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The synthesis and fluorescence of *N*-substituted 1- and 2-aminopyrenes

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Abstract

N-Acetyl and *N*-triazinyl 1- and 2-aminopyrenes were prepared and their absorption and fluorescence spectra as well as fluorescence quantum yield (q_{Fl}) in different solvents were measured. The dependence of fluorescence quantum yield on both structure and solvent polarity is discussed. The photophysical properties of 1- and 2-aminopyrenes and their *N*-derivatives are compared.

Keywords: 1-Aminopyrene and 2-aminopyrene *N*-derivatives; Synthesis; Absorption and fluorescence spectra; Fluorescence quantum yield; Influence of the structure and solvent

1. Introduction

Molecular structure control of intramolecular electronic energy transfer has been an area of recent interest, inspired by biology and optoelectronics, e.g. [1]. In earlier papers we presented the spectral and photophysical properties of a bichromophoric compound containing 1-aminopyrene as a donor, 3-aminobenzanthrone as an acceptor and 1,3,5-triazine as a spacer [2,3]. A better understanding of unexpected features of electronic energy transfer in this system needs investigation of the potential role of photophysics of aminobenzathrone and aminopyrene chromophores in such a system. In a previous paper [4], we reported on the synthesis, absorption and fluorescence spectra of *N*-(1,3,5-triazine-2-yl)-3-aminobenzanthrone derivatives. More recently, we have reported on a solvent dependence of absorption and fluorescence spectra, fluorescence lifetimes and fluorescence quantum yields of various 3-substituted benzanthrone derivatives [5]. The experimental data together with the results of semi-empirical quantum chemical calculations indicate that the main channel of the fluorescent $S_1(\pi,\pi^*)$ excited state of studied compounds is an intersystem crossing to an upper (n,π^*) triplet state. Previously, we reported on the spectroscopic behaviour of several *N*-derivatives of 1-aminopyrene [6,7].

Direct nitration of pyrene leads almost exclusively to 1-nitropyrene [10]. Depending on the reaction conditions, 1,6- and 1,8-dinitro derivatives were prepared [11]. Graebe [12] and Goldschmiedt [13] carried out the nitration in boiling diluted nitric acid; Vollmann et al. [14] in 65% nitric acid in acetic acid at 50 °C. When the nitration proceeds in heterogeneous phase, its course strongly depends on pyrene particle size [15].

1-Aminopyrene can be prepared by reduction of 1-nitropyrene with various reduction agents: Sn in HCl [13], 10–40% solution of NaHS in boiling ethanol [14,15], NH_2–$NH_2 \cdot H_2O$ in ethanol [16]. Hydrogenation of 1-nitropyrene with PtO_2 catalyst has been described [17,18]. A mixture of 1- and 2-aminopyrenes is produced by a reaction of 1-bromopyrene with potassium amide in liquid ammonia [19].

The synthesis of 2-aminopyrene is more complicated. Vollmann et al. [13,14] developed a synthesis from 2-nitropyrene carboxylic acid. 2-Aminopyrene can be synthesized from 2-nitropyrene according to Scheme 2. 4,5,9,10-Tetrahydropyrene (THPy) was prepared by catalytic hydrogenation of pyrene

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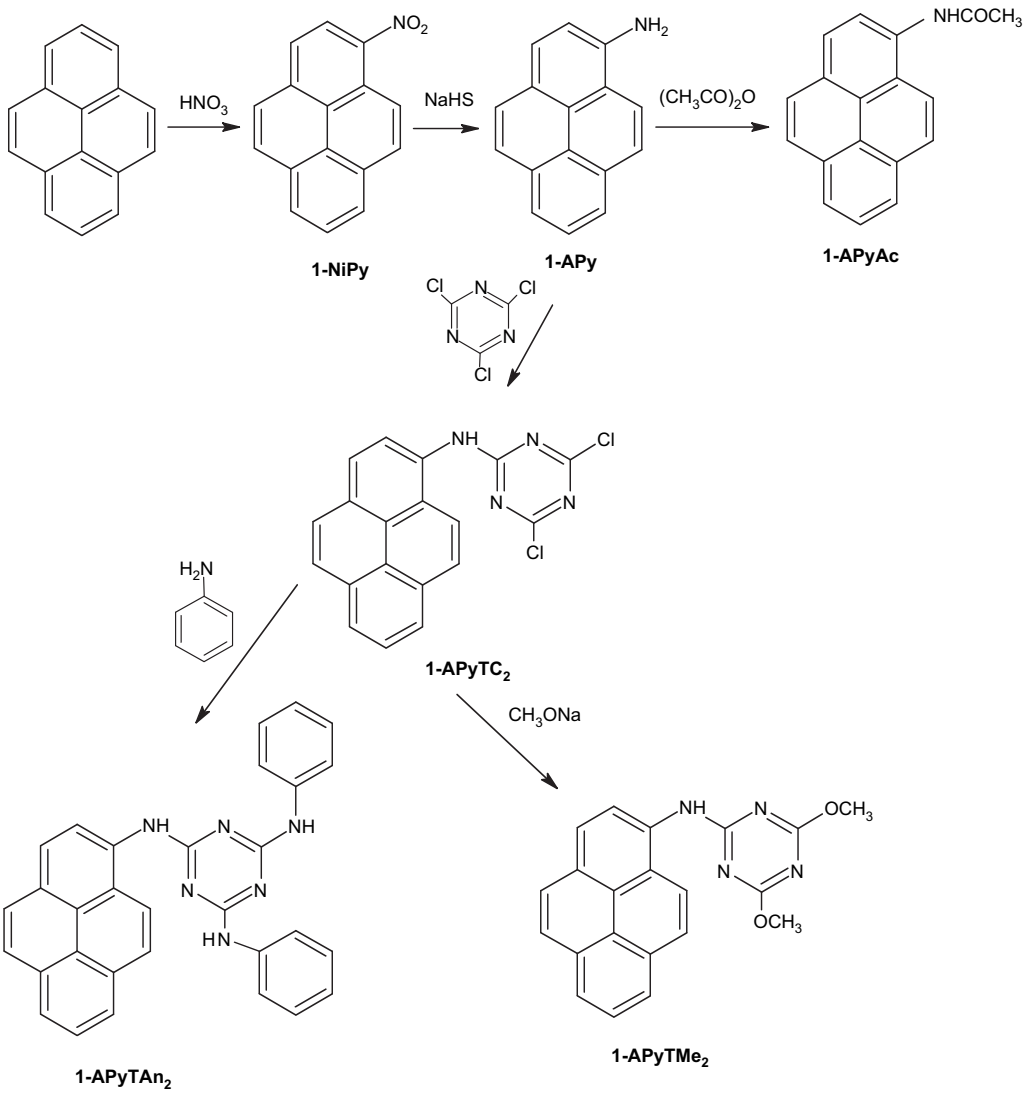


