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Solvatochromism of 3-[2-(aryl)benzoxazol-5-yl]alanine derivatives

Katarzyna Guzow[a], Mariusz Szabelski[a], Jerzy Karolczak[b], Wiesław Wiczk[a,*]

[a] *Faculty of Chemistry, University of Gdańsk, Sobieskiego 18, Gdańsk 80-952, Poland*
[b] *Quantum Electronics Laboratory, Faculty of Physics, Adam Mickiewicz University, Umultowska 85, Poznań 61-614, Poland*

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Abstract

The photophysical properties of *N*-Boc-3-[2-(9-anthryl)benzoxazol-5-yl]-L-alanine methyl ester (BoxAnt) and *N*-Boc-3-[2-[4-(9′-(10′-butyl)anthryl)phenyl]benzoxazol-5-yl]-L-alanine methyl ester (BoxPhAnt) were studied in a series of solvents. Their absorption spectra are less sensitive to the solvent polarity than the corresponding fluorescence spectra which show a pronounced solvatochromic effect leading to large Stokes shifts. Using an efficient solvatochromic method, based on the empirical solvent polarity parameter E_T^N, a large change of the dipole moment on excitation for BoxPhAnt has been found. From an analysis of the solvatochromic behaviour of the absorption and fluorescence spectra in terms of bulk solvent polarity functions, $f(\varepsilon_r, n)$ and $g(n)$, a larger excited-state dipole moment (about 8 D, $\psi = 56$) was obtained for BoxPhAnt than for BoxAnt (about 3 D, $\psi = 0$). Both applied methods gave similar values of the excited-state dipole moments for both compounds studied.

Keywords: Solvatochromism; Fluorescence; Dipole moment; Benzoxazole; Amino acid

1. Introduction

The 2-phenylbenzoxazoles are known as photo-stable highly efficient UV dyes [1]. They are used as organic brightening agents [2], laser dyes [1], organic plastic scintillators [3] and optical fibre sensors [4]. An electron-donor substituent in a phenyl ring of 2-phenylbenzoxazole shifts the absorption and emission spectra to the longer wavelengths because of a charge transfer in the excited-state from a phenyl ring to the benzoxazole moiety [5]. Absorption and emission spectra of 2-phenylbenzoxazole and its derivatives with electron-donor substituents in para position of the phenyl ring possess well-resolved vibrational structure in non-polar solvents. This is a result of partially double C_1–C_1' bond which restricts rotation of two aromatic subunits of 2-phenylbenzoxazole [5]. Moreover, their absorption and emission spectra are affected by a solvent polarity [1].

The solvatochromic effect is frequently used in biophysical studies of the polarity of microenvironment of peptides, proteins and lipid bilayers using an intrinsic or extrinsic fluorescent probes [6,7]. Among the proteinogenic aromatic amino acids only tryptophan shows an evident solvatochromic effect [8,9]. To bypass the limitation connected with tryptophan, we synthesized non-proteinogenic aromatic amino acids based on the (benzoxazol-5-yl)alanine skeleton which are characterized by high fluorescence quantum yields [10–13]. In this paper, we present an influence of solvents on the photophysical properties of BoxAnt and BoxPhAnt (Fig. 1) as well as the application of solvatochromic methods

Abbreviations: BoxAnt, *N*-Boc-3-[2-(9-anthryl)benzoxazol-5-yl]-L-alanine methyl ester; BoxPhAnt, *N*-Boc-3-[2-[4-(9′-(10′-butyl)anthryl)phenyl]benzoxazol-5-yl]-L-alanine methyl ester; MeOH, methanol; EtOH, ethanol; 1-BuOH, 1-butanol; *i*-PrOH, 2-propanol; 1-PeOH, 1-pentanol; 1,2-Pr(OH)$_2$, propane-1,2-diol; TFE, 2,2,2-trifluoroethanol; *i*PrOH-6F, 1,1,1,3,3,3-hexafluoro-2-propanol; MeCN, acetonitrile; Cx, cyclohexane; Hex, *n*-hexane; MeCx, methylcyclohexane; *iso*-Oct, *iso*-octane; AcOEt, ethyl acetate; THF, tetrahydrofuran; DMF, *N*,*N*-dimethylformamide; DMSO, dimethylsulphoxide; PC, propylene carbonate; di-MeOEt, 1,2-dimethoxyethane

* Corresponding author. Tel.: +48 58 3450353; fax: +48 58 3450472.
E-mail address: ww@chem.univ.gda.pl (W. Wiczk).

