Investigation of the photoisomerisation process in four *p*-benzoxazoyl-substituted stilbenes†

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Fluorescence properties and *trans–cis* photoisomerisation of the benzoxazole derivatives 2-[4-(*E*)-(styryl)phenyl]benzoxazole (**I**), 2-{4-[(*E*)-2-(4-methoxyphenyl)vinyl]phenyl}benzoxazole (**II**), {4-[(*E*)-2-(4-benzoxazol-2-yl-phenyl)vinyl]phenyl}dimethylamine (**III**) and {4-[(*E*)-2-(4-benzoxazol-2-yl-phenyl)vinyl]phenyl}diphenylamine (**IV**) have been investigated in solvents of different polarities. It was found that these compounds exhibit efficient fluorescence with quantum yields and lifetimes strongly dependent on solvent polarity, although only compounds **III** and **IV** possess a significant charge transfer character in solvents of medium and high polarities. In addition, the photoisomerisation quantum efficiency depends strongly on the substitution of the phenyl ring in the electron donor moiety. A strong dependence of the quantum efficiency of the photoisomerisation on solvent was established. That quantity depends linearly on the non-radiative quantum yield of the deactivation of the excited singlet state for all investigated compounds. These results are consistent with a singlet state mechanism of the photoprocess. For compounds **III** and **IV**, with strong electron donors (*N,N*-dimethylaniline and triphenylamine), the molecule in the excited state *trans* configuration is more stabilized by solvent polarity than in the perpendicular form which causes more efficient isomerisation in nonpolar solvents. For compounds **I** and **II** the energy of the perpendicular configuration decreases more rapidly than that of the *trans* configuration when solvent polarity increases. In this case the energy barrier decreases with increasing solvent polarity. This makes the photoisomerisation process easier in polar solvents.

Introduction

trans–cis photoisomerisation of olefinic compounds, especially stilbenes, has been a subject of numerous investigations and reviews.[1,2] In the ground state a large activation barrier (corresponding to the perpendicular geometry of the molecule) exists between the *trans* and *cis* isomers, which prevents the twist around the ethylenic double bond. In other words, the *trans–cis* isomerisation cannot proceed in the ground state at room temperature, but may proceed at higher temperatures.[3] In the excited state a minimum exists on the potential energy surface when the molecular geometry is perpendicular (p* state, Fig. 1).[4] A much smaller activation barrier exists between the *trans* and perpendicular conformers which is small enough to allow the photochemical process of isomerisation. On the *cis* side there is a very small or no barrier to torsional motion.[5] When the *cis* or *trans* excited conformer achieves the perpendicular geometry the decay to the ground state is very fast due to the proximity of the excited and ground state energies. In this decay process the probability to reach the *trans* or

cis conformer is almost equal, in the second case we observe the photochemical process of isomerisation. Several investigators have studied the conversion of the *cis* to *trans* stilbenes in the singlet excited state.[6,7] Excitation of the pure *cis*-stilbene in hydrocarbons leads to the formation of the perpendicular state, from which the formation of 4a,4b-dihydrophenanthrene and photoisomerisation occurs. A small fraction of the excited *cis*-stilbene reaches the excited *trans* conformation *via* adiabatic conversion.[7] Saltiel and coworkers estimated the lifetime of the p* state at 0.3 ps.[7]
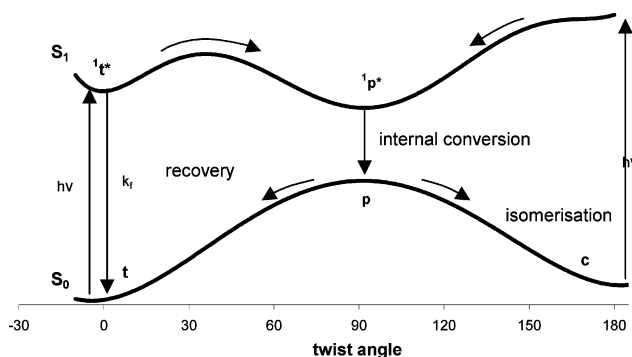
Fig. 1 Energy *vs.* dihedral angle (twist around the ethylenic bond) for stilbene-like compounds. The reaction pathways are introduced in Scheme 1.

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As pointed out in several publications, the quantum efficiency of a photoprocess depends strongly on solvent polarity,[8] solvent viscosity,[9] temperature,[10] and varies with the nature of substituents.[11] When heavy atoms (for example bromine) are present in the molecule a triplet isomerisation pathway becomes operative.[2,10,12] Lewis and coworkers investigated photophysical and photochemical behaviour of *trans*-stilbenes substituted by a strong electron donor (amine) in the *para* and *meta* positions.[13] They found high fluorescence quantum yields and long fluorescence lifetimes when the amino group was attached to the *ortho* and *meta* position of the phenyl ring in stilbene; for these compounds very small isomerisation quantum yields were found. The fluorescence decay time of the *para* isomer is less than one hundred picoseconds and also fluorescence quantum yield is substantially smaller than that of *ortho* and *meta* isomers (less than 0.05). The photoisomerisation of the *para* compounds proceed with a high quantum yield in solvents of low and high polarities. This is a consequence of larger torsional barriers in the excited state for the *ortho* and *meta* substituted aminostilbenes (*ca.* 7 kcal mol^{-1}) compared to that of the *para* isomer (3.5 kcal mol^{-1}).