Scheme 1. Synthesis of 1-aminopyrene and its derivatives.

with various catalysts: MoS/C [19], Pd/C [20–22], Raney nickel [23,24], tetrapropyldiborane [25]. 2-Nitro-THPy was synthesized by the nitration of THPy with nitric acid in acetic anhydride [26] or by the reaction of THPy with copper(II) nitrate in acetic anhydride at room temperature for 7 h with the yield of 90% [27].

Dehydrogenation of 2-nitro-THPy to 2-nitropyrene was carried out with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in nitrobenzene [27] or in benzene [28], or with iodine in boiling nitrobenzene [26]. Reduction of 2-nitropyrene to 2-aminopyrene with hydrazine hydrate and with Pd/C catalyst in benzene or in ethanol was described by Bolton [26].

This work presents the synthesis and the spectral and photophysical characteristics of 1- and 2-aminopyrene *N*-derivatives. The relationships between structure, properties of compounds and solvent polarity are discussed. While substitution in 1- and 4-positions causes large changes of character of pyrene electronic states, their character remains almost unchanged in the case of 2-pyrene derivatives [8,9]. Therefore, a comparison of photophysical properties of 1- and 2-aminopyrene derivatives could be interesting and also useful from the point of view of study of excitation energy transfer in bichromophoric compounds with an aminopyrene moiety and from the point of view of practical applications of triazinyl reactive fluorescent dyes as probes and labels in biochemistry.