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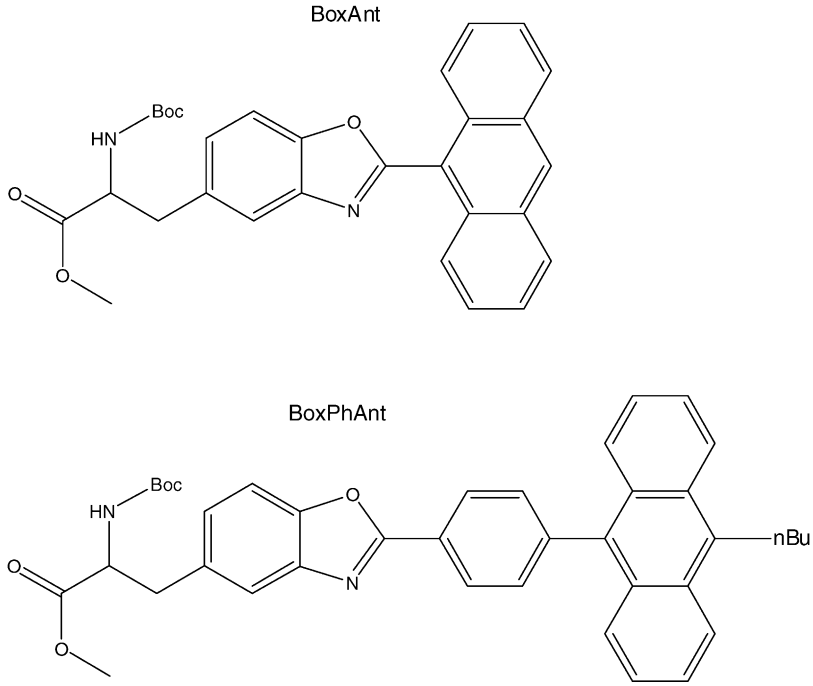

Fig. 1. Structures of compounds studied.

to determine excited-state dipole moments of the compounds studied.

2. Theory

It is commonly acknowledged that solvent-dependent spectral band shifts can arise from either general and/or specific solvent effects [14]. The first effect results from isotropic interactions of the chromophore dipole moment with the reaction field induced in the surrounding solvent. Specific effects result from the short-range anisotropic interactions between the chromophore with one or more solvent molecules in its first solvation shell such as hydrogen bonds. It is thus of interest to quantify the relative contributions from these two effects. As a result, many empirical solvent polarity parameters are used to correlate spectral or photophysical properties of a solute [15,16]. One of the most frequently used is Dimroth–Reichardt $E_T(30)$ [17] or E_T^N introduced by Reichardt [18]. These parameters are mostly used to correlate the absorption or emission transition energies, however, the fluorescence lifetimes as well as the Stokes shifts are also used in such correlations [19–24]. The correlation of the Stokes shift with the microscopic solvent polarity parameter E_T^N can be applied to calculate the dipole moment change between the excited- and ground-state (μ_e–μ_g) according to the equation proposed by Ravi et al. [23]:

$$\tilde{\nu}_a - \tilde{\nu}_f = 11307.6\left[\left(\frac{\Delta\mu}{\Delta\mu_B}\right)^2\left(\frac{a_B}{a}\right)^3\right] \times E_T^N + \text{const} \quad (1)$$

where $\tilde{\nu}_a$ and $\tilde{\nu}_f$ are the absorption and emission band shifts (in wavenumbers) in a solvent, $\Delta\mu_B$ and a_B are the dipole moment change and Onsager's cavity radius, respectively, for a pyridinium *N*-phenolate betaine dye ($\Delta\mu_B$ = 9 D and a_B = 6.2 Å [24]), whereas $\Delta\mu$ and a are the corresponding values for the molecule under study. This method minimizes the problem associated with the Onsager's radius estimation since a ratio of two Onsager's radii is involved. The excited-state dipole moment can also be calculated from an analysis of the absorption and emission band shifts in solvents of different relative permittivities ε_r and refractive indices n. According to Bilot and Kawski [25], Kawski [26] and Bakshiev [27], for a spherical molecule with the isotropic polarizability, the following equations hold:

$$\tilde{\nu}_a - \tilde{\nu}_f = m_1 f(\varepsilon_r, n) + \text{const} \quad (2)$$

$$\tilde{\nu}_a + \tilde{\nu}_f = -m_2[f(\varepsilon_r, n) + 2g(n)] + \text{const} \quad (3)$$

$$m_1 = \frac{2(\vec{\mu}_e - \vec{\mu}_g)^2}{hca^3} = \frac{2(\mu_e^2 + \mu_g^2 - 2\mu_e\mu_g \cos\,\psi)}{hca^3} \quad (4)$$

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3}, \quad (5)$$

where μ_e and μ_g are the dipole moments in the excited- and ground-state, respectively, h is Planck's constant, c the velocity of light in vacuum, $f(\varepsilon_r, n)$ and $g(n)$ are the solvent polarity functions given by Eqs. (6) and (7).

$$f(\varepsilon_r, n) = \frac{2n^2 - 1}{n^2 + 2}\left(\frac{\varepsilon_r - 1}{\varepsilon_r + 2} - \frac{n^2 - 1}{n^2 + 2}\right) \quad (6)$$

$$g(n) = \frac{3}{2}\frac{n^4 - 1}{(n^2 + 2)^2}. \quad (7)$$

Generally, the dipole moments μ_e and μ_g are not parallel to each other but make an angle ψ. The use of Eqs. (4) and (5) leads then to Eqs. (8) and (9) [26,28]:

$$\mu_e = \left(\mu_g{}^2 + \tfrac{1}{2}m_2 hca^3\right)^{1/2} \quad (8)$$

$$\cos\,\psi = \frac{1}{2\mu_e\mu_g}\left[(\mu_g^2 + \mu_e^2) - \frac{m_1}{m_2}(\mu_e^2 - \mu_g^2)\right]. \quad (9)$$