Some attention has been paid to investigations of the substituent effects on fluorescence and isomerisation quantum yields in series of stilbenes. Likhtenshtein and coworkers investigated fluorescence parameters of a large class of *trans*-4,4′-disubstituted stilbenes.[14] For compounds which do not possess strong electron donor acceptor and/or substituents, the isomerisation rate constant increased with increasing solvent polarity. Introducing a strong donor substituent (N(CH$_3$)$_2$) in the *para* position on the aromatic ring causes a large shift in the fluorescence spectra which is attributed to the strong charge transfer character of these molecules in the excited singlet state. The donor stabilizes the excited *trans* state relative to the perpendicular state. Thus, on increasing the solvent polarity, the torsional energy barrier increases making radiationless torsional relaxation less favorable. For the compounds that do not have significant charge transfer character in the excited state, the perpendicular state is more stabilized than the *trans* state, which in consequence reduces the intrinsic energy barrier to photoisomerisation when solvent polarity increases. They found that the lifetimes and quantum yields of fluorescence depend on the donor–acceptor properties and correlate with the Hammett σ-constants.

One effect should be taken into account in substituted stilbenes with strong electron donor–acceptor subunits, which exhibit strong charge transfer character in the excited singlet state. Rettig and coworkers[15] investigated the fluorescence behavior of bridged 4-(dimethyl-amino)-4′-cyanostilbenes. Bridging affects the fluorescence lifetimes and quantum yields significantly. Based on the experimental results the authors concluded that the three state model must be operative in such compounds (called push–pull molecules) as presented in Scheme 1. Upon excitation of the planar molecule to the singlet state, a twist of the aniline group occurs (leading to twisted intra-molecular charge transfer (TICT) conformation) which lowers the energy of the system.[16] Thus, in consequence, this leads to an increase of the torsional barrier for the transition from the TICT to perpendicular configuration. The authors also postulated that for unsubstituted stilbenes the perpendicular geometry accessible by twisting the double bond has a zwitterionic character (thus of larger polarity) whereas for push–
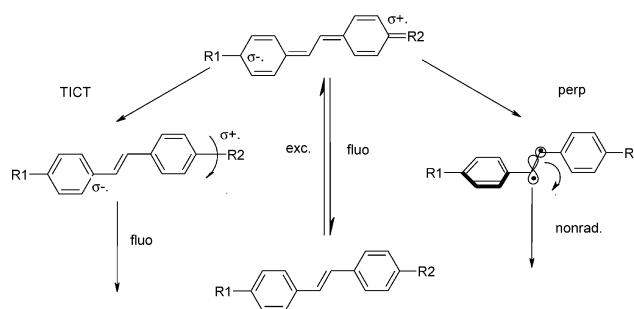
Scheme 1

pull stilbenes biradical (weakly polar) structures are predicted to be favoured.

Yang and coworkers investigated the fluorescence and isomerisation processes of a series of methyl- and ethylene-bridge-substituted *trans*-4-(N-(4-cyanophenyl)amino)stilbenes.[17] They also showed that formation of the highly polar TICT state, which is responsible for the dual fluorescence in acetonitrile, strongly reduces photochemical isomerisation. Fluorescence behaviour of the similar molecule (2-p-dimetylaminostyryl)benzoxazole) has been investigated by Fayed.[18] Fluorescence quantum yield of this compound in all exploited solvents of various polarities turned out to be very low, but also strongly temperature and solvent viscosity dependent.

We have studied the isomerisation process of four compounds that belong to the group of benzoxazole derivatives. Special attention has been focused on the influence of the substituent on the quantum yields of the photochemical and photophysical processes as well as the solvent polarity and viscosity dependence on these processes. The structures of the investigated compounds are given in Scheme 2.

Experimental

Chemicals were purchased from commercial suppliers (Aldrich, Fluka and POCh-Polish Chemical Company) and used as received. Solvents (n-hexane (HEX), cyclohexane (CHX), dibutyl ether (DBE), ethyl acetate (EtAc), glycerol triacetate (GTA), tetrahydrofuran (THF), methylene dichloride (MeCl$_2$), acetone (Ace), acetonitrile (ACN), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethyl iodide (EtI), propylene carbonate (PC) and alcohols methanol (MeOH), ethanol (EtOH), n-propanol (PrOH), n-butanol (BuOH), n-pentanol (PeOH), n-hexanol (HxOH), n-heptanol (HpOH) and n-octanol (OcOH)) were purchased from Aldrich and Fluka. Melting points were measured on Melt-temp apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian VXR 300 in CDCl$_3$ solution.