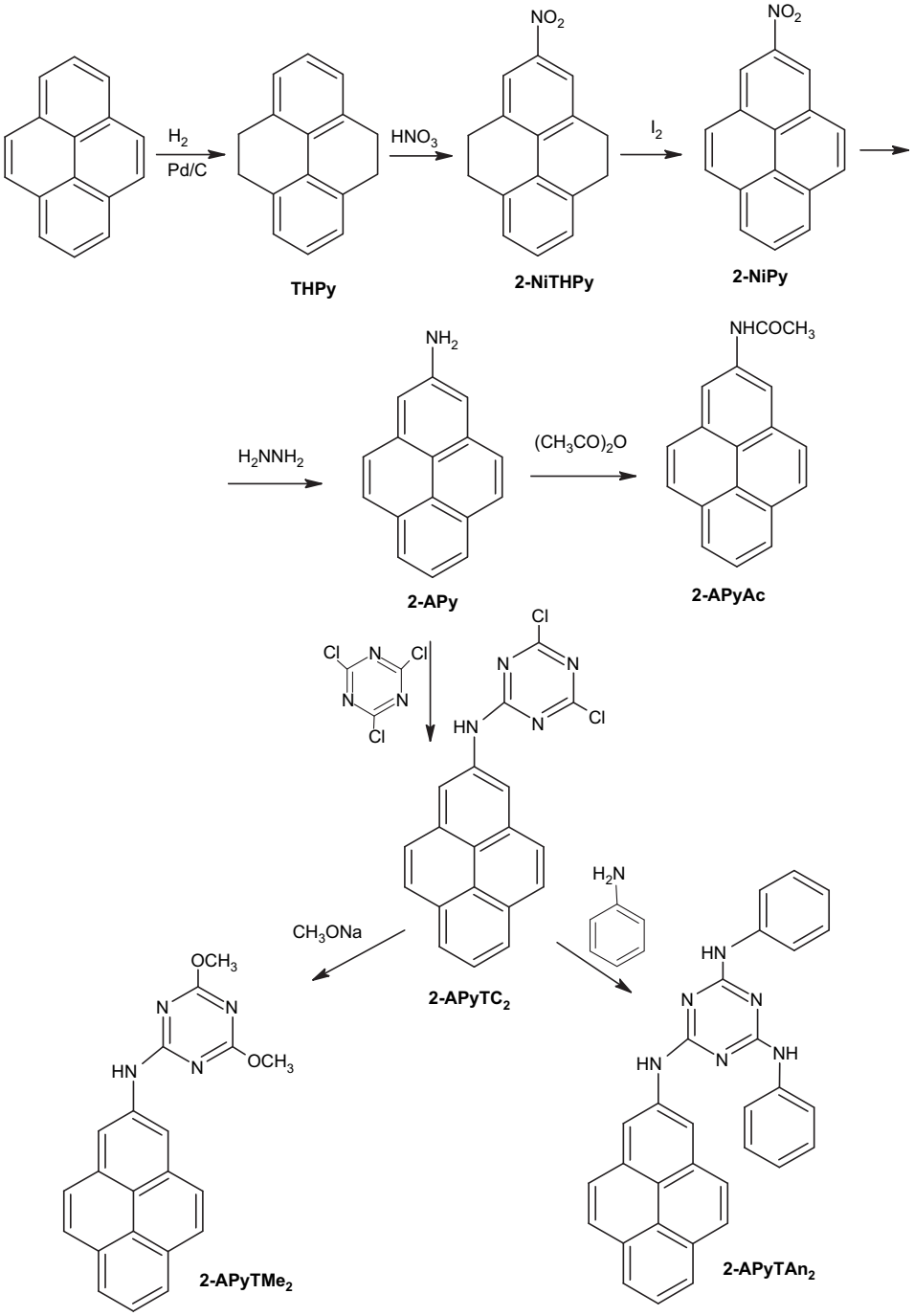
2. Experimental

2.1. Syntheses

The route of synthesis of *N*-derivatives of 1-aminopyrene is shown in Scheme 1, the synthesis of *N*-derivatives of 2-aminopyrene is shown in Scheme 2.

2.1.1. 1-Nitropyrene (1-NiPy)

1-Nitropyrene was prepared by the nitration of pyrene with 65% HNO_3 in acetic acid. The product forms yellow crystals with m.p. 152–153 °C (153–154 °C [7,14]).



Scheme 2. Synthesis of 2-aminopyrene and its derivatives.

2.1.2. 1-Aminopyrene (1-APy)

1-NiPy (55 g, 222.4 mmol) was refluxed in ethanol for 15 min. Then, during 30 min, 210 mL aqueous solution of sodium hydrosulphide (conc. = 1.82 mol/L) was added; the reaction mixture was heated for 90 min and after cooling, the precipitated crystals of 1-aminopyrene were filtered off. The filtrate was concentrated on a vacuum rotary evaporator; cooling of the concentrate gave a second portion of the product. Both the portions of 1-aminopyrene were united and recrystallized from cyclohexane to yield 41.2 g (85%) of crystals with m.p. 116–117 °C (117–118 °C [7,11,14]). Anal. calcd. for $C_{16}H_{11}N$: C 88.45%, H 5.10%, N 6.45%; found: C 88.41%, H 5.07%, N 6.52%.

2.1.3. 4,5,9,10-Tetrahydropyrene (THPy)

4,5,9,10-Tetrahydropyrene was synthesized by catalytic hydrogenation of pyrene in ethyl acetate in an autoclave at 90 °C and 14 MPa for 7 h with Pd/C catalyst [22]; the reaction mixture was filtered, the filtrate was concentrated on a rotary evaporator; the yield 19.5 g of chromatographically pure product with m.p. 138–140 °C (138 °C [20,29–31]) was obtained from 20 g of pyrene.

Table 1
^{1}H and ^{13}C chemical shifts in 1-APy measured in hexadeuteriodimethyl sulphoxide

H/C	δ (^{1}H)	δ (^{13}C)	H/C	δ (^{1}H)	δ (^{13}C)
1	[a]	144.5	5a[1]	–	125.3
2	7.44	113.2	6	8.03	123.0[b]
3	8.03	126.7[b]	7	7.91	122.5[b]
3a	–	121.5	8	8.03	126.0[b]
3a[1]	–	125.8	8a	–	131.8
4	7.75	121.9	9	7.97	124.3
5	7.92	127.6[b]	10	8.33	122.3
5a	–	132.1	10a	–	114.8

[a] $\delta(NH_2) = 6.42$.
[b] The assignment can be interchanged.

2.1.4. 2-Nitro-4,5,9,10-THPy (2-NiTHPy)

2-Nitro-4,5,9,10-THPy was prepared by the nitration of THPy with 65% HNO_3 in acetic anhydride according to Bolton [26]; m.p. 109–110 °C (111–112 °C [26,30]).

2.1.5. 2-Nitropyrene (2-NiPy)

2-Nitropyrene was synthesized according to Bolton [26] by oxidation of 2-nitro-4,5,9,10-THPy with iodine in nitrobenzene; m.p. 199–201 °C (201–202 °C [26,28]).

2.1.6. 2-Aminopyrene (2-APy)

2-Aminopyrene was prepared by reducing 2-NiPy with hydrazine hydrate in boiling mixture ethanol–benzene and with an addition of $FeCl_3$; m.p. 220–222 °C (222–223 °C [19]). Anal. calcd. for $C_{16}H_{11}N$: C 88.45%, H 5.10%, N 6.45%; found: C 88.39%, H 5.12%, N 6.49%.

2.1.7. N-Acetyl-1-aminopyrene (1-APyAc)

1-APy (5 g, 23 mmol) was dissolved in 50 mL acetone and 5 mL (53 mmol) acetic anhydride was added. The mixture was refluxed for 1 h. After cooling, the precipitated yellowish product was filtered off, washed with water and with a small amount of cool acetone; yield 5.07 g (85%); m.p. 265–266 °C (266 °C [7], 261 °C [14]); ^{1}H NMR chemical shifts: 10.39 (s, 1H, NH), 8.09–8.32 (m, 9H, aromatic protons), 2.34 (s, 3H, $COCH_3$), ^{13}C NMR chemical shifts: 169.2 (CO), 132.1, 130.9, 130.6, 128.2, 124.5, 124.0, 123.7 (all C), 127.3, 127.1, 126.6, 126.5, 125.3, 125.0, 124.9, 123.4, 122.5 (all CH), 23.7 (CH_3). Anal. calcd. for $C_{18}H_{13}NO$: C 83.38%, H 5.05%, N 5.40%, O 6.17%; found: C 83.25%, H 5.18%, N 5.30%.

