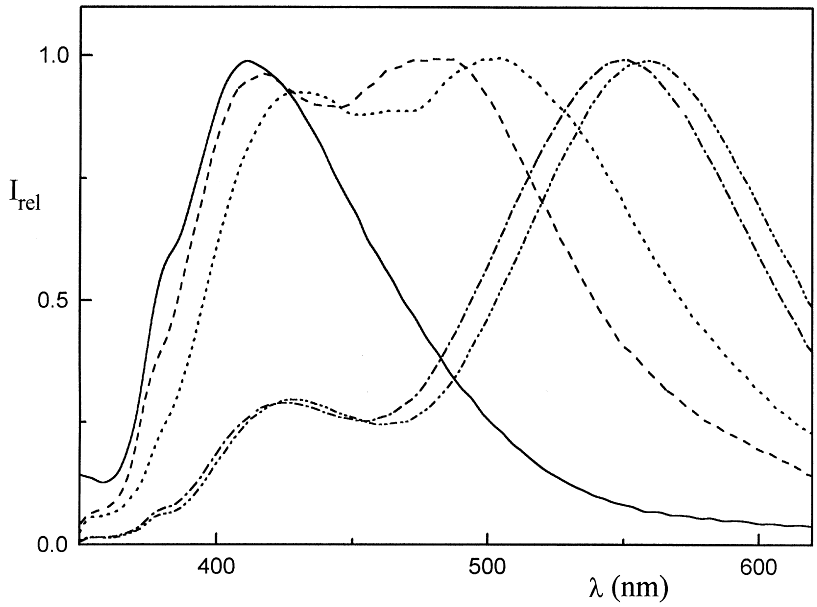


Fig. 4. Fluorescence emission spectra of 2,3-NIE in presence of 0.8 M ethylamine in: toluene (———) $E_T(30) = 33.9$, ethylacetate (- - -) $E_T(30) = 38.1$, $CH_2Cl_2$ (. . .) $E_T(30) = 41.1$, propionitrile (– · –) $E_T(30) = 43.7$ and acetonitrile (– ·· –) $E_T(30) = 46.0$. The spectra were normalised at the emission maximum.

strongly quenched by the amine with the concomitant formation of a new band peaking at 440–450 nm for 2,3-NIE and 460–470 nm for 1,3-NIE. Once again the $\lambda_{max}$ of the emission induced by primary and secondary amines is higher than that observed in the presence of tertiary amines.

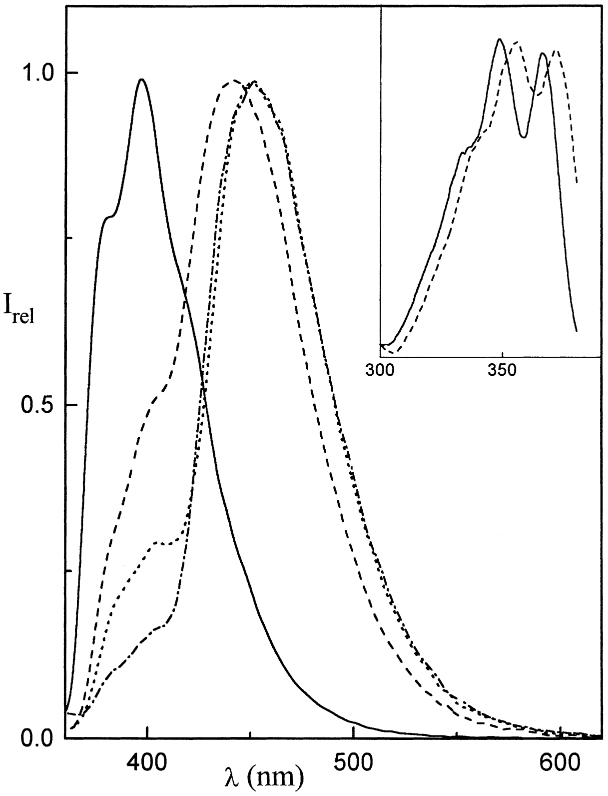


Fig. 5. Normalised emission spectra of 2,3-NIE in butyronitrile matrix at 77 K: alone (———) and in the presence of 0.9 M ethylamine (– · –), diethylamine (. . .) and triethylamine (- - -). Inset: fluorescence excitation spectra of 2,3-NIE in the absence ($\lambda_{em} = 400$ nm) (———) and in the presence of 0.9 M ethylamine ($\lambda_{em} = 460$ nm) (- - -).

