Steric Effects in the Electronic Spectra of the 3,5-Diarylaminobenzene Derivatives

A. Balter, W. Nowak, P. Milart*, and J. Sepioł*
Institute of Physics, N. Copernicus University, Grudziądzka 5, 87-100 Toruń, Poland

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Absorption and fluorescence properties, excited state lifetimes and fluorescence quantum yields were determined for a series of 3,5-diarylaminobenzene derivatives in solvents of different polarities. The role of the nitrile, methyl, phenyl and naphthyl substituents is discussed. Especially the steric effects on the spectroscopic behaviour of the investigated molecules are studied.

1. Introduction

Electronic spectral properties of polyphenyls, in particular terphenyls, have been a subject of numerous studies [1 – 5]. In 1985 a new and efficient method of the synthesis of 3,5-diarylaminobenzenes and their derivatives was developed by Sepioł and Milart [6]. Some fluorescent compounds belonging to this group, presented in Fig. 1, were chosen as a model set for the investigation of several important photophysical problems:

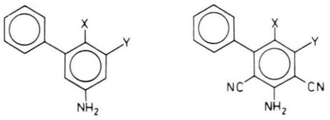
1. What are the conformations of the side aryls in the ground and excited states and how are they influenced by the presence of the methyl group in the X position (see Figure 1)?
2. What is the influence of the nitrile groups on the spectral properties of 3,5-diarylaminobenzenes?
3. What is the role of the size (naphthyl vs. phenyl) and the mode of binding (α-naphthyl vs. β-naphthyl) of the side aryl substituents?
4. How does the electronic excitation influence the charge distribution in such compounds?

In order to answer these questions, absorption and fluorescence properties, fluorescence lifetimes and quantum yields of the compounds shown in Fig. 1 were studied in three solvents of different polarity (cyclohexane, methanol and acetonitrile) at concentrations of $5 \cdot 10^{-5}$ M. Some of the absorption spectra were already reported [6 – 8].

A possible application of the investigated 3,5-diarylaminobenzene solutions as laser media was checked.

2. Experimental

3,5-diarylaminobenzenes were prepared in the Institute of Chemistry, Jagiellonian University, Cracow and their synthesis was described in [6, 9]. The spectroscopic grade solvents were non-fluorescent and transparent in the range of the excitation wavelengths used (313 nm to 366 nm). The samples were saturated with air and measured at 293 K. Absorption spectra were recorded using a Specord UV-VIS (Carls Zeiss, Jena, GDR) spectrophotometer. A home-built photon-counting spectrofluorimeter, equipped with a 200 W mercury high pressure lamp and two SPM-2 double prism mono-



An Bn

n	X	Y
1	H	phenyl
2	CH$_3$	phenyl
3	H	α-naphthyl
4	H	β-naphthyl

Fig. 1. Structural formulas of the investigated 3,5-diarylaminobenzenes and their derivatives:
A 1: 5′-amino-1,1′:3′,1″-terphenyl,
A 2: 5′-amino-2′-methyl-1,1′:3′,1″-terphenyl,
A 3: 3-amino-5-(1-naphthyl)biphenyl,
A 4: 3-amino-5-(2-naphthyl)biphenyl,
B 1: 5′-amino-1,1′:3′,1″-terphenyl-4′,6′-dicarbonitrile,
B 2: 5′-amino-2′-methyl-1,1′:3′,1″-terphenyl-4′,6′-dicarbonitrile,
B 3: 3-amino-5-(1-naphthyl)biphenyl-2,4-dicarbonitrile,
B 4: 3-amino-5-(2-naphthyl)biphenyl-2,4-dicarbonitrile.

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* Institute of Chemistry, Jagiellonian University, Cracow, Poland.

Reprint requests to Dr. A. Balter, Institute of Physics, N. Copernicus University, Grudziądzka 5, 87-100 Toruń, Poland.

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Table 1. Positions of the first absorption and fluorescence bands, their half-widths, Stokes shifts ($\Delta\tilde{\nu}_{af}$), all in 1000 cm^{-1}, lifetimes (c_F) and quantum yields φ_F of the investigated 3,5-diarylaminobenzenes in cyclohexane (c), methanol (m) and acetonitrile (a), * shoulder.