Table 2
^{1}H and ^{13}C chemical shifts in 2-APy, 2-APyAc, 2-APyTC$_2$ and 2-APyTMe$_2$ measured in hexadeuteriodimethyl sulphoxide

H/C	2-APy		2-APyAc		2-APyTC$_2$		2-APyTMe$_2$	
	δ (^{1}H)	δ (^{13}C)	δ (^{1}H)	δ (^{13}C)	δ (^{1}H)	δ (^{13}C)	δ (^{1}H)	δ (^{13}C)
1 = 3	7.49	110.7	8.56	115.7	8.49	118.0	8.66	117.0
2	–	147.9	–	137.8	–	135.1	–	137.4
3a = 10a	–	132.1	–	131.3	–	131.2	–	131.1
3a[1]	–	116.9	–	120.5	–	121.4	–	120.4
4 = 10	7.93	126.6	8.14	127.2	8.15	127.1	8.11	127.0
5 = 9	8.03	127.3	8.16	127.9	8.22	128.2	8.22	127.9
5a = 8a	–	129.1	–	130.1	–	130.3	–	130.1
5a[1]	–	124.5	–	124.5	–	123.6	–	123.8
6 = 8	8.14	124.9	8.14	123.8	8.33	125.6	8.33	125.3
7	7.87	123.9	8.01	125.6	8.09	126.2	8.09	125.7
N*H*R	5.77	–	10.35	–	11.68	–	10.68	–
NHC	–	–	–	168.9	–	164.2	–	166.4
N=C–N	–	–	2.26[a]	24.3[a]	–	169.9	–	172.2
						169.0		
OCH_3	–	–	–	–	–	–	4.02	54.7

[a] CH_3.

Table 3
Absorption and fluorescence maxima and fluorescence quantum yields of 1- and 2-aminopyrenes and their *N*-derivatives in various solvents

Solvent	A_{max}	F_{max}	q_{Fl}	A_{max}	F_{max}	q_{Fl}	A_{max}	F_{max}	q_{Fl}
	1-APy			2-APy			1-APyAc		
Bu_2O	361	417	61	338	432	19	341	385	27
CH_3CN	361	425	62	338	438	14	339	386	23
CH_3OH	357	428	56	336	445	17	338	383	13
	2-APyAc			1-APyTC$_2$			2-APyTC$_2$		
Bu_2O	336	389	10	341	–	–	336	374	6
CH_3CN	334	388	9	341	–	–	336	–	–
CH_3OH	334	387	7	340	–	–	334	–	–
	1-APyTM$_2$			2-APyTM$_2$			1-APyTAn$_2$		
Bu_2O	341	388	57	336	393	15	342	394	61
CH_3CN	340	390	24	336	393	13	342	395	72
CH_3OH	340	388	2	334	392	13	340	395	50
	2-APyTAn$_2$								
Bu_2O	336	397	21						
CH_3CN	336	398	19						
CH_3OH	336	399	21						

The fluorescence was excited at corresponding absorption maxima of the compounds (A_{max} absorption maximum (nm), F_{max} fluorescence maximum (nm), q_{Fl} fluorescence quantum yield (%), – no fluorescence was found).

2.1.8. N-Acetyl-2-aminopyrene (2-APyAc)

2-APy (0.32 g, 1.46 mmol) was dissolved in hot ethyl acetate (40 mL), 0.9 mL acetic anhydride was added, and the

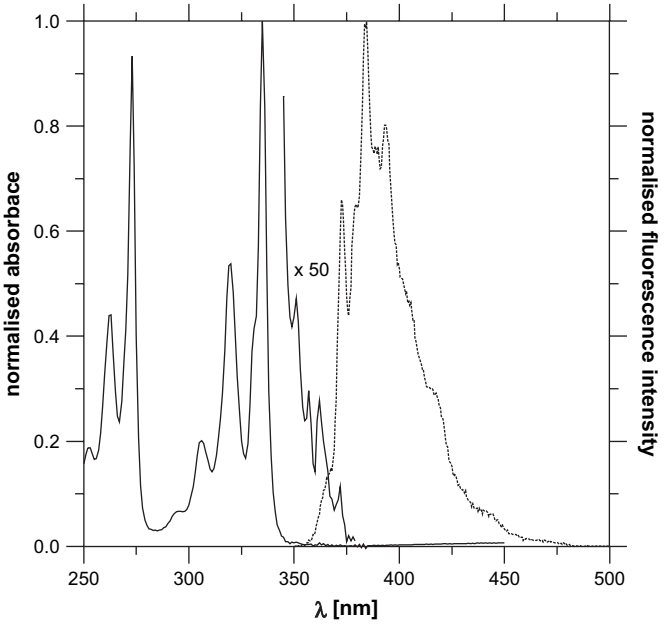


Fig. 1. Absorption (solid line) and fluorescence (dashed line) spectra of pyrene in cyclohexane.