Synthesis procedures

2-(4-(E)-Styrylphenyl)benzoxazole I, (2-{4-[(E)-2-(4-methoxyphenyl)vinyl]phenylbenzoxazole) II and {4-[(E)-2-(4-benzoxazol-2-yl-phenyl)vinyl]phenyl}dimethylamine III. Compound **I** was prepared using the literature procedure for stilbene anil synthesis developed by Siegrist.[19]

Compounds **II** and **III** were prepared as described in our previous paper.[20]

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I

II

III
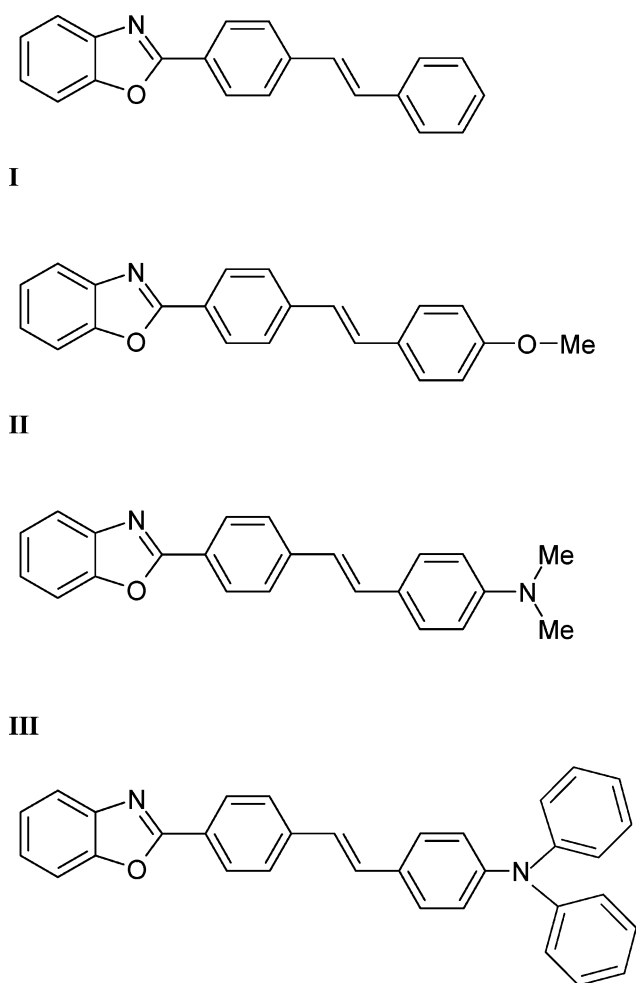
IV

Scheme 2 Structures and chemical names of the investigated compounds. **I**: 2-(4-(*E*)-styrylphenyl)benzoxazole. **II**: 2-{4-[(*E*)-2-(4-methoxyphenyl)vinyl]phenyl}benzoxazole. **III**: {4-[(*E*)-2-(4-benzoxazol-2-yl-phenyl)vinyl]phenyl}dimethylamine. **IV**: {4-[(*E*)-2-(4-benzoxazol-2-yl-phenyl)vinyl]phenyl}diphenylamine.

{4-[(*E*)-2-(4-Benzoxazol-2-yl-phenyl)vinyl]phenyl}diphenylamine IV. The synthesis of stilbene **IV** is shown in Scheme 3. The bromomethyl derivative **4** was prepared as described in our previous paper.[20] Reaction of compound **4** with triphenylphosphine (PPh₃) gave phosphonium bromide **5** in quantitative yield. This salt was subjected to the Wittig reaction with 4-diphenylamino benzaldehyde yielding a 1 : 3 mixture of *Z* and *E* isomers **6**. An attempt to separate the isomers failed due to very close R_f values. Boiling in toluene with an iodine crystal isomerized the mixture. The final compound **IV** was purified on column packed with silica gel using toluene as eluent.

2-(p-Triphenylmethylphenylphosphonium)benzoxazoyl bromide 5. 2-(*p*-Bromomethylphenyl)benzoxazole **4** (3.83 g, 1.32 mmol) was heated with triphenylphosphine (3.7 g, 1.4 mmol) in boiling xylene (20 mL) for 2 h. After cooling the precipitate was filtered of, washed with toluene and dried.

Colorless crystals, yield 7 g, 95%, mp >300 °C (dec).
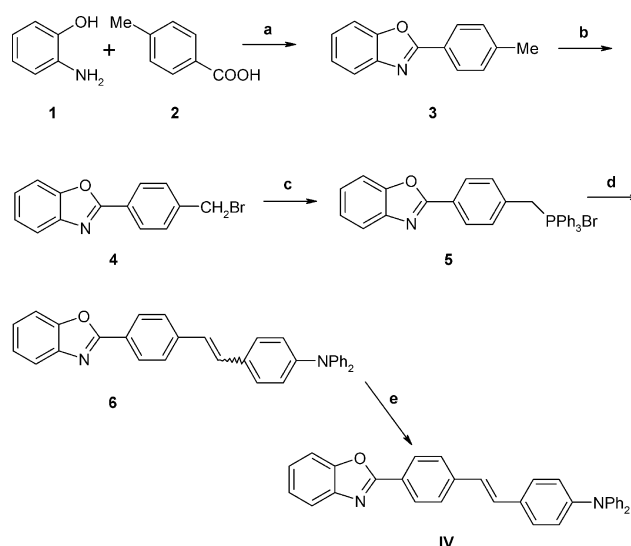
Scheme 3 (a) Polyphosphoric acid PPA/120 °C/12 h; (b) *N*-bromosuccinimide (NBS)/CCl₄/8 h; (c) PPh₃/xylene/boiling/2 h; (d) ArCHO/DMF/*tert*-BuOK; (e) iodine/toluene/boiling.