If the ground and excited-state dipole moments are parallel, based on Eqs. (4) and (5), the following equations are obtained:

$$\mu_g = \frac{m_2 - m_1}{2}\left(\frac{hca^3}{2m_1}\right)^{1/2} \quad (10)$$

$$\mu_e = \frac{m_2 + m_1}{2}\left(\frac{hca^3}{2m_1}\right)^{1/2} \quad (11)$$

or

$$\mu_e = \frac{m_1 + m_2}{m_2 - m_1}\mu_g \quad \text{for} \quad (m_2 > m_1). \quad (12)$$

From Eqs. (10) and (11) arise that for parallel orientated dipole moments in the ground and excited-state there is no need to estimate Onsager's cavity radius for the calculation of μ_e and μ_g as well as μ_e can be calculated directly from the spectroscopic measurements.

3. Experimental

The synthesis and purification of the compounds studied is described in [13]. The absorption spectra of BoxAnt and BoxPhAnt in all solvents studied (spectroscopic or HPLC grade) were measured with a Perkin-Elmer Lambda 40P spectrophotometer, whereas emission spectra were measured using a Perkin-Elmer LS 50B spectrofluorimeter. Fluorescence quantum yields (ϕ) were calculated with quinine sulphate in 0.5 M H_2SO_4 (ϕ = 0.53 ± 0.02) as reference and were corrected for different refractive indices of solvents [6]. In all fluorimetric measurements the optical density of solution does not exceed 0.1.

The fluorescence intensity decays were measured using a time correlated single-photon counting apparatus at Centre for Ultrafast Laser Spectroscopy, Adam Mickiewicz University (Pozná, Poland). The excitation source (λ_{ex} = 277 nm) was pico/femtosecond laser system (Ti: Sapphire "Tsunami" laser pumped with an argon ion laser "BeamLok" 2060 and equipped with cooled 3809U-05 MCP PMT). The half-width of the instrument response function was about 35 ps [29]. All fluorescence measurements were carried out with the emission polariser set at 54.7° with respect to the excitation polarisation. The channel width (δt) was set to 24.4 ps/ch in all measurements. The desired emission wavelength was selected using a monochromator ($\Delta\lambda$ = 4.8 nm). A Ludox solution was used to collect the instrument response. Fluorescence decays for the sample and reference were measured to 1×10^4 and 4×10^4 counts in the channel, respectively. The fluorescence decay data were fitted by the iterative convolution to the sum of exponents:

$$I(t) = \sum_i \alpha_i \exp\left(\frac{-t}{\tau_i}\right), \quad (13)$$

where α_i is the pre-exponential factor obtained from the fluorescence intensity decay analysis and τ_i is the decay time of the ith component, using a software supplied by Edinburgh Analytical Instruments. The adequacy of the exponential decay fitting was judged by visual inspection of the

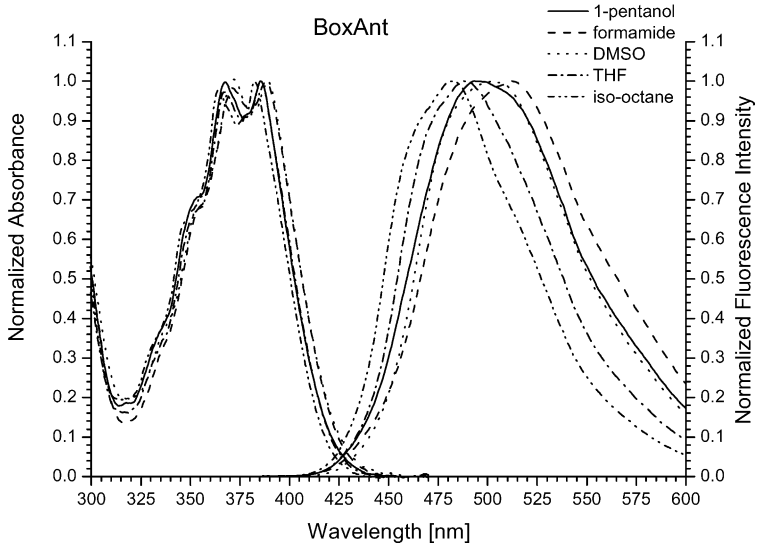

Fig. 2. Absorption and emission spectra of BoxAnt in different solvents.

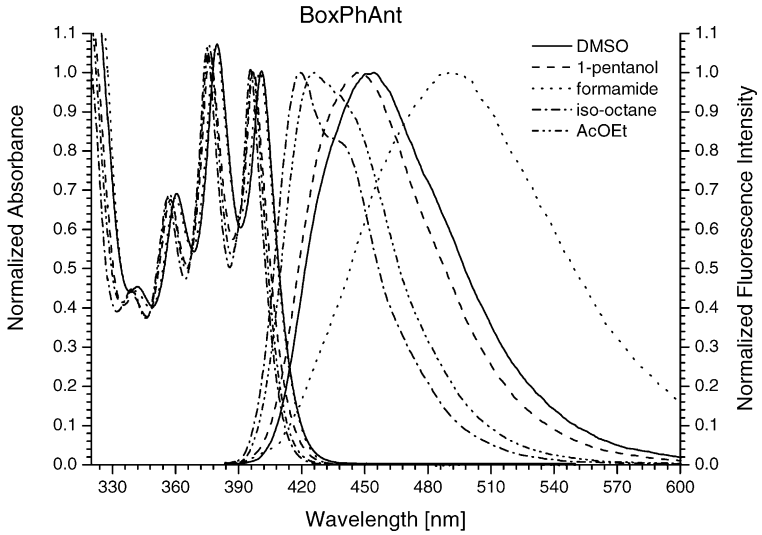

Fig. 3. Absorption and emission spectra of BoxPhAnt in different solvents.