We suggest that an hydrogen bonded NIE–amine ground state complex is responsible for the bathochromic emission at low-temperature. This implies that the calculated $k_q$ values for the fluorescence quenching, above reported, are higher than the real values because they include the contribution of the ground state complexation.

At room temperature, the shift to the red of the emission $\lambda_{max}$ with the increasing [amine] suggests the presence of at least another long-wavelength-emitting excited species, besides the H-bonded ground state complex. Some hypotheses can be put forward to explain the multiple nature of the *red*-emission. (i) The H-bonding properties of the indole moiety are strengthened by light excitation [23–25] and, in solution, a H-bonded complex can be formed by the diffusion controlled interaction of the excited NIE and the amine: this complex should emit at wavelengths longer than those of the light-excited ground state complex. A similar behaviour is exhibited by the system carbazole-aliphatic amines, for which fluorescence decay measurements gave clear evidence of the presence of two different excited complexes: the light excited ground-state complex and the complex formed by the interaction of the amines with the excited carbazole [22]. (ii) A charge-transfer process in the excited state could be operative. When the quenchers were tertiary amines, which have a low oxidation potential and a low hydrogen affinity, the CT process should have more weight than H-bonding and the position of the long wavelength emission did not change with increasing [amine]. When the quenchers were the primary amines, which have high oxidation potentials and high hydrogen affinities, the contribution of H-bonding prevails and the red-shift of the emission with the increasing [amine] mirrors the increased importance of

Table 3

Fluorescence decay lifetimes (in nanoseconds) of 1,3-NIE and 2,3-NIE in acetonitrile and methanol. The relative abundances are given in parenthesis

| | 1,3-NIE | | | 2,3-NIE | | | 2,3-NIE + 1 M EA | | | | | | 2,3-NIE + 1 M $OH^-$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 435 nm | | | 435 nm | | | 435 nm | | | 550 nm | | | 435 nm | | | 550 nm | | |
| | $\tau_1$ | $\tau_2$ | $\chi^2$ | $\tau_1$ | $\tau_2$ | $\chi^2$ | $\tau_1$ | $\tau_2$ | $\chi^2$ | $\tau_1$ | $\tau_2$ | $\chi^2$ | $\tau_1$ | $\tau_2$ | $\chi^2$ | $\tau_2$ | $\tau_2$ | $\chi^2$ |
| $CH_3OH$ | 0.25 (90) | 4.5 (10) | 0.985 | 0.20 (98) | 4.0 (2) | 1.010 | 0.20 (97) | 2.65 (3) | 1.14 | 1.05 (59)[a] | 1.7 (41) [a] | 1.00 | 0.20 (97) | 3.0 (3) | 1.009 | 1.15 (70)[a] | 1.8 [a] (30) | 0.825 |
| ACN | 0.20 (92.5) | 3.7 (7.5) | 1.00 | 0.20 (97) | 2.3 (3) | 0.85 | 0.15 (96) | 2.1 (4) | 0.88 | 0.20 (17.5) | 2.70 (82.5) | 0.865 | – | – | | – | – | |

[a] A monoexponential decay ($\tau = 1.35$ and $\chi^2 = 0.88$) fits the observed data as well as the biexponential one.

this process in the excited state. Secondary amines have an intermediate behaviour, as suggested by the smaller red-shift. (iii) Different conformeric (NIE–amine)$^*$, characterised by different *red*-emission, are present. This situation was also found in methylcyclohexane solutions of the system *trans* 1-(2-naphthyl)-2-phenylethene/tri-*n*-butylamine in which two exciplexes with $\lambda_{max} = 453$ and 475 nm have been identified [26]. Moreover, the fluorescence of the two conformeric *trans* ethyl-2-naphthylacrylate in *n*-hexane and acetonitrile was quenched without exciplex emission, but at a different rate, by aliphatic amines [27].

To obtain more informations about the nature of the species responsible of the *red*-fluorescence, the fluorescence decays at 435 and 550 nm were measured on degassed solutions containing 2,3-NIE and various [EA]. At both the wavelengths the fluorescence decay was described by a linear combination of two exponential terms and positive pre-exponential factors, whatever the amine concentration used: in Table 3 are reported the data obtained in presence of 1 M EA, an amine concentration for which $I \approx 0.4\ I_0$ at 435 nm. On the basis of the decay times data, an interaction in the excited state between the NIE and the amine originating an exciplex-type behaviour could be discarded. However it should be stressed that most of the emission of the NIEs is due to a species living ≈0.2 ns, which is the detection limit of our apparatus, and that the species generated by the interaction of NIE with the amine have lifetime similar to those of the NIE itself: this makes the analysis of our system, in which two short-living components (conformers) potentially interact both in the ground and in the excited singlet state with the amines, too complicated to give useful information about the number and the nature of the emitting species.

