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Electronic structure, spectra and photophysical properties of *N*-triazinylderivatives of 1-aminopyrene. Semi-empirical theoretical study

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ABSTRACT

The geometry and excited state characteristics of five *N*-triazinyl derivatives of 1-aminopyrene were calculated using AM1, CNDO/S and ZINDO/S methods. For the optimized structures of the studied molecules, L_b, L_a and B_b transitions (localized on the amino pyrene moiety) were found, as well as charge-transfer states characterized by a charge transfer from the amino pyrene to the triazinyl ring. The energy of such strongly polar charge-transfer states depends on the chemical structure of the compound and on the solvent polarity. The relationships among each charge-transfer-to-emitting state energy gap, solvent polarity and fluorescence quantum yield of the studied compounds are discussed.

1. Introduction

It has been both experimentally and theoretically confirmed a long time ago [1] that the S_0–S_1 transition of pyrene corresponds to the excitation to the L_b state with diminishing extinction coefficient and with transition polarization along the short molecular axis; S_0–S_2 transition corresponds to the excitation to the L_a state with a high extinction coefficient and the long molecular axis polarization. Recently, theoretical investigation (AM1 and ZINDO calculations) of the excited states involved in the HOMO–LUMO transition (L_a band) was carried out [2] for pyrene with a variety of substituent at different positions.

Fiebig et al. [3] reported on the absorption and fluorescence spectra of several bichromophoric systems containing phthalic acid ester, isophthalic ester, and benzoic ester (as electron acceptors) linked to pyrene (acting as an electron donor) at the 1- position via a phenyl group. On the basis of CNDO/S calculations, they discussed the mechanism of charge-transfer (CT) state formation, the magnitude of electronic coupling and the relative energy of CT states in relation to the structure of those compounds.

In their theoretical study, Mitchell and Netzel [4] analyzed the structure-to-electronic spectra relationship for 1-pyrenyl substituted 1-methyluracil-5-carboxamide nucleoside model compounds and discussed the character of the compound's excited states. Besides the states localized on the pyrenyl moiety, this study has revealed the states connected with a significant pyrenyl-to-uracil transition. Taking into account a different character of the excited states, they discussed the mechanism of the fluorescence quenching for the studied compounds in polar solvents.

Dobkowski et al. [5] investigated the character of 4-(pyren-1-yl) benzonitrile excited states both experimentally and theoretically. Their INDO/S calculations showed that a highly polar TICT state could be generated by rotating the benzonitrile group, but they found that the stabilization of such a state in polar solvents is not sufficient to down-shift the TICT state energy below that of the lowest emitting singlet state. They also stated that when a π-conjugated substituent is directly linked to the 1-position of pyrene, the symmetry of the original system (D_{2h}) is reduced (C_1); this results in removing of strict symmetry forbiddance of S_o–S_1 transition of pyrene which leads to intensity increase of the corresponding absorption band (L_b). Simultaneously, depending on the character of the substituent, the S_0–S_2 transition (L_a band) is bathochromically shifted. Due to these changes, the S_2–S_1 energy gap is reduced, resulting in a stronger mixing of the both states by

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a vibronic coupling. Consequently, the electronic nature of the states may become unclear.

In our earlier papers, we presented the synthesis, spectral, and photophysical properties of bi- and tri-chromophoric compounds containing 1-aminopyrene as an excitation energy donor, 3-aminobenzanthrone as an acceptor, and 1,3,5-triazine as a spacer [6–8]. For a better understanding of the electronic excitation energy transfer mechanism in such Donor-Spacer-Acceptor systems, it was necessary to investigate the photo-physical properties of each chromophoric subsystem. We have reported on the solvent dependence of the spectral and photophysical characteristics of various *N*-substituted 3-aminobenzanthrone derivatives [9]. On the basis of experimental results and semi-empirical quantum chemical calculations, we have concluded that the main deactivation channel of the fluorescent S_1 ($\pi\pi^*$) excited state of *N*-substituted 3-aminobenzathrone derivatives is an intersystem crossing to an upper ($n\pi^*$) triplet state.

Recently, we have published the synthesis, spectral, and photophysical characteristics of *N*-triazinyl derivatives of 1- and 2-aminopyrenes, and we have discussed the dependence of these characteristics on the solvent polarity [10]. We have found that the number of chlorine atoms on the triazinyl ring and solvent polarity are determining factors for the fluorescence quantum yields (q_F) of *N*-triazinyl derivatives. Extremely strong fluorescence quenching of the dichlorotriazinyl derivative is the most remarkable feature. Among many processes that could lead to the fluorescence quenching in these compounds, most of them can be excluded as a possible major quencher in this case. All the compounds are photostable, thus photochemical reactions can be ruled out. The presence of a heavy atom (Cl) can enhance the spin-orbit coupling; it could increase the S (π,π^*)—T (π,π^*) transition rate constant, but this mechanism does not explain the strong influence of the solvent polarity on q_F. Besides, 1-(dichloro-1,3,5-triazinyl)-pyrene, i.e. the compound with triazinyl ring directly bonded to pyrene, exhibits high q_F in both non-polar and polar solvents [11].