Table 1
Photophysical properties of BoxAnt in all solvents studied

No.	Solvent	$\tilde{\nu}_a$ (cm−1)	$\tilde{\nu}_f$ (cm−1)	Quantum yield	Lifetime and pre-exponential factor			Quality of fit (χ^2_R)
					τ (ns)	$\langle\tau\rangle$[a] (ns)	α	
1	MeOH	26041.7	19685	0.223	3.93	–	1	1.18
2	EtOH	25990.9	20020	0.381	4.88	–	1	1.17
3	1-BuOH	25948.8	20222.4	0.404	5.56	–	1	1.05
4	*i*-PrOH	26007.8	20325.2	0.376	5.49	–	1	1.23
5	1-PeOH	25940.3	20263.4	0.4	5.49	–	1	1.23
6	$HCONH_2$	25740	19512.2	0.263	4.06	–	1	1.12
7	HCONHMe	25873.2	19900.5	0.371	5.77	–	1	1.14
8	1,2-Pr$(OH)_2$	25859.8	20161.3	0.308	4.90		1.000	22.43
					5.02		0.777	
					0.61	4.87	0.223	1.19
9	TFE	26143.8	19565.4	0.068	–	–	–	–
10	*i*PrOH-6F	25967.3	18873.1	0.011	–	–	–	–
11	Water	25906.7	19417.5	0.017	0.49		1.000	436
					0.36	1.2	0.971	1.13
					3.85		0.029	
12	Acetone	25987.5	20366.6	0.456	6	–	1	0.99
13	MeCN	25974	20345.9	0.407	5.97	–	1	1.09
14	C_6H_5CN	25706.9	20060.2	0.441	5.72		1.000	3.22
					6.03	5.78	0.826	
					1.72		0.174	1.11
15	CH_2Cl_2	25871.6	20366.6	0.608	6.36	–	1	0.99
16	$CHCl_3$	25841.5	20242.9	0.577	5.94	–	1	1.09
17	Cx	26075.6	20661.2	0.637	5.46	–	1	1
18	CCl_4	25881.6	20512.8	0.63	5.69	–	1	1.04
19	Hex	26133.5	20682.5	0.567	5.36	–	1	1.04
20	MeCx	26075.6	20661.2	0.589	5.14	–	1	1.08
21	*iso*-Oct	26143.8	20703.9	0.615	5.17	–	1	1.24
22	AcOEt	26007.8	20491.8	0.525	5.69	–	1	1.17
23	THF	25940.3	20491.8	0.526	5.79	–	1	1.18
24	DMF	25806.5	20181.6	0.447	6.19	–	1	0.99
25	DMSO	25706.9	19900.5	0.493	6.27	–	1	1.19
26	PC	25839.8	20202	0.463	6.57	–	1	1.24
27	1,4-dioxane	25873.2	20408.2	0.542	6.17	–	1	1.16

[a] $\langle\tau\rangle = \sum_i \frac{\alpha_i \tau_i^2}{\alpha_i \tau_i}$.

plots of weighted residuals, and the statistical parameter χ^2_R and shape of the autocorrelation function of the weighted residuals and serial variance ratio (SVR).

4. Results and discussion

Absorption and fluorescence spectra of BoxAnt and BoxPhAnt in representative solvents are presented in Figs. 2 and 3, respectively. The spectral and photophysical parameters (maxima of absorption and emission spectra in wavenumbers, fluorescence quantum yields (ϕ), fluorescence lifetimes (τ) and quality of fit parameter (χ^2_R)) in all solvents studied are presented in Table 1 for BoxPhAnt and Table 2 for BoxAnt. Absorption spectra of compounds studied show vibrational structure, even in polar solvents. Emission spectra do not show vibrational structure in any solvent used, except for saturated hydrocarbons in which diffuse vibrational structure can be seen, especially for BoxPhAnt (Figs. 2 and 3). An increase of solvent polarity causes a bathochromic shift of the absorption and fluorescence bands, however, the shift of emission band is substantially greater (Figs. 2 and 3, Tables 1 and 2). The energies of absorption ($\tilde{\nu}_a$) and ($\tilde{\nu}_f$) emission transitions of BoxAnt and BoxPhAnt were correlated with the E_T^N solvent polarity parameter. These correlations revealed that both, non-specific and specific, interactions contribute to the solvation process of both compounds studied. According to obtained correlations, ($\tilde{\nu}_a$) is almost independent on E_T^N:

for BoxAnt: $\tilde{\nu}_a = 25970(\pm40) - 70(\pm80) \times E_T^N$, ($r = 0.1750$, Np = 27)
for BoxPhAnt: $\tilde{\nu}_a = 25020(\pm50) + 244(\pm94) \times E_T^N$ ($r = 0.5040$, Np = 21).