In the attempt to distinguish the ground state H-bonding effects from the diffusive processes in the excited state, some experiments were done in methanol which has a dielectric constant value ($\varepsilon = 32.7$) similar to that of acetonitrile ($\varepsilon = 37.5$). Methanol is either a good H-bonding donor and a H-bonding acceptor [28] solvent so that the H-bonding interactions between NIE and amines should be hampered by the formation of complexes between the amine and the solvent (where methanol acts as H-bonding donor) and by the solvation of the NIE, where methanol behaves as H-bonding acceptor [29,30].

The presence of EA, up to 1.5 M, does not affect the room temperature absorption spectrum of NIEs in methanol nor the fluorescence emission in a rigid matrix at 77 K suggesting that H-bonding ground state NIE–amine complexes are not formed in this solvent. However, at room temperature, the NIEs emission is modified by high amine concentrations, as shown in Fig. 6 for the couple 2,3-NIE–EA. It should be noted that, for all the amines, the yields of the long wavelength emission steadily increase with the increasing [amine] and fit the Stern–Volmer equation.

$$\Phi^{-1} = K(1 + 1/K_{SV}[Q]) \qquad (1)$$

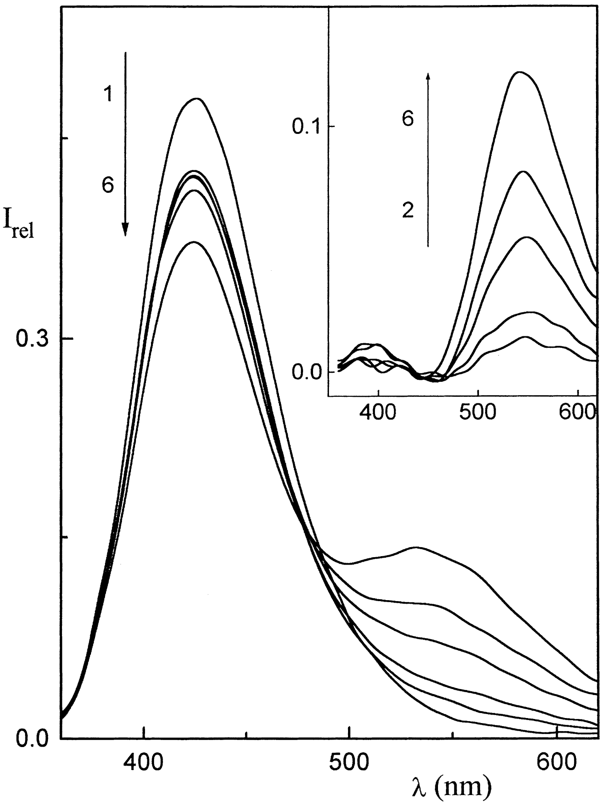


Fig. 6. Fluorescence emission spectra of 2,3-NIE in methanol containing different concentrations of ethylamine. [ethylamine]: 0, 0.153, 0.306, 0.612, 0.918 and 1.45 M. Inset: difference emission spectra.

where *K* is constant in an experimental run. The obtained SV constants are in the range 0.002–0.007 $M^{-1}$. In contrast, the variations of the 2,3-NIE original fluorescence does not follow a Stern–Volmer behaviour: the $\lambda_{max} \approx 545$ nm of the amine induced emission does not depend on the degree of substitution at the amine nitrogen nor on the amine concentration.

The anomalous characteristics of the red emission in methanol, non-dependence of the $\lambda_{max}$ on the oxidation potential of the amines and non-Stern–Volmer behaviour of the quenching of the original NIE fluorescence, frustrate the attribution of the emission to a charge transfer process.

A possible source of the amine-induced emission in alcohols could be the deactivation of the NIE anion formed by proton transfer to the amines in the singlet excited state. It is well known that the indole has a very weak acidic character and that light excitation increases its acidity [31–33]: a similar behaviour is expected for NIEs. In fact, the addition of KOH to a methanolic solution of 2,3-NIE caused the quenching of its fluorescence and the growth of an emission with maximum at 550 nm, due to the radiative deactivation of the deprotonated molecule, shown in Fig. 7. The very similar spectral characteristics of the amine and the $OH^-$ induced emission of the NIEs in methanol suggest the same identity for the fluorescent species.