Previously, according the INDO/S calculations, Kapusta et al. [12] revealed a highly dipolar optically forbidden state corresponding to electron transition from the aminopyrene moiety to the triazinyl ring,

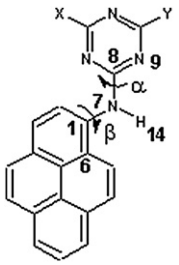
As the chlorine atoms can enhance the electron withdrawing character of the triazinyl ring, the excited states connected with π-electron transfer from the aminopyrene moiety to the triazinyl ring (CT state) could exist and open a new efficient deactivation channel. To investigate the role of such a state in fluorescence quenching in detail, we present here the theoretical characteristics of electronic transitions in the studied compounds, obtained through semiempirical quantum chemical calculations. The major goal of this study is to show the relationships among q_F, molecular structure, and characteristics of the electronic transitions in the studied compounds, and to investigate the influence of the solvent polarity.

2. Results and discussion

2.1. Experimental results

In contrast with pyrene, the absorption spectra of the compounds studied in this work (Scheme 1) exhibit a spectral broadening. The fluorescence bands show a clear cut vibronic structure. Positions and shapes of the absorption and fluorescence spectra of the compounds reported here are practically identical to those of $APyTM_2$ (Fig. 1).

From the shape of the absorption spectra of *N*-derivatives of 1-aminopyrene, strong overlap of L_b and L_a bands is evident in the 340–390 nm range [10], (Fig. 1). Previously, we investigated



	$APyTC_2$	APyTCM	$APyTM_2$	APyTCAn	$APyTAn_2$
X	Cl	Cl	OCH_3	Cl	NHPH
Y	Cl	OCH_3	OCH_3	NHPH	NHPH

Scheme 1.

a fluorescence anisotropy for 1-acetylaminopyrene (APyAc) [13] and $APyTM_2$ [14] in ethylacetate (EtAc). It was found that the anisotropy degree was practically constant (0.3) in the aforementioned spectral region. It may prove that the transition moment orientations of the both absorption bands are very close to each other. It is in agreement with the calculations presented here that predict the angle between L_b and L_a moments of optimized structure of about 10° for $APyTC_2$ and smaller than 5° for $APyTM_2$ and $APyTAn_2$. Therefore, the problem of a sequence and the character of L_b and L_a Franck–Condon states remains open.

The substitution on the amino group of 1-aminopyrene (APy) by an acetyl group decreases the APyAc fluorescence quantum yield q_F by two to four times, depending on the solvent polarity (Table 1). But, the same substitution on amino group by a cyanuric chloride causes a total quenching of the $APyTC_2$ fluorescence. For APyTCM, a very weak fluorescence was found and only in non-polar dibutyl ether (DBE); otherwise no measurable fluorescence was detected. The substitution of one chlorine atom by a phenylamino group increases q_F slightly in DBE, nevertheless, either of those compounds does not fluoresce in polar solvents at all. The substitution of both of the chlorine atoms by methoxy groups results in high q_F of $APyTM_2$ though an influence of solvent polarity is still evident. Only when both of the chlorine atoms are substituted by the phenylamino groups does q_F stay high in polar solvents. Hence, with increasing number of chlorine atoms on the triazinyl ring, i.e. with its increasing electronegativity, and with increasing solvent polarity, the q_F is dramatically reduced.

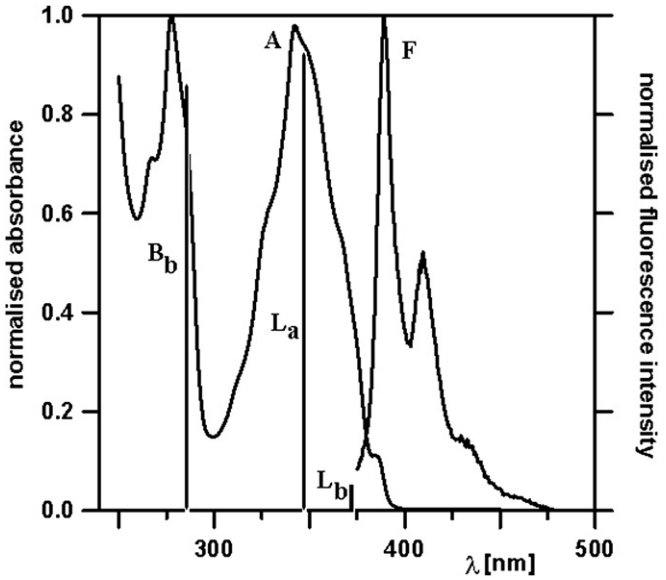


Fig. 1. Absorption (A) and fluorescence (F) spectra of $APyTM_2$ in dibutyl ether; the straight lines denote the CNDO/S transitions.