In the case of ($\tilde{\nu}_f$), the following linear correlations with E_T^N (Figs. 4 and 5) for aprotic solvents were obtained:

for BoxAnt: $\tilde{\nu}_f = 25650(\pm50) - 1140(\pm190) \times E_T^N$ ($r = 0.8480$, Np = 16),
for BoxPhAnt: $\tilde{\nu}_f = 23890(\pm1300) - 3890(\pm460) \times E_T^N$ ($r = 0.9316$, Np = 13).

Also for protic solvents, ($\tilde{\nu}_f$) correlates linearly with E_T^N:

for BoxAnt: $\tilde{\nu}_f = 21630(\pm250) - 2410(\pm320) \times E_T^N$ ($r = 0.9248$, Np = 11),
for BoxPhAnt: $\tilde{\nu}_f = 22750(\pm490) - 970(\pm670) \times E_T^N$ ($r = 0.5343$, Np = 8).

A double linear correlation in the case of fluorescence indicates that the nature of the emitting state is considerably different in these two classes of solvents.

The change of the solvent polarity influences, not only energies of absorption and emission transition, but also the

Table 2
Photophysical properties of BoxPhAnt in all solvents studied

No.	Solvent	$\tilde{\nu}_a$ (cm^{-1})	$\tilde{\nu}_f$ (cm^{-1})	Quantum yield	Lifetime and pre-exponential factor			Quality of fit χ^2_R
					τ (ns)	$\langle\tau\rangle$ (ns)	α	
1	MeOH	25274.9	21575	0.265	2.11	–	1	1.13
2	HCONHMe	25064.5	21786.5	0.38	2.25	–	1	1.26
3	1-BuOH	21184.5	22296.5	0.5	2.22		1.000	1.42
					2.26	2.2	0.858	1.08
					0.45		0.142	
4	*i*-PrOH	25244.2	22396.4	0.497	2.1	–	1	1.19
5	1-PeOH	25154.1	22421.5	0.531	2.25		1.000	1.29
					2.28	2.23	0.874	1.05
					0.45		0.126	
6	$HCONH_2$	24975.7	20345.9	0.287	2.52	–	1	1.08
7	1,2-$Pr(OH)_2$	25094.7	21953.9	0.529	2.12		1.000	74.3
					2.26	2.06	0.595	
					0.45		0.405	0.98
8	*i*PrOH-6F	25518.7	22002.2	0.015	–	–	–	–
9	MeCN	25184.5	22371.4	0.401	2.19	–	1	1.16
10	C_6H_5CN	24919.2	22123.9	0.413	2.39		1.000	11.8
					2.96	2.43	0.457	
					1.59		0.543	1.23
11	$CHCl_3$	25184.5	22753.1	0.623	2.35	–	1	1.04
12	Cx	24975.7	23781.2	0.654	2.76	–	1	1.08
13	MeCx	25035.1	23781.2	0.646	2.7	–	1	1.08
14	*iso*-Oct	25094.7	23866.3	0.576	2.58	–	1	1.17
15	AcOEt	24887.4	23474.2	0.571	2.52	–	1	1.09
16	THF	25094.7	23364.5	0.591	2.53	–	1	1.12
17	DMF	25124.4	22246.9	0.544	2.29	–	1	1.01
18	DMSO	25244.2	22002.2	0.536	2.21	–	1	1.2
19	PC	25005.6	22173	0.464	2.29	–	1	1.23
20	1,4-dioxane	25184.5	23557.2	0.576	2.83	–	1	1.18
21	di-MeOEt	25154.1	22831.1	0.505	2.11	–	1	1.17

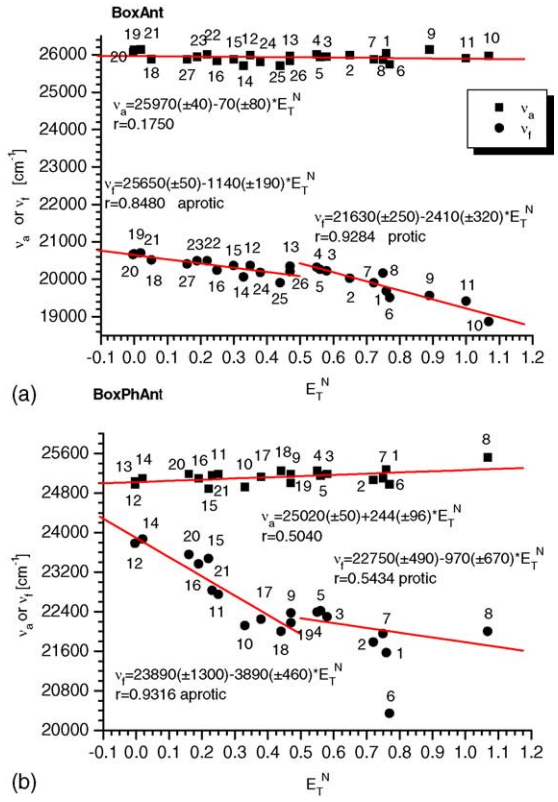

Fig. 4. Plot of ($\tilde{\nu}_a$) and ($\tilde{\nu}_f$) vs. the solvent polarity parameter E_T^N: (a) for BoxAnt and (b) for BoxPhAnt.