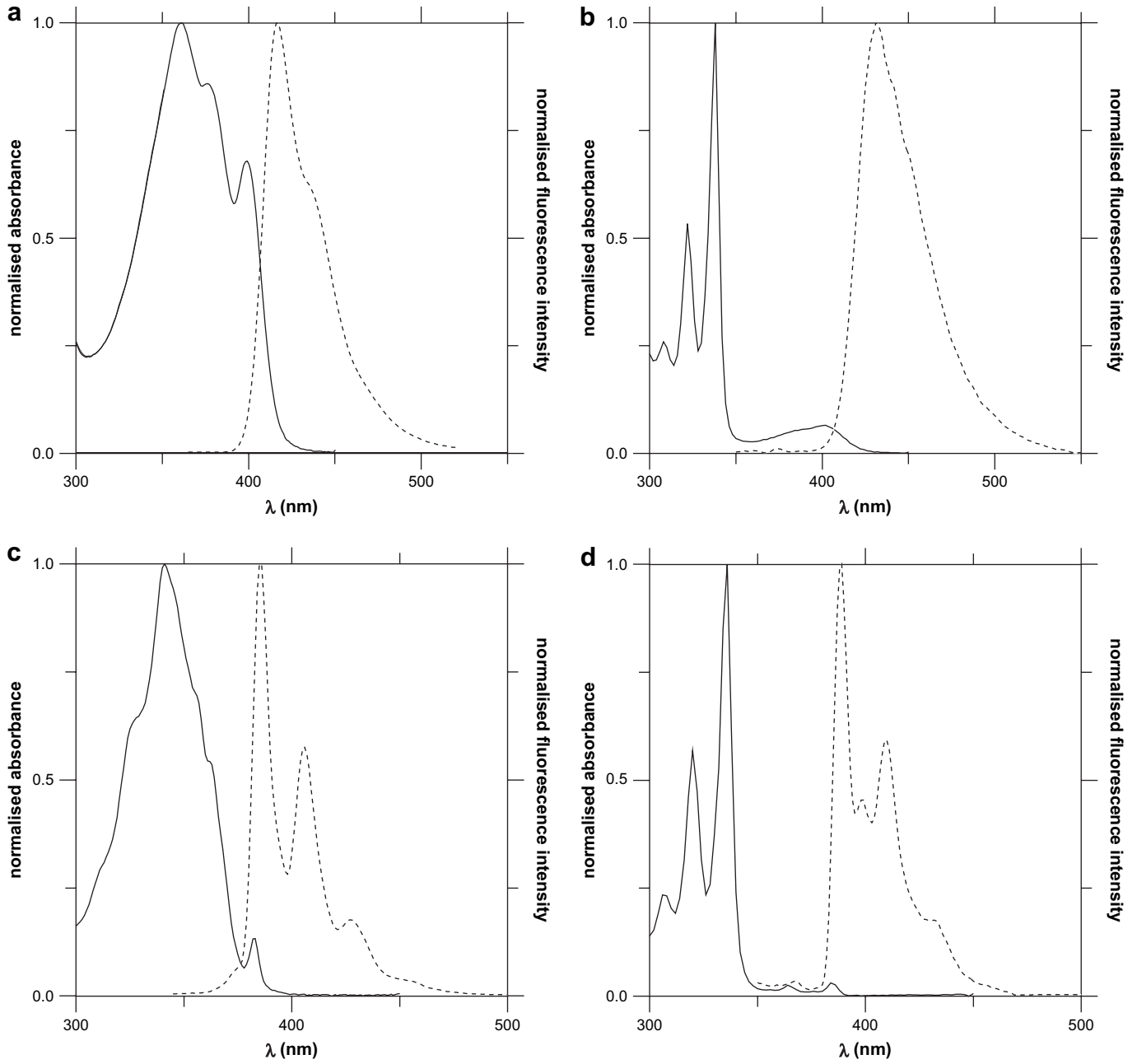


Fig. 2. The absorption (solid line) and fluorescence (dashed line) spectra of 1-APy (a), 2-APy (b), 1-APyAc (c), and 2-APyAc (d) in dibutyl ether.

reaction mixture was refluxed for 3 h. After partial removal of solvent on a vacuum rotary evaporator and cooling, the separated solid was filtered off, washed with a small amount of acetone and dried; yield 0.33 g (88%); m.p. 236–237 °C (234–235 °C [26]). Anal. calcd. for $C_{18}H_{13}NO$: C 83.38%, H 5.05%, N 5.40%, O 6.17%; found: C 83.45%, H 5.17%, N 5.49%.

2.1.9. N-(4,6-Dichloro-1,3,5-triazin-2-yl)-1-aminopyrene (1-APyTC$_2$)

1-Apy (2.7 g, 12.5 mmol) and cyanuric chloride (2.3 g, 12.5 mmol) were dissolved in acetone. After cooling to 5–10 °C, sodium hydrogen carbonate in a small amount of water was added; the mixture was kept at this temperature and stirred for 1 h, whereupon the precipitated solid was collected by filtration, washed with water and with a small amount of acetone and dried at 40 °C. After recrystallization from toluene, 3.8 g (84%) white substance was obtained; m.p. 236–237 °C (237 °C [7]); ^{1}H NMR chemical shifts: 11.62 (s, 1H, NH), 8.13–8.40 (m, 9H, aromatic protons), ^{13}C NMR chemical shifts: 169.9, 169.3, 166.0, 130.8, 130.5, 129.8, 129.7, 125.8, 124.4, 123.7 (all C), 128.0, 127.6, 127.2, 126.7, 125.8, 125.6, 125.1, 124.9, 122.4 (all CH). Anal. calcd. for $C_{19}H_{10}N_4Cl_2$: C 62.49%, H 2.76%, N 15.34%, Cl 19.41%; found: C 62.55%, H 2.81%, N 15.31%, Cl 19.33%.