^{1}H NMR (CDCl₃, 300 MHz, δ (ppm)): 7.78–7.74 (m, 8H); 7.71–7.65 (m, 3H); 7.70–7.65 (m, 7H); 7.35–7.32 (m, 1H); 7.26–7.16 (m, 5H); 5.76 (AB, J_{AB} = 15.3 Hz, 2H).

Anal. calcd for C₃₂H₂₆BrNOP: C 69.70; H 4.75; N 2.54%. Found C 69.56; H 4.51; N 2.32%.

{4-[(E)-2-(4-Benzoxazol-2-yl-phenyl)vinyl]phenyl}diphenyl-lamine IV. To a solution of compound **5** (1 g, 1.8 mmol) and *tert*-BuOK (0.2 g, 1.8 mmol) in DMF (10 mL) *p*-diphenylaminobenzaldehyde was added (0.54 g, 2.0 mmol). The solution was stirred at room temperature for 12 h and poured into an ice/water mixture. The yellow precipitate was filtered off and dried. The mixture of *Z* and *E* isomers **6** was boiled with iodine in toluene for 2 h. Toluene was evaporated and the residue was subjected to column chromatography on silica gel (Merck 60, 70–230 mesh) using toluene as eluent.

Bright yellow crystals, yield 540 mg, 58%, mp. 225–226 °C (toluene).

^{1}H NMR (CDCl₃, 300 MHz, δ (ppm)): 8.20–8.17 (m, 2H); 7.74–7.71 (m, 1H); 7.60–7.57 (m, 2H); 7.55–7.52 (m, 1H); 7.38–7.35 (m, 2H); 7.32–7.21 (m, 6H); 7.14 (d, *J* = 16.3 Hz, 1H); 7.09–7.07 (m, 4H); 7.04–6.96 (m, 5H).

^{13}C NMR (CDCl₃, 75 MHz, δ (ppm)): 163.65; 151.40; 148.55; 148.05; 142.91; 141.54; 131.40; 130.94; 129.97; 128.60; 128.28; 127.28; 126.41; 126.16; 125.64; 125.36; 125.20; 123.91; 123.81; 120.54; 111.15.

Anal. calcd for C₃₃H₂₄N₂O; C 85.32; H 5.21; N 6.03%. Found C 85.01; H 5.13; N 5.84%.

Fluorescence measurements

The fluorescence arrangement was described in a previous paper.[21] The samples (prepared in darkness) were degassed before experiments using the freezing–pumping–thawing technique. The fluorescence quantum yields were determined and corrected for spectral sensitivity fluorescence spectra using quinine sulfate in 0.1 N H₂SO₄ as an actinometer (Φ_{fl} = 0.51).[22] The fluorescence lifetimes were estimated from the decay curves measured by

time-resolved single photon counting technique. As an excitation source a picosecond diode laser ($\lambda = 400$ nm, 70 ps pulse duration) or nanosecond diode ($\lambda = 310$ nm, 1 ns pulse duration) (both from IBH-UK) were used. Analyses of the decay functions were performed by a convolution method using our own FORTRAN programs. The decay functions were mono-exponential except that of compound **III** in alcohols, where a clear rise of fluorescence on the red side of the fluorescence spectrum has been observed. On the blue side of the fluorescence, the double exponential behavior of the decay function was observed. This may be attributed to a solvation effect due to proportionality of the rise time to the longitudinal relaxation time of the alcohols.

Actinometric studies

The *trans–cis* isomerisation process was monitored by measuring the absorption spectra of the compound upon irradiation of the sample by a 365 nm (for compound **I** and **II**) photographic flash lamp (ELEKTRONIKA 85-24) equipped with a suitable interference filter. For compounds **III** and **IV** a 405 nm interference filter was used. As a reference the *trans–cis* isomerisation of *trans*-4-dimethylamino-4-nitrostilbene in cyclohexane was used ($\Phi_{t-c} = 0.14$).[23] To determine the quantum efficiency of isomerisation the equation derived by Gauglitz and Hubig is usually applied:[24]

$$\frac{dA}{dt} = QI(A - A_\infty)\frac{1-10^{-A'}}{A'} = QI*F(A, A') \quad (1)$$

where A and A_∞ are the absorbances at the observation wavelength (maximum of the 0-0 absorption band) at times t and infinity, respectively, A' is the absorbance at the irradiation wavelength, I is the irradiation in einsteins per square centimetre per second and Q is the pseudophotochemical quantum yield defined as:

$$Q = \varphi_{t-c}\varepsilon'_t + \varphi_{c-t}\varepsilon'_c. \quad (2)$$

In the above equation φ_{c-t} and φ_{t-c} are the partial quantum yields of the *cis–trans* and *trans–cis* isomerisations, respectively, and ε'_c and ε'_t are the extinction coefficients of the *cis* and *trans* isomers at the irradiation wavelength. However, this approach requires the extinction coefficients of the *cis* conformer which may be directly inaccessible. Therefore we analysed the initial reaction velocities, related to the *trans–cis* isomerisation quantum yields (Φ_{t-c}) according to the equation:

$$\frac{dA_{trans}}{dt} \approx -I*\varepsilon_{trans}(1-10^{-A'})\Phi_{t-c} \quad (3)$$