Compound			A1	A2	A3	A4	B1	B2	B3	B4
absorption	$\tilde{\nu}^a_{max}$	c	31.6	32.6	31.8	31.8	27.80	28.2	27.8	27.8
		m	31.3	32.6	~31.3*	~31.3*	27.4	27.4	27.4	27.4
		a	30.8	32.0	30.8	30.8	27.5	27.8	27.5	27.5
	$\Delta\tilde{\nu}^a_{1/2}$	c	3.5	3.4	–	–	2.9	2.9	3.2	3.3
		m	3.5	3.5	–	–	3.2	3.1	3.5	3.4
		a	3.7	3.6	–	–	3.2	3.1	3.4	3.4
fluorescence	$\tilde{\nu}^f_{max}$	c	26.8	26.5	26.3	26.3	25.0	25.3	24.7	24.7
		m	24.7	24.3	22.5	22.7	23.1	23.7	22.7	22.7
		a	25.0	24.7	23.1	23.1	23.7	24.2	23.1	23.1
	$\Delta\tilde{\nu}^f_{1/2}$	c	3.0	4.8	3.2	3.2	2.9	3.1	2.8	2.8
		m	3.2	4.7	4.5	4.4	3.1	2.8	3.1	3.1
		a	3.2	4.6	4.1	4.1	3.1	2.9	2.9	2.9
$\Delta\tilde{\nu}_{af}$		c	5.0	6.1	5.5	5.6	2.8	2.9	3.1	3.1
		m	6.6	8.3	8.8	8.6	4.3	3.7	4.7	4.7
		a	5.8	7.3	7.7	7.7	3.9	3.6	4.4	4.4
τ_F (ns)		c	5.5	2.3		4.6	3.6	0.7		3.3
		m	4.4	3.5		6.3	2.8	1.0	3.3	3.4
		a	4.4	3.3		5.9	2.6	0.7		3.4
φ_F		c	0.44	0.10		0.35	0.17	0.03		0.26
		m	0.15	0.12	0.27	0.52	0.23	0.07	0.25	0.33
		a	0.17	0.10		0.33	0.24	0.06		0.26

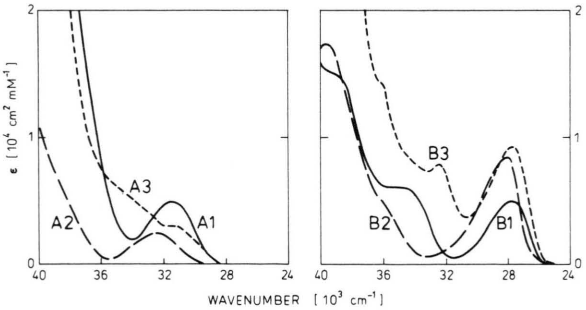

Fig. 2. Absorption spectra of the **A 1**, **A 2**, **A 3** and **B 1**, **B 2**, **B 3** compounds in cyclohexane (ε = the molar decadic absorption coefficient).

chromators (C. Zeiss, Jena) for the selection of the excitation and emission wavelengths was used to measure the corrected fluorescence spectra and quantum yields.

Excited state lifetimes were measured using a home-built phase fluorometer with an accuracy of ± 0.1 ns [10]. The accuracy of the quantum yield determination relative to a quinine standard was about ± 0.1 [11].

3. Results and Discussion

The wavenumbers of the absorption and fluorescence maxima, spectral half-widths (FWHM), Stokes shifts, lifetimes and quantum yields are presented in Table 1.

3.1. Conformations of the side phenyl rings and steric effects

The substitution of hydrogen by a methyl group at the central phenyl ring in the X position is accompanied by the following spectral effects. The first absorption bands of the compounds **A 2** and **B 2** exhibit a hypsochromic shift compared with **A 1** and **B 1**, respectively, in all solvents (Figure 2). Usually, the substitution of benzene with the methyl group causes a bathochromic shift of the absorption spectrum [3]. The hypsochromic shift observed in our case can be explained by steric hindrance leading to a reduced conjugation of the amino group with the aromatic system [7]. This reduction is connected with a lowering of the conjugation of the side phenyl rings, which adopt a more twisted conformation. Thus the polar resonance effect of the phenyl groups in the meta positions on the nitrogen lone electron pair is eliminated.

The shapes of the first absorption bands indicate some charge transfer character of the $S_0 \rightarrow S_1$ transitions. The amino group acts as an electron donor, while the central ring and, to some extent, also the side rings accept the electronic charge as a result of the excitation.

The fluorescence quantum yields and lifetimes of the methylated compounds are significantly lower than those of their parent compounds. Presumably the excited-state energy surface along the side phenyls twisting angle coordinates is steeper for methylated compounds, which allows for a more efficient radiationless deactivation in this case.

It is interesting to note that the fluorescence maxima of the **A** compounds shift toward red on methylation, while the **B** compounds exhibit a blue shift in this case (Figure 3).

The most striking effect is the increase of the FWHM of the **A 2** fluorescence band compared with **A 1** (cf. Figure 3). The absence of this broadening in the **B** compounds will be discussed later.

As one can seen, the **A 1**, **A 2**, **B 1** and **B 2** compounds may be treated as derivatives of meta-terphenyl (m-TP). The main structural problem in this group of compounds is the conformation of the terminal phenyls in the ground and excited states.

An extensive discussion of existing experimental data and CS INDO calculations by Baraldi et al. [12] result in the conclusion that in the gas phase m-TP has two conformers (of D_{2h} or C_2 symmetry). The torsional angles along the inter-annular bond are ± 35°. It is well established that in solvents such molecules are usually flatter [13].