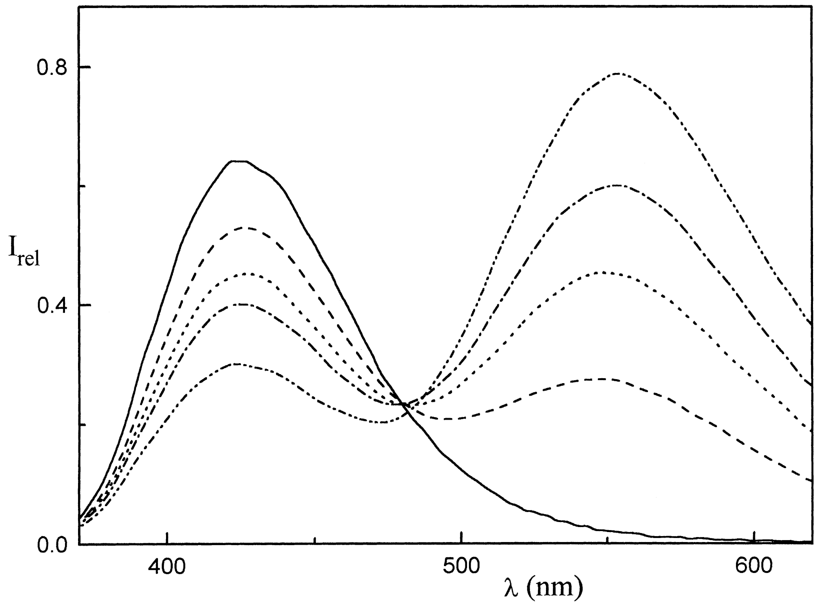


Fig. 7. Fluorescence emission spectra of 2,3-NIE in methanol containing different concentrations of KOH. [KOH]: 0 (———), 0.215 (- - -), 0.43 (. . .), 0.645 (– · –) and 0.175 (– ·· –) M.

To verify this hypothesis some time-resolved experiments on the NIE–amine and NIE–KOH systems in methanol have been carried out. In $CH_3OH$ the lifetime and the relative abundance of the short-lived conformer of the two NIEs are unchanged ($\tau \approx 0.2$ ns) with respect to $n$-hexane and ACN solutions; the lifetime of the long-lived forms increases to 4.5 ns (1,3-NIE) and 4.0 ns (2,3-NIE). The emission of 2,3-NIE in presence of 1 M EA or KOH has been analysed at 435 nm ($\lambda_{max}$ of the NIE emission) and at 550 nm ($\lambda_{max}$ of the red emission). In methanol, as well as in ACN, at both the analysis wavelengths the fluorescence decay was well described by a linear combination of two exponential terms with positive pre-exponential factors: the obtained values are reported in Table 3. Once again, as in ACN, the different lifetimes found from the analysis of the decay of the two bands and the sign of the pre-exponential factors lead to kinetic schemes different from those describing an equilibrium between two species in the excited state. However, the similarly of the lifetimes of the long-wavelength fluorescence induced by the addition of $OH^-$ or amines suggests the anionic nature of the emitting species in both the cases.

We propose that the anomalous quenching of the NIEs fluorescence in methanol is due to a local change in the polarity of the medium caused by the high amine concentration (aliphatic amines have a dielectric constant value $\varepsilon \sim 2.5$): this agrees with the blue shift of the original emission of the two NIEs, ensuring the amine addition. The emission quantum yield of NIEs in low polarity solvents is higher than in polar ones, possibly due to a change in the conformeric equilibrium, as found for 3-styrylquinoline [34] and *trans* 2-(2-(2-pyridyl)ethyl)indole [25], so that the quenching effect of the amines should balance the increase of the emission yield due to the polarity change.

### 3.3. Photoisomerization

Exciplex formation is a key step in the photoreduction and photoaddition reactions of diarylethenes and aliphatic amines [10]. Amines also affect the *trans*→*cis* photoisomerization quantum yield $\Phi_c$ of diaryl-ethenes and their aza-analogues [11,12,35].