In some cases the photostationary states (pss) were achieved and the ratios of the concentrations of *trans* and *cis* isomers were determined. In such cases the quantum yields of the *cis–trans* isomerisation (Φ_{c-t}) were calculated using Fischer's method for determination of the absorption spectrum of the *cis* isomer[25] (Table S1 in the ESI†) according to the formula:

$$\left(\frac{[trans]}{[cis]}\right)_{pss} = \frac{\Phi_{c-t}\varepsilon'_c}{\Phi_{t-c}\varepsilon'_t} \quad (4)$$

Results

Absorption

The syntheses solely yield the *trans* isomers of the compounds. The absorption spectra recorded on freshly prepared solutions are presented in Fig. 2.
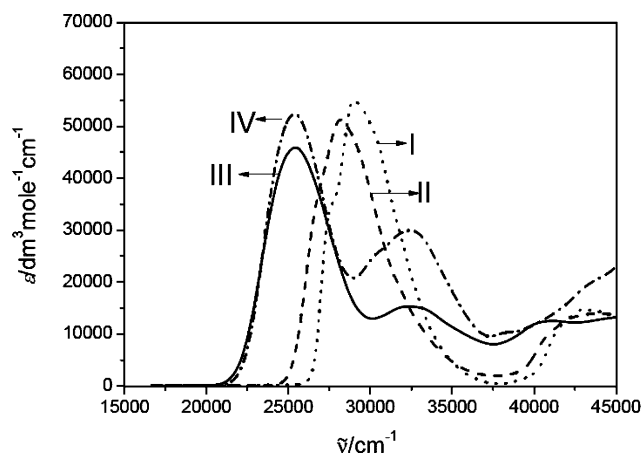

Fig. 2 Absorption spectra of compounds **I**, **II**, **III** and **IV** in acetonitrile.

The molar absorptivity of the first absorption bands of the fluorophores are very high. Substitution of the *para* hydrogen atom by electron-donating methoxy and amino groups leads to a bathochromic shift of the position of the first absorption band. This situation is common for many substituted stilbenes.[26] As we described in our previous paper, the amine-containing dyes also show a solvatochromic shift of the position of the absorption band with increasing solvent polarity. For **I** and **II** this shift is not pronounced and subtle vibration structure of the first absorption band is observed even in a polar solvent (acetonitrile).

trans–cis isomerisation

Irradiation of the *trans* compounds causes a photoisomerisation process as monitored by changes in the absorption spectra. The results shown in Fig. 3 for **II** in acetonitrile are representative.

We can see a decrease of the first absorption band with simultaneous increase of the broad absorption band located at *ca.* 39 000 cm^{-1}. This is consistent with formation of the *cis* isomer. Irradiation of the isomer mixture at 33 000 cm^{-1} leads to a partial recovery of the *trans* isomer. The absorption changes due to irradiation are observed in all investigated compounds, but the solvent polarity dependence of the isomerisation quantum yield is different for each compound. This result is discussed in detail below.

Fluorescence

The fluorescence spectra of compounds **I**–**IV** are presented in Fig. 4.

Consistent with the behavior observed in the absorption spectra, the position of the maximum of fluorescence intensity shifts to the red as the electron-donating ability of the substituent increases. Moreover, the vibrational structure which is discerned in the emission spectra of compounds **I** and **II** vanishes in the spectra
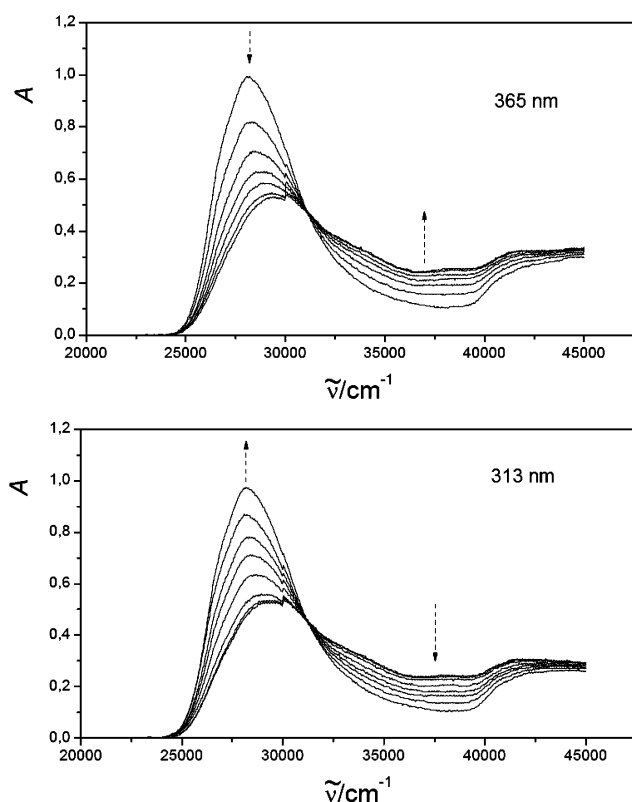
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Fig. 3 Irradiation of compound **II** in acetonitrile at 365 nm (bottom) and 313 nm (top) by a flash lamp.
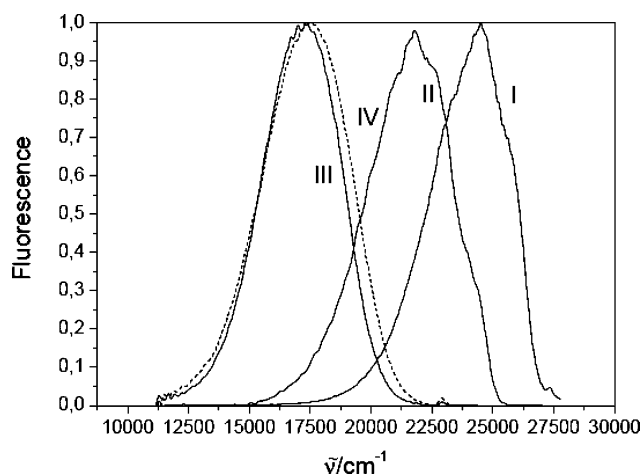