Since, in our opinion, amino and nitrile substituents have no significant influence on the twisting of the terminal aryls, the value of 20° for these torsional angles in solutions of **A 1**, **A 3**, **A 4**, **B 1**, **B 3** and **B 4** seems to be a reasonable estimation [14].

A different situation arises for the **A 2** and **B 2**, where the methyl group in the ortho position to the phenyl substituents introduces a substantial steric hindrance already noticed in the NMR spectra of these compounds [6]. Therefore, the twisting angle should be larger than the mentioned angle of 20°. On the other hand, since the interaction of the CH_3 group with the side phenyl rings is not so strong as the phenyl-phenyl interaction in o-TP, the ground-state twisting angle is probably lower than about 55° estimated for o-TP by Baraldi et al. [12].

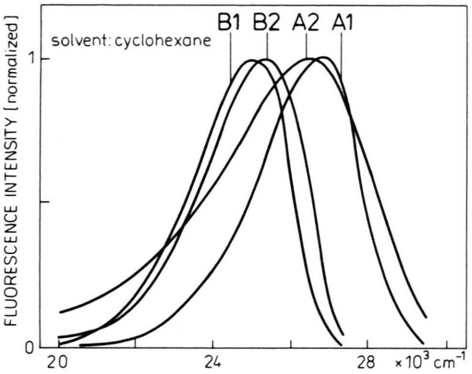

Fig. 3. Fluorescence spectra of the **A 1**, **A 2**, **B 1** and **B 2** compounds.

Studies of the phosphorescence spectra of m-TP in propylene glycol indicate a substantial change of geometry after excitation [15]. Fujii et al. [15] assumed that m-TP in its S_1 state is nearly flat. This assumption fits quite well with our spectral data; so we are convinced that our derivatives of m-TP become flatter in their excited states, too. This flattening is sterically hindered in the case of **A 2** and **B 2**.

The broadening of the **A 2** fluorescence spetra with respect to **A 1** (cf. Fig. 3) may be interpreted as a result of the presence of many rotational isomers of different energies in the S_1 excited state. The absence of this broadening for the nitrile compounds (**B 2** vs. **B 1**) is caused by the evident localization of the first electronic transition which reduces the influence of the side aryl conformation.

3.2. *Role of the Nitrile Groups*

This localization, connected with the strong electron withdrawing character of the CN groups, manifests itself also in other spectral properties. The first absorption band, which is of the charge transfer character, exhibits a bathochromic shift (ca. 3000 cm^{-1}) for all the **B** compounds (in all the three solvents). The FWHM slightly decreases, while the oscillator strength increases twofold as a result of the CN groups attachment. The fluorescence spectra of the **B** compounds are also red-shifted (ca. 1000 cm^{-1}). As a result the Stokes shift is significantly reduced. The FWHM of the fluorescence bands, the lifetimes and the quantum yields are smaller for the **B** compounds. It is interesting to note, that this effect is especially pronounced for derivatives with the methyl group in the X position (cf. **A 2** and **B 2** in Figure 3).

In general, the presence of the nitrile groups diminishes spectral effects caused by changes of substituents in the X and Y positions.

Since for all the **A** compounds the values of the Stokes shift are twice those of the **B** compounds, one may infer a larger dipole moment and/or a substantial intramolecular structural relaxation in their excited states. The change of the dipole moment after the excitation, estimated from the spectral solvent shifts [16], is similar for all compounds, being the largest for **A 3** and **A 4**. This correlates with the dimensions of these two derivatives.

3.3. Effects Caused by the Naphthyl Substituents

The absorption and emission spectra of the α- and β-naphthyl compounds do not exhibit any differences due to the mode of binding (α vs. β). On the other hand, the size of the aryl substituent has a very profound effect. While the position of the first absorption band remains almost unchanged, the second absorption band is strongly red-shifted in the naphthyl compounds (Figure 2). This red-shift, caused by the increase of the substituent π-electron system, suggests that side aryls are strongly involved in the second $\pi^* \leftarrow \pi$ transition, while the first transition is localized primarily on the central ring. The fluorescence spectra of the naphthyl derivatives in polar solvents exhibit a blue-shift compared with those of the phenyl compounds. In contrast to the **B** compounds, the **A** derivatives exhibit an about $1100\ \mathrm{cm}^{-1}$ increase of the FWHM.

4. Conclusions

The investigated 3,5-diarylaminobenzenes exhibit large differences in spectral properties between compounds with and without the methyl substituent caused by the steric hindrance preventing the flattening of the side aryls in the excited states.

The nitrile groups reduce the ground state dipole moments and localize the first transition in the region of the central ring, thus weakening the spectral effects induced by the changes of substituents in the X and Y positions.

The naphthyl derivatives have qualitatively similar properties as the phenyl ones, although their absorption spectra are different and their dipole moments are larger.

We did not find any significant differences between the α- and β-naphthyl derivatives. Our search for laser action in solutions of the investigated compounds excited by a pulsed nitrogen laser gave negative results.

We are planning to investigate the rotational diffusion of these compounds in the excited states in order to find a possible correlation with their conformation.

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