Isomerization of the olefinic double bond is the most important photoreaction of NIEs, as demonstrated by the maintenance of the *cis–trans* isosbestic points for irradiation times prolonged by far after the attainment of the photostationary state. In all the solvents the *trans*→*cis* photoisomerization remained the only photochemical process also in the presence of amines, at variance of the system stilbenes-aliphatic amines in which the photoaddition of the amines to the olefin was observed [10,36,37]. In $n$-hexane/$CH_2Cl_2$ (9/1) and in $CH_2Cl_2$, $\Phi_c$ was unaffected by the presence of 1 M amine: this indicates the same photoreactivity of the ground-state H-bonded complex and of the free NIE in low polarity media. In ACN a decrease of the photoisomerization yield was generally observed: the values obtained in the presence of 1 M amine are collected in Table 4 together with the *red*-fluorescence yields calculated from Eq. (1). In general, there is an inverse correlation between the decrease of the photoisomerization quantum yield and the limit *red*-fluorescence yield. However, the photoisomerization quenching is lower than that of the fluorescence: this indicates that the $(\text{NIE–amine})^*$ complex is photoreactive in ACN too. The $\Phi_c^{obs}$ reported in Table 4 are the sum of two contributions: that of the free NIE molecules ($\Phi_c$), which can be evaluated from the $K_{SV}$ and the yield in the absence of amine ($\Phi_f^0/\Phi_f = \Phi_c^0/\Phi_c = 1 + K_{SV}$ [amine]), and that of the complexed NIE ($\Phi_{ca}$) which is ($\Phi_c^{obs} - \Phi_c$) [12]. As one can

Table 4
Experimental *trans→cis* photoisomerization quantum yields ($\Phi_c^{obs}$) in acetonitrile containing 1 M amine; $\Phi_c$ and $\Phi_{ca}$ are the contributions of the free and complexed molecule, respectively. $\Phi_f$ are the limiting fluorescence quantum yields calculated from Eq. (1) of the text

| | 1,3-NIE | | | | 2,3-NIE | | | |
|---|---|---|---|---|---|---|---|---|
| | $\Phi_c^{obs}$ | $\Phi_c$ | $\Phi_{ca}$ | $\Phi_f$ | $\Phi_c^{obs}$ | $\Phi_c$ | $\Phi_{ca}$ | $\Phi_f$ |
| – | 0.55 | – | – | | $0.58_5$ | – | – | |
| Ethylamine | 0.54 | $0.20_5$ | $0.33_5$ | 0.015 | 0.49 | $0.23_5$ | $0.25_5$ | 0.073 |
| Diethylamine | $0.48_5$ | $0.30_5$ | 0.18 | $0.014_5$ | $0.50_5$ | 0.22 | $0.28_5$ | 0.052 |
| Triethylamine | – | – | – | $0.007_5$ | 0.5 | 0.39 | 0.19 | 0.019 |
| Piperidine | – | – | – | 0.028 | 0.49 | $0.21_5$ | $0.27_5$ | 0.04 |
| *N*-Methyl-piperidine | – | – | – | $0.007_5$ | 0.60 | $0.29_5$ | 0.31 | 0.017 |
| Pyrrolidine | – | – | – | 0.023 | – | – | – | 0.09 |
| *N*-Methyl-pyrrolidine | – | – | – | 0.012 | – | – | – | 0.032 |
| Ethylendiamine | $0.49_5$ | $0.24_5$ | 0.25 | $0.03_5$ | 0.43 | 0.22 | 0 .21 | 0.72 |

see from the data of Table 4, the two contributions are comparable, as found in [12] for the two isomeric styrylnaphthalenes.

The charge-transfer interaction between diarylethenes and amines in low polarity solvents induces intersystem crossing which favours the *trans→cis* photoisomerization in the triplet state. By contrast, in ACN, the photoisomerization does not occur because the charge-transfer leads to non-isomerizable negative radical ions [38,39]. In fact, the *cis→trans* isomerization of the diarylethene radical ions is a one-way process [40,41]. The *trans→cis* photoisomerization of NIEs is scarcely affected by the amines and the fluorescence emission is a non-negligible deactivation channel for the (NIE–amine)$^*$ in ACN, so that the formation of the triplet state and of the non-isomerizable radical anions can be ruled out. This fact, together with the lack of correlation between the fluorescence quenching and the ionisation potential of the amines, support the hypothesis that the photochemistry of NIEs in the presence of amines is mainly driven by a H-bonding interaction.

## 4. Conclusions

It is difficult to give an univocal interpretation of the experimental results obtained in this work. However, one can conclude that in non-hydroxylated solvents of low and high polarity, H-bonding between the indolic >N-H and the lone pair of the aliphatic amines is the most important interaction in the system NIE–aliphatic amines. The complex, either formed in the ground- or in the excited state, has a photochemical reactivity very similar to that of the unbound NIEs. The fluorescence properties of the bound NIEs cannot be described in terms of a mixed ground- and excited-state kinetics likely because multiple conformer-amine equilibria are active and, possibly, influenced by the microenvironment changes induced by the high concentrations of amines necessary to bring about the interaction. In methanol, the formation of the NIE anion by prototropic equilibration in the singlet excited state rationalises the observed phenomena.

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