Fig. 4 Fluorescence spectra (corrected for spectral sensitivity and normalized to their maximal intensities) of the compounds **I**, **II**, **III**, and **IV** (dashed line) in DMSO.

of compounds **III** and **IV**. Differences in the solvent polarity dependencies of the positions of the fluorescence maxima of these compounds are informative.

The strong charge transfer character in the excited states of **III** and **IV** leads to much greater sensitivity to solvent polarity in these compounds. The dependence of the position of the fluorescence maximum on the solvent polarity function is described by the well-known Lippert–Mataga equation (eqn (5)).[27]

$$\tilde{v}_{flu} = \tilde{v}_{flu}(vacuo) - \frac{\vec{\mu}_e(\vec{\mu}_e - \vec{\mu}_g)}{2\pi\varepsilon_0 hca^3} f(n^2, \varepsilon_s)$$

$$f(n^2, \varepsilon_s) = \left(\frac{\varepsilon_s - 1}{2\varepsilon_s + 1} - \frac{n^2 - 1}{2(2n^2 + 1)} \right)$$

(5)

The parameters appearing in the above equation have the following meaning: $\vec{\mu}_g$ and $\vec{\mu}_e$ are the dipole moments of the molecule in the ground and excited states, respectively, a is the Onsager radius of the molecule and ε_s and n are the dielectric constant and refraction index of the solvents.

For compounds **III** and **IV** the solvent dependence is almost identical, as can be seen in Fig. 5. This is not surprising in view of similar oxidation potential of the attached electron donors (*N,N*-dimethylaniline and triphenylamine), which are equal to 0.81 V[28] and 0.89 V,[29] respectively (*vs.* SCE in acetonitrile).
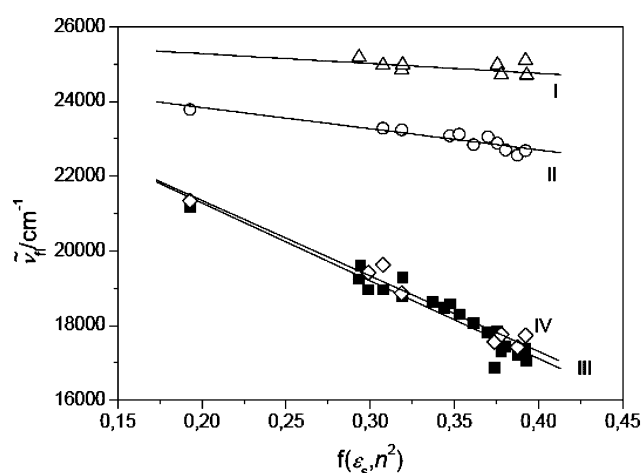

Fig. 5 Dependence of the position of the fluorescence maximum on the solvent polarity function for **I** (open triangles), **II** (open circles), **III** (black squares) and **IV** (open diamonds).

Assuming that the dipole moments in the ground state are equal to 1.6, 2.4, 5.8 and 3 D‡ respectively for compounds **I–IV**, and the angle between the ground and excited state is equal to 46.4°,[20] and that the Onsager radii are equal to 6.0, 6.2, 6.3 and 6.8 Å for compounds **I–IV**, the calculated excited state dipole moments from the slopes in Fig. 5 are equal to 7.4 ± 2 D, 13.1 ± 1.2 D, 26.3 ± 1.7 and 27.4 ± 1.6 D for **I**, **II**, **III** and **IV**, respectively.

We also performed time-resolved fluorescence measurements of the investigated systems. The results of the fluorescence measurements and quantum yields of the isomerisation are gathered in Table S1 in the ESI.†

The rather short fluorescence lifetimes are strongly solvent polarity dependent in all cases. The fluorescence decay functions are mono-exponential, but for system **III** in alcohols become bi-exponential (in alcohols of larger viscosity), which indicates a solvation behavior, meaning that excitation leads to the non-equilibrated excited state, which relaxes to achieve its minimum potential. The rise time, observed on the red side of the fluorescence band, and the fast decay contribution, observed on the blue side

‡ Calculated using the DFT method with the B3LYP potential with the cc-pVDZ basis set.

of the fluorescence band, correspond roughly to the longitudinal relaxation times (or viscosity parameters) of the alcohols.