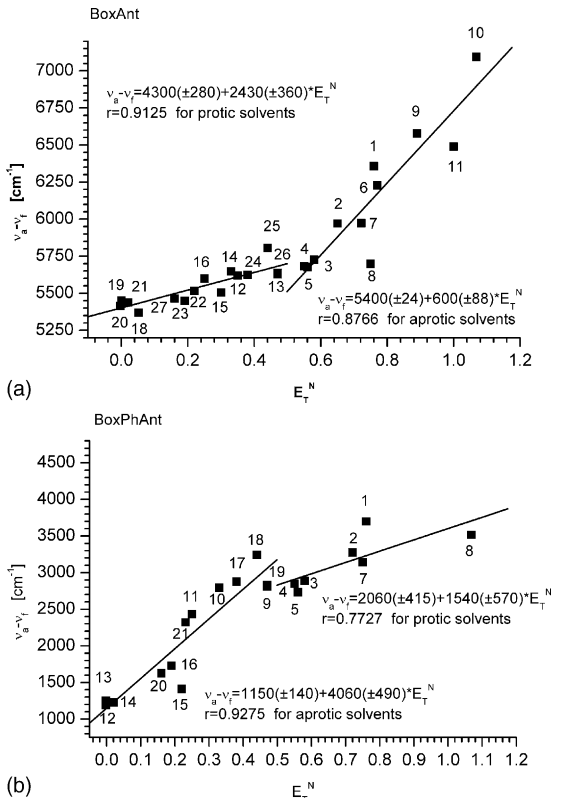

Fig. 5. Plot of the Stokes shift vs. the solvent polarity parameter E_T^N: (a) for BoxAnt and (b) for BoxPhAnt.

fluorescence quantum yield as well as the fluorescence lifetime (Tables 1 and 2). As in the case of fluorescence transition energy, similar correlations with E_T^N were obtained for fluorescence quantum yields and fluorescence lifetimes (Figs. 6 and 7). Both compounds, BoxAnt and BoxPhAnt, have high fluorescence quantum yields in all solvents studied, except for fluorinated alcohols and water (BoxAnt). The fluorescence intensity decays of BoxAnt and BoxPhAnt in aprotic solvents are mono-exponential, except for benzonitrile in which some specific interactions, probably the charge-transfer between the solute and the solvent, take place. For protic solvents, the fluorescence intensity decays are more diversified. For BoxAnt, the bi-exponential fluorescence intensity decay is observed in propane-1,2-diol and water, whereas for BoxPhAnt additionally in 1-butanol and 1-pentanol. The fluorescence lifetimes of BoxAnt are generally two-times longer as compared with those of BoxPhAnt (Tables 1 and 2).

According to Eq. (1), the linear correlation of the Stokes shift with the empirical solvent polarity parameter E_T^N allows to calculate the excited-state dipole moment when the Onsager's cavity radius and the ground-state dipole moment are known. The following correlations of ($\tilde{\nu}_a - \tilde{\nu}_f$) with E_T^N for both compounds studied were obtained (Fig. 5):

aprotic solvents:

for BoxAnt: $\tilde{\nu}_a - \tilde{\nu}_f = 5400(\pm24) + 600(\pm88) \times E_T^N$ (r = 0.8766, Np = 16),

for BoxPhAnt: $\tilde{\nu}_a - \tilde{\nu}_f = 1150(\pm150) + 4070(\pm490) \times E_T^N$ (r = 0.9319, Np = 13),

protic solvents:

for BoxAnt: $\tilde{\nu}_a - \tilde{\nu}_f = 4300(\pm280) + 2430(\pm360) \times E_T^N$ (r = 0.9125, Np = 11),
for BoxPhAnt: $\tilde{\nu}_a - \tilde{\nu}_f = 2060(\pm415) + 1540(\pm570) \times E_T^N$ (r = 0.7727, Np = 8).

Using values of Onsager's cavity radius and ground-state dipole moment for BoxAnt (μ_g = 1.6 D and a = 4.5 Å [13]) and BoxPhAnt (μ_g = 2.1 D and a = 6.5 Å [13]) and appropriate data for betaine ($\Delta\mu$ = 9 D, a = 6.2 Å [24]), the following changes of dipole moment in the excited-state were obtained: $\Delta\mu$ = 1.3 D (μ_e = 2.9 D) for BoxAnt and $\Delta\mu$ = 5.8 D (μ_e = 7.9 D) for BoxPhAnt in aprotic solvents.