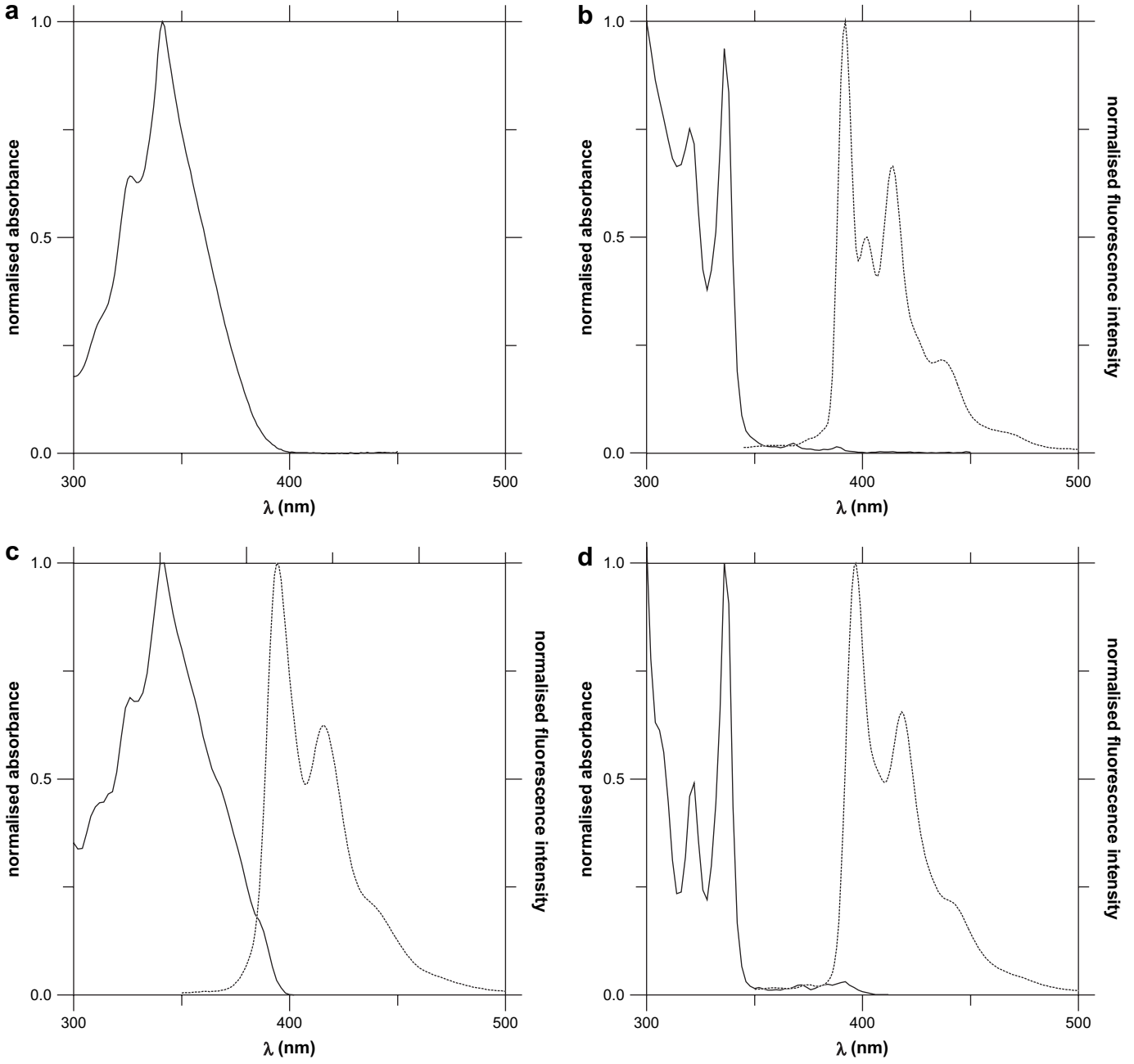


Fig. 3. The absorption (solid line) and fluorescence (dashed line) spectra of 1-APyTC$_2$ (a), 2-APyTC$_2$ (b), 1-APyTAn$_2$ (c), and 2-APyTAn$_2$ (d) in dibutyl ether.

2.1.10. N-(4,6-Dichloro-1,3,5-triazin-2-yl)-2-aminopyrene (2-APyTC$_2$)

This compound was prepared by the same procedure as described above for 1-ApyTC$_2$; m.p. 242–246 °C. Anal. calcd. for $C_{19}H_{10}N_4Cl_2$: C 62.49%, H 2.76%, N 15.34%, Cl 19.41%; found: C 62.68%, H 2.84%, N 15.32%, Cl 19.16%.

2.1.11. N-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-1-aminopyrene (1-APyTMe$_2$)

(a) Preparation of sodium methanolate solution: finely cut sodium (5 g) was slowly added into 100 mL methanol, and the mixture was filtered. The content of sodium methanolate in solution (2.025 mol/L) was estimated by potentiometric titration.

(b) 1-APyTC$_2$ (1.0 g, 2.74 mmol) was mixed with 3.3 mL sodium methanolate (6.7 mmol) in 20 mL methanol, and the mixture was refluxed for 1 h. After cooling, the mixture was diluted with water; the precipitated product was collected by filtration, washed with water and with a small amount of acetone, and dried at 40 °C. After recrystallization from methanol, the yield was 0.7 g (72%) white substance; m.p. 176–178 °C (171–172 °C [7]). Anal. calcd. for $C_{21}H_{16}N_4O_2$: C 70.78%, H 4.53%, N 15.72%, O 8.98%; found: C 70.92%, H 4.65%, N 15.55%.