The fluorescence lifetimes of compounds **I** and **II** decrease with increasing solvent polarity. The opposite behavior is observed (Fig. 6, top) for **III** and **IV**. Rate constants of the non-radiative deactivation of the excited singlet state, calculated from the fluorescence quantum yields and lifetimes, are also plotted as a function of the solvent polarity parameter (Fig. 6, bottom). We can observe an increase of the non-radiative rate constant k_{nr} (calculated as $k_{nr} = (1 - \Phi_{fl})/\tau_{fl}$) with increasing solvent polarity for compounds **I** and **II**, *i.e.* for the compounds not having the charge transfer character in the first excited state.

state is reflected in excited state dipole moments based on strong solvatochromic shift of the fluorescence maximum. We previously showed that this charge transfer character for compound **III** also exists in the ground state in polar solvents.[20]

All the compounds are efficient fluorophores, *i.e.* they possess relatively high fluorescence quantum yields, although they behave differently with respect to the dependence of the fluorescence lifetimes on the solvent dielectric constant. In the flash photolysis experiments it has been found that the population of the triplet state is negligible in all cases and all solvents of different polarities. At 77 K no phosphorescence was detected in all investigated systems. Thus, the excited singlet state depopulates only *via* radiative and non-radiative $S_1 \rightarrow S_0$ transitions. From our actinometrical studies we can conclude that the nature of the non-radiative transition is the *trans–cis* isomerisation for compounds **I–III** on the basis of the linear dependence of the isomerisation quantum yield (Φ_{t-c}) on the quantum yield of non-radiative deactivation ($1 - \Phi_{fl}$) (Fig. 7). In these cases the relation $\Phi_{fl} + 2\Phi_{t-c} = 1$ is roughly fulfilled. Some deviations from this dependence were found for compound **IV**.

Fig. 6 Solvent polarity dependencies of the fluorescence lifetimes of **I** (open triangles), **II** (open circles), **III** (black squares) and **IV** (open diamonds) (top) and those of the non-radiative deactivation rates (bottom). The correlation lines are drawn only for presentation purposes.
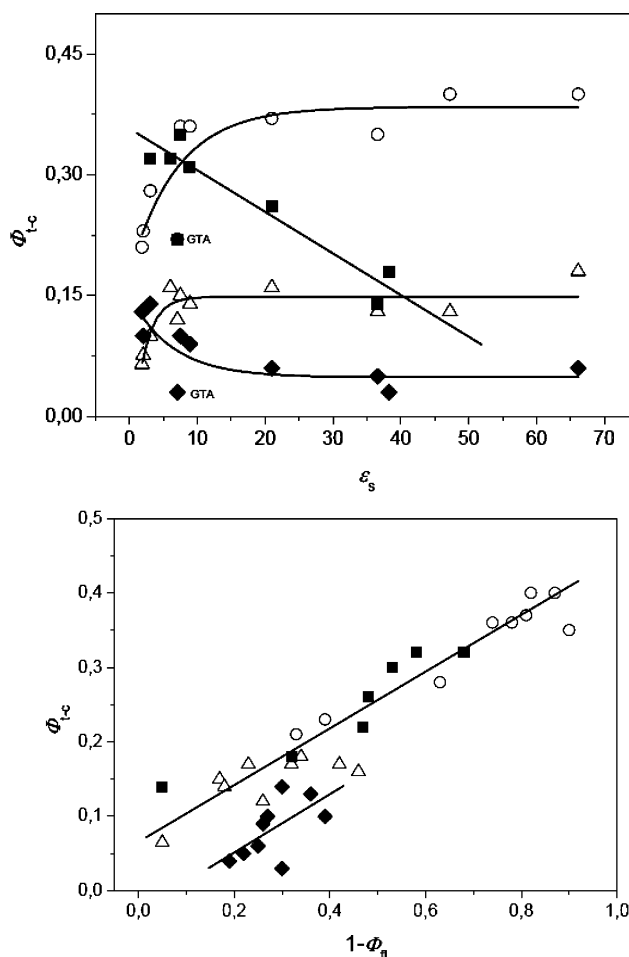
Discussion

Fluorescence and isomerisation data

The replacement of hydrogen by the electron-donating groups methoxy and amino shifts the position of the first absorption and fluorescence bands to lower wavenumbers. Significant charge transfer character in the amino substituents in the excited singlet

Fig. 7 Dependence of the photoisomerisation quantum efficiency on solvent dielectric constant (top). Dependence of the photoisomerisation quantum efficiency on the non-radiative deactivation quantum yield (bottom). **I** (open triangles), **II** (open circles), **III** (black squares) and **IV** (black diamonds).

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The difference between the individual systems with respect to the non-radiative deactivation and consequently the difference in the dependence of photochemical reactivity on the solvent polarity, remain to be explained.