Figs. 8 and 9 show the solvatochromic spectral shifts of BoxAnt and BoxPhAnt versus the solvents polarity functions $f(\varepsilon_r, n)$ and $f(\varepsilon_r, n) + 2g(n)$, respectively. The slopes obtained from the fitted lines presented in Figs. 8 and 9 for aprotic solvents were found to be m_1 = 240 ± 40 (r = 0.8584), m_2 = 830 ± 140 (r = 0.8457) for BoxAnt and m_1 = 1540 ± 190 (r = 0.9140), m_2 = 1840 ± 240 (r = 0.9139) for BoxPhAnt, respectively. Using Eq. (8) and theoretically calculated ground-state dipole moment and Onsager's cavity radius, the excited-state dipole moment for BoxAnt was determined to be μ_e = 3.1 D and μ_e = 7.4 D for BoxPhAnt. Applying Eq. (9), the angle

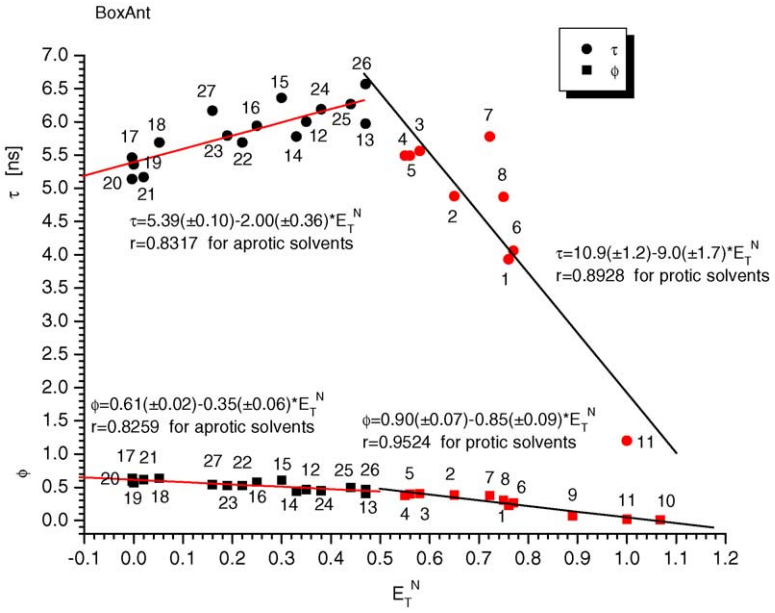

Fig. 6. Plot of the fluorescence quantum yield (ϕ) and fluorescence lifetime (τ) vs. the solvent polarity parameter E_T^N for BoxAnt.

between ground and excited-state dipole moments can be calculated. For BoxAnt its value is equal to $\psi \approx 0^\circ$ ($\cos\psi$ = 1.04), whereas for BoxPhAnt $\psi \approx 56^\circ$ ($\cos\psi$ = 0.548). In the case when the ground- and excited-state dipole moments are parallel, Eq. (10) allows to calculate the ground-state dipole moment from the spectroscopic data only. For BoxAnt, calculated from this equation, μ_g is equal to 1.8 D, which is in good agreement with the theoretically calculated value [13]. Thus, the excited-state dipole moments values obtained using two different methods are in good agreement. A method proposed by Ravi et al. [23] does not allow calculating the angle between dipole moment in the ground and excited-state, however, gives a correct value of μ_e regardless of their mutual orientation. A large dependence of the emission band on solvent polarity indicates that the excited-state for both compounds is a state with the internal charge-transfer (ICT). Moreover, the phenyl linker, increasing a distance between benzoxazolyl-acceptor unit and aromatic-donor unit, causes a substantial increase of the excited-state dipole moment of BoxPhAnt. The values of excited-state dipole moments obtained from an analysis of the solvatochromic effect are not in agreement with those calculated theoretically using a semiempirical PM3 method using a SCRF approximation with Onsager solvation model [13]. Such

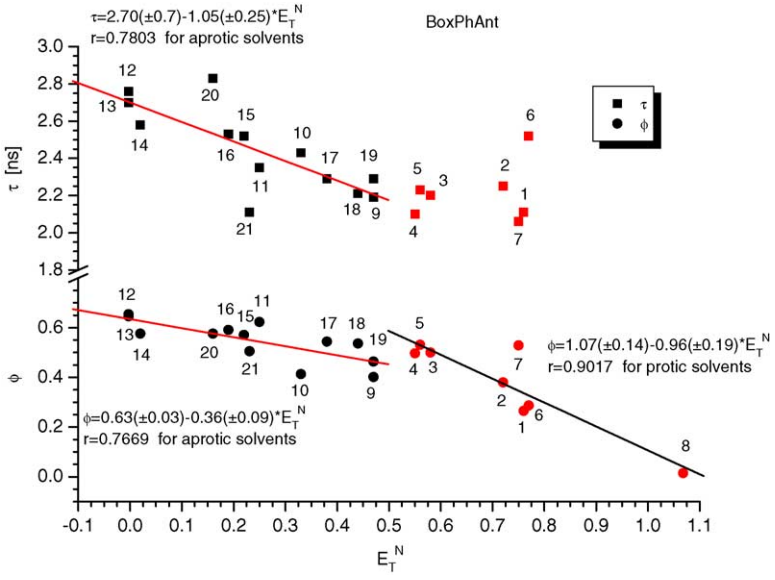

Fig. 7. Plot of the fluorescence quantum yield (ϕ) and fluorescence lifetime (τ) vs. the solvent polarity parameter E_T^N for BoxPhAnt.