Table 4
Fluorescence lifetimes of pyrene, aminopyrenes, and *N*-substituted derivatives

Compound	Fluorescence lifetime (ns)	Compound	Fluorescence lifetime (ns)
Pyrene	462[a]	2-APy	41.8[a]
1-APy	5.6[c]	2-APyAc	107.6[a]
1-APyAc	6.9[b]	2-APyTC$_2$	122.5[a]
1-APyTM$_2$	6.3[b]	2-APyTM$_2$	112.0[a]
1-APyTAn$_2$	4.3[a]	2-APyTAn$_2$	101.6[a]

Solvents:
[a] *n*-Heptane.
[b] Ethyl acetate.
[c] Cyclohexane.

2.1.12. N-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-2-aminopyrene (2-APyTMe$_2$)

This compound was prepared by the same procedure as described above for 1-APyTMe$_2$; m.p. 223–224 °C. Anal. calcd. for $C_{21}H_{16}N_4O_2$: C 70.78%, H 4.53%, N 15.71%, O 8.98%; found: C 70.97%, H 4.79%, N 15.40%.

2.1.13. N-(4,6-Dianilino-1,3,5-trazin-2-yl)-1-aminopyrene (1-APyTAn$_2$)

A 0.72 g (1.97 mmol) portion of 1-APyTC$_2$, 0.38 g (4.52 mmol) sodium hydrogen carbonate, 6.45 mL aniline and 2 mL water were added to 65 mL acetone. The mixture was refluxed for 6 h, whereupon it was diluted with water; the precipitated product was collected by suction, washed with water and with a small amount of acetone, and dried at 40 °C; this procedure gave 0.814 (86%) pure product with m.p. 267–269 °C. MS: $[M-H]^-$ *m/z* 477 (M.W. 478 g/mol). Anal. calcd. for $C_{31}H_{22}N_6$: C 77.81%, H 4.63%, N 17.56%; found: C 77.59%, H 4.65%, N 17.46%.

2.1.14. N-(4,6-Dianilino-1,3,5-trazin-2-yl)-2-aminopyrene (2-APyTAn$_2$)

This compound was prepared by the same procedure as described above for 1-APyTAn$_2$. Yield 95%; m.p. 237–239 °C. MS: $[M+H]^+$ *m/z* 479 (M.W. 478 g/mol). Anal. calcd. for $C_{31}H_{22}N_6$: C 77.81%, H 4.63%, N 17.56%; found: C 77.48%, H 4.96%, N 17.37%.

The course of the reactions and purity of the substances were checked by TLC (Silufol UV 254, mobile phase cyclohexane–ethyl acetate 3:1), HPLC (Thermo Separation Products PC 1000 with a reverse-phase column 250 × 4 mm Nucleosil C18 and absorption UV/VIS detector, liquid phase acetonitrile–water 9:1) and by comparison of fluorescence excitation spectra with absorption spectra of the final substances.

The elemental analyses were carried out at the Department of Organic Chemistry, the University of Pardubice.

2.2. Spectra

Mass spectra were measured on a Bruker Daltonics Esquire 3000 and on Micromass Platform spectrometers at the Institute of Analytical Chemistry, the University of Pardubice.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 spectrometer operating at 500.13 MHz for ^{1}H and 125.76 MHz for ^{13}C. The samples were dissolved in hexadeuteriodimethyl sulphoxide and measured at room temperature. The ^{1}H and ^{13}C chemical shifts were referenced to the central signal of the solvent ($\delta = 2.55$ (^{1}H) and 39.6 (^{13}C)). The positive values of chemical shifts denote shifts of signals to higher frequencies with respect to the standard. The two-dimensional experiments (gradient-selected H,H-COSY, H,C-HSQC and H,C-HMBC) were performed with the aim to assign ^{1}H and ^{13}C chemical shifts.

The absorption spectra were measured on a Perkin–Elmer 555 spectrophotometer. Typical concentrations were of the order of 10^{-5} mol/L, which yielded optical density ~0.5 at the main absorption maximum in a 1-cm cell.

The steady-state fluorescence spectra were measured using a Hitachi Perkin–Elmer LS 5 spectrophotometer. The instrument provides corrected excitation spectra directly; the fluorescence emission spectra were corrected for the characteristics of the emission monochromator and for the detection of photomultiplier response. During fluorescence measurements, very weakly absorbing solutions (optical density ~0.05 at the exciting wavelength in 1-cm cell) were used. The fluorescence quantum yields (q_{Fl}) were measured using quinine sulphate (fluorescence quantum yield $q_{Fl} = 0.54$ in 0.5 mol/L H_2SO_4) [32,33] as the standard. Deoxygenation of the samples by bubbling through N_2 or Ar did not make any difference in the spectra and quantum yield recorded; therefore the data reported here correspond to aerated solutions.

The samples for fluorescence measurements were prepared by preparative TLC on Silufol UV 254 plates. All solvents used were of spectral grade and were checked for their own fluorescence under relevant conditions.

The fluorescence decay kinetics was measured using an Edinburgh Instruments FL900 spectrofluorimeter with ns-excitation flashlamp nF900. With a time-correlated single-photon counting (TCSPC) detection channel the instrument provided sub-ns time resolution.

3. Results and discussion

The syntheses of 1- and 2-aminopyrenes and their *N*-acetyl derivatives were carried out by procedures described in literature. The elemental analyses of compounds were in accordance with theory and melting points were in agreement with literature. Because of the importance for the synthesis of reactive dyes, the reactions of cyanuric chloride with amino and hydroxy compounds are well known. The syntheses of triazinyl derivatives were carried out by well-tried procedures only modified for our type of compounds; their structure was confirmed by elemental analyses, MS and ^{1}H and ^{13}C NMR spectra (Tables 1 and 2 and Section 2).