Upon excitation of the *trans* isomer the system starts to twist around the double bond to achieve the perpendicular configuration from which the non-radiative deactivation process occurs (Fig. 1). We thus expect that twisting of the heavier subunit containing triphenylamine (**IV**) is more difficult than the rotation of the dimethylaniline subunit (**III**). This effect seems to be responsible for larger fluorescence decay times and smaller photoisomerisation quantum efficiencies for **IV**. Goerner reported a similar observation for nitro- and dinitro-substituted diarylethylenes. Photoisomerisation quantum efficiency decreases drastically when the anthracene moiety is attached to the nitro- or dinitro-styryl subunit[30] instead of the naphthalene substituent.

At the present time, only an intuitive explanation for the different photochemical behavior can be given regarding the differences between the compounds which do not posses charge transfer character in the excited singlet state (**I** and **II**) and those exhibiting a large excited state dipole moment in *trans* configuration (**III** and **IV**). This can be inferred from the difference of the excited state dipole moment in the *trans* and perpendicular conformations.[14] To enhance this explanation, the energetic scheme (Fig. 1) that describes the energy potential dependence on the twisting angle for all the investigated systems in the ground and excited singlet state is employed. It can be seen that in the ground state, at an angle roughly equal to 90° a high activation barrier exists which cannot be overcome, making isomerisation in the ground state at room temperature improbable. However, in the excited state a minimum exists at the same geometry and the proximity of the excited and ground states allows for an efficient non-radiative transition, which leads to the *trans–cis* isomerisation. Now let us assume that for compounds **I** and **II** the *trans* conformer in the singlet excited state is less polar than in the perpendicular structure: thus, increasing solvent polarity will decrease the energy of the *trans* state more than that of the perpendicular geometry. In consequence, this will lead to a decrease of the activation barrier (which corresponds to a twist angle somewhere between −90 and −180°) making the excited-singlet state isomerisation easier in polar solvents. Contrary to that, the opposite situation has been found in compounds **III** and **IV**—the excited singlet state in the *trans* geometry is more polar than that in the perpendicular configuration. In this case the increasing solvent polarity will increase the activation barrier suppressing the excited-state isomerisation in solvents of larger polarities. For the description of the processes, occurring in the excited singlet state of the investigated molecules, the two-state model is sufficient. No dual fluorescence has been detected in these compounds, which possibly would be expected for systems **III** and **IV**. The molecules remain planar prior to the twist around the C=C double bond to form the perpendicular structure.

It seems that in this class of the compounds the solvent polarity has greater influence on the rate constants of the non-radiative transitions than the solvent viscosity as can be judged from the results obtained for very viscous triacetine and less viscous dichloromethane. Both solvents possess comparable dielectric constants (7.11 and 8.93, respectively) but significantly differ in viscosity coefficients (23 and 0.413 mPa s, respectively).

Surprisingly the non-radiative deactivation rate constants of the molecules **III** and **IV** in both solvents are similar.

Some attention should be paid to system **IV**. As we can see from Fig. 7, the *trans–cis* isomerisation quantum yields for this compound do not match the correlation line predicted for the values obtained for other systems. In other words, beside the non-radiative deactivation channel connected with a twist around the ethylenic double bond, an additional deactivation channel must be operative. It may be an electron back-transfer leading to the ground state recovery. Our preliminary analysis of the fluorescence spectra of compound **IV** shows a significantly larger internal reorganization energy connected with the transition $^1CT \rightarrow$ ground state than that for compound **III**. This in consequence leads to an increase of the back electron transfer rate constants for compound **III**, as can be predicted from electron transfer theory for the transitions in the inverted Marcus region. Further investigations in this area are planned.

Conclusions

Fluorescence and chemical behavior of the four benzoxazole derivatives were investigated using steady state and time-dependent techniques. These compounds differ with respect to the electron-donating properties of the donor groups attached *via* the stilbene system to phenyl-benzoxazole. When the attached donors do not posses strong electron donating properties (phenyl **I** and *p*-methoxyphenyl **II**) the systems do not exhibit strong charge transfer character in the fluorescing state. This is supported by weak dependence of the position of the fluorescence maximum on the solvent polarity function. Attachment of the amino derivative (compounds **III** and **IV**) causes a strong electron transfer character in the excited state as can be judged from the clear-cut solvent polarity shift of the fluorescence. However, in all cases strong solvent polarity dependence of fluorescence quantum yields and decay times is observed. It means that the non-radiative transitions in compounds **I** and **II** are accelerated by increasing solvent polarity but in **III** and **IV** the retardation of the non-radiative deactivation in polar solvents is observed.

These results also show a clear-cut solvent polarity dependence of the photoisomerisation quantum efficiency and non-radiative deactivation quantum yields of the excited singlet state on the solvent polarity. However, the character of these dependencies (increase or decrease) depends on the nature of the substituent. When the excited molecule possesses a charge transfer character then both above-mentioned quantities tend to decrease with increasing solvent polarity. When the molecule in the excited state does not exhibit a charge transfer character the opposite trend is observed. In the first case the stabilization of the excited *trans* configuration is greater than that of the perpendicular state, which makes the activation barrier greater in polar solvents. For the second class of the investigated compounds the opposite situation is true, which was confirmed experimentally by acceleration of the photoisomerisation process in polar solvents.

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