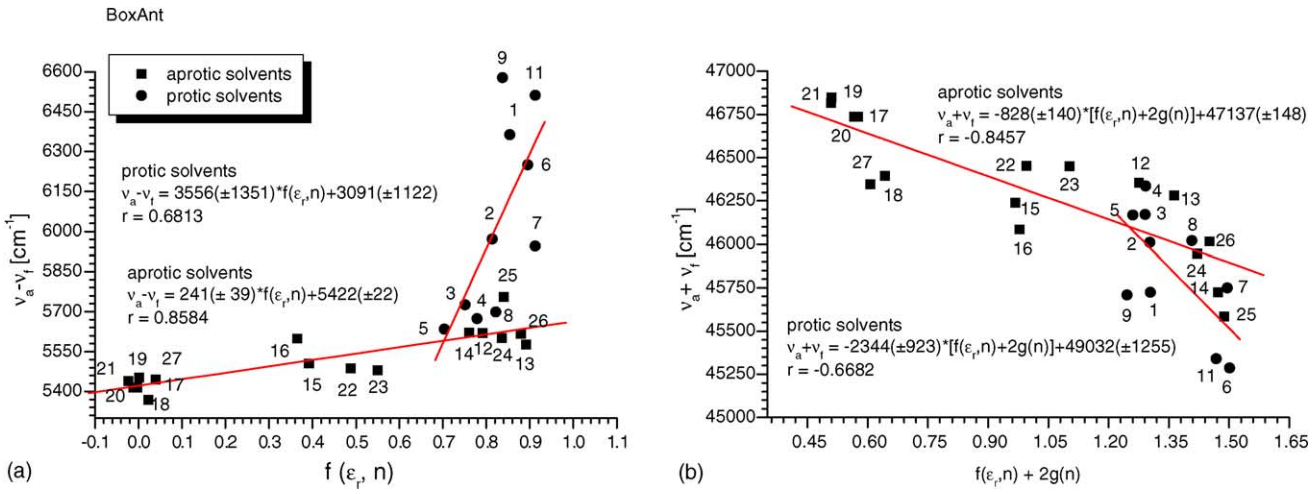

Fig. 8. Plot of (a) the Stokes shift vs. $f(\varepsilon_r, n)$ and (b) $\tilde{\nu}_a + \tilde{\nu}_f$ vs. $f(\varepsilon_r, n) + 2g(n)$ for BoxAnt.

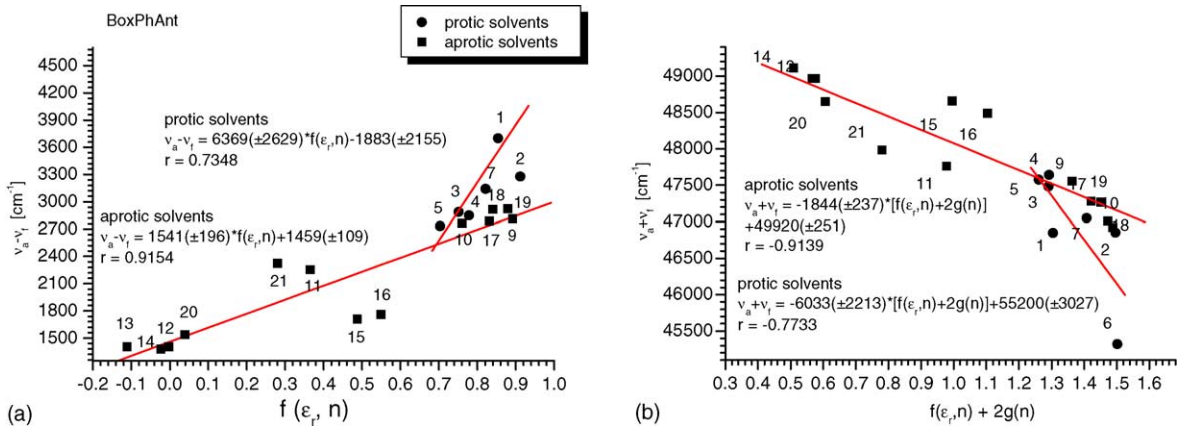

Fig. 9. Plot of (a) the Stokes shift vs. $f(\varepsilon_r, n)$ and (b) $\tilde{\nu}_a + \tilde{\nu}_f$ vs. $f(\varepsilon_r, n) + 2g(n)$ for BoxPhAnt.

difference indicates that the semi-empirical methods should be used with caution for the calculations of the excited-state properties of compounds consisting of two-electron subunits separated by one single bond.

5. Conclusion

A simple correlation of the Stokes shift with an empirical solvent polarity parameter E_T^N is useful in the calculation of the excited-state dipole moment regardless of its mutual orientation to the ground-state one.

Benzoxazol-5-yl-alanine derivatives substituted in position 2 by 4-(9-anthryl)phenyl is characterized by a large change of the dipole moment on excitation as well as high fluorescence quantum yield and solvent-dependent fluorescence lifetime. Because of that it seems to be a useful fluorescent probe. Moreover, the presence of amino acid moiety allows incorporating it into a peptide/protein chain. Thus, it could be used in the studies of microenvironment polarity of biologically active compounds.

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