The spectral characteristics and fluorescence quantum yields (q_{Fl}) of the studied substances in dibutyl ether (Bu_2O), in acetonitrile (MeCN) and in methanol (MeOH) are summarized in Table 3. Absorption and fluorescence spectra are presented in Figs. 1–3.

The substitution in 2-position retains the character of L_b and L_a states of pyrene and absorption spectra of 2-derivatives

are very similar to the spectrum of pyrene: well separated very weak first absorption band (L_b) and strong L_a band with clear-cut vibronic structure. The substitution in position 1 removes a symmetrical forbiddance of $S_o \rightarrow L_b$ transition of the pyrene, which results in an increased intensity of the L_b band and in its strong overlapping with bathochromically shifted L_a band. The substitution on NH_2 group with electron withdrawing acetyl or triazinyl groups has practically no influence on the character of absorption spectra of 2-derivatives, while a hypsochromic shift of L_a band was found for 1-derivatives. A solvent influence on absorption spectra is insignificant.

The fluorescence spectra of 1-APy and 2-APy are formed by one broad band, the fluorescence band of *N*-derivatives shows a clear-cut vibronic structure. The shape and the position of the fluorescence bands of both amines and their *N*-derivatives are practically independent of the type of *N*-substituents and of the solvent polarity.

The order of magnitude of the radiation lifetime can be estimated from the relation $\tau_o \sim 10^{-4}/\varepsilon_{max}$ for absorption bands in the near UV. Thus, allowed transitions (strong absorption bands, $\varepsilon \sim 10^{-5}$) will give rise to excited states having an approximate lifetime of $\sim 10^{-9}$ s (ns); τ_o will be much longer for forbidden transitions (weak absorption bands).

The character of absorption spectra and fluorescence lifetimes (Table 4) show that 1-derivatives of pyrene fluoresce from solvent relaxed L_a state, whereas the 2-derivatives fluoresce from L_b state (as in the case of pyrene).

In contrast to the absorption and fluorescence spectra, the q_{Fl} of studied compounds is significantly influenced by the character of *N*-substituents and by the solvent polarity. In comparison with 1-APy, the q_{Fl} of 2-APy is about three times lower. The q_{Fl} of both aminopyrenes is reduced about twice by *N*-acetylation. No dependence on solvent polarity was observed.

The substitution on amino group by cyanuric chloride causes a dramatic effect on q_{Fl}: 1-APyTC$_2$ does not fluoresce at all, 2-APyTC$_2$ exhibits only weak fluorescence in non-polar dibutyl ether. The substitution of chlorine atoms by methoxy groups results in a high q_{Fl} of 1-APyTM$_2$ in non-polar dibutyl ether, but q_{Fl} is significantly reduced in polar solvents; q_{Fl} is practically constant for 2-APyTM$_2$ in the solvents used. 1-APyTAn$_2$ exhibits a high q_{Fl} even in polar solvents and q_{Fl} of 2-APyTAn$_2$ is about three times lower and solvent independent.

The presented experimental results show a dependence of q_{Fl} of the studied compounds on solvent polarity and on the presence of chlorine atoms in the triazine ring. These phenomena are more pronounced for 1-derivatives (L_a fluorescent state) than for 2-derivatives (L_b fluorescent state). The strong fluorescence quenching of dichlorotriazinyl derivatives is the most remarkable feature. There are a variety of processes leading to fluorescence quenching; some can be excluded in our case. All the compounds are photo-stable, thus photochemical reactions can be ruled out. The presence of chlorine atoms can enhance the spin–orbit coupling and so it could increase $S \rightarrow T$ transition rate constant. But this mechanism (intersystem crossing) cannot account for the dependence of q_{Fl} on solvent polarity, especially for the dramatic fluorescence quenching of 1-APyTM$_2$ in methanol. Besides, 1-(dichloro-1,3,5-triazinyl)-pyrene, i.e. the compound with triazinyl ring directly bonded to pyrene, exhibits remarkable fluorescence properties: high q_{Fl} in non-polar and polar solvents and strong solvatochromism [34]. These facts rule out an $S \rightarrow T$ transition as an efficient deactivation nonradiative process.

For this reason, another deactivation process probably exists. As the chlorine atoms enhance the electron withdrawing character of triazinyl ring, an excited state connected with π-electron transfer from the aminopyrene moiety to the triazinyl ring and with simultaneous changing of geometry of the molecule could operate. Due to a solvent relaxation, the energy of such a state could decrease to the vicinity of, or even below, a fluorescent state. Hence, a new efficient deactivation channel could be opened. Rigorous explanation of the fluorescence features of the presented group of compounds requires a more detailed discussion of the character and the energy of molecular states. Quantum chemical calculations on semi-empirical level are now in progress.

4. Conclusions

The aim of this research was to synthesize the series of *N*-derivatives of 1- and 2-aminopyrenes and to investigate their fluorescence characteristics. The syntheses of compounds were carried out in part by methods described in literature; in part new procedures were developed. The constitution of compounds was confirmed by the elemental analyses, MS, and NMR spectra.

The UV/vis absorption spectra and fluorescence characteristics (spectra, quantum yields, and lifetimes) were measured in various solvents. A strong influence of the character of *N*-substituents (acetyl, *s*-triazinyl ring with various substituents) and of the solvent polarity on fluorescence quantum yields and lifetimes has been found. Some relationships between structure and fluorescence properties were revealed.

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