Table 1
Fluorescence quantum yields of studied compounds [10,15,16].

Compound	DBE	EtAc	MeCN	MeOH	2-MTHF	2-MTHF −190°
APy	0.61	0.52	0.62	0.56		
APyAc	0.27	0.27	0.23	0.13		
$APyTC_2$	–	–	–	–	–	0.21
APyTCM	0.01	–	–	–	–	0.65
$APyTM_2$	0.57	0.35	0.24	0.02	0.42	0.93
APyTCAn	0.18	0.01	–	–		
$APyTAn_2$	0.61	0.72	0.72	0.50		

–, no fluorescence was observed.

For all the reported compounds, their q_F does not depend on the excitation wavelength in the region of 300–370 nm. No dual fluorescence was found.

2.2. Theoretical results

The equilibrium conformations of molecules depicted in Scheme 1 in electronic ground state and excited state characteristics have been calculated using the semi-empirical AM1 and CNDO/S methods with modified Nishimoto–Mataga gamma integrals as implemented in WinMOPAC 2.0 Package and using ZINDO/CI method implemented in ArgusLab 4.0 [17].

The 1-aminopyrene *N*-triazinyl derivative's geometry optimization converges to the geometries presented in Table 2.

From the data in Table 2 it is evident that:

- in dependence on a substituent, the angle β is 1.8–2.9 times greater than angle α;
- β is decreasing and α slightly increasing with decreasing electronegativity of the triazinyl ring;
- the bond Tr-NH is either somewhat shorter than Py-NH bond, or both bonds are practically the same;
- a markedly smaller twisting around the Tr-NH bond than around the Py-NH bond and somewhat shorter Tr-NH bond demonstrate a stronger π-electronic interaction of the amino group with the triazinyl ring than with pyrene.

The MO energies for APy and its *N*-derivatives are shown in Table 3 and schematically depicted in Fig. 2. The orbitals included in Table 3 are expected to be those important for an understanding of the spectra and photophysics of the compounds under study, all MOs are of a π-type. The frontier orbitals HOMO and LUMO of all compounds are localized on the amino pyrene moiety; their energy is practically independent on a type of *N*-substituent. But, an attachment of the triazinyl ring to the aminopyrene results in the creation of two new orbitals (π_{-2} and π_{-3}) largely localized on the triazinyl ring (Fig. 3). Their energy is between the π_{-1} and π_{-2} MOs of unsubstituted APy and the energy significantly decreases with a successive substitution of methoxy or anilino groups by chlorine atoms (Fig. 2).

Table 2
Optimized geometry of the studied compounds.

Compound	α°	β°	Py-NH (A)	Tr-NH (A)
APyTC2	12	35	1.42	1.39
APyTCM	12	34	1.42	1.39
APyTM2	14	33	1.41	1.40
APyTCAn*	14	32	1.42	1.40
APyTAn2*	17	31	1.41	1.41

Tr denotes the triazinyl ring.
α° denotes the dihedral angle 9N8C7N14H.
β° denotes the dihedral angle 6C1C7N14H.
*, the planes of triazinyl and phenyl rings contain the angle 36°.

Table 3
Orbital energies of studied compounds for optimized structures.

No.	Energy (eV)	Labelling*	No.	Energy (eV)	Labelling*
APy			*APyAc*		
43	−0.874	π_{-3}	52	−1.065	π_{-4}
42	−1.468	π_{-2}	51	−1.188	π_{-3}
41	−2.179	π_{-1}	50	−1.682	π_{-2}
40	−7.585	π_1	49	−2.393	π_{-1}
39	−8.734	π_2	48	−7.884	π_1
			47	−8.886	π_2
$APyTC_2$			*APyTCM*		
65	−1.026	π_{-5}	68	−0.958	π_{-5}
64	−1.616	π_{-4}	67	−1.547	π_{-4}
63	−2.028	π_{-3} (Tr)	66	−1.831	π_{-3} (Tr)
62	−2.174	π_{-2} (Tr)	65	−1.960	π_{-2} (Tr)
61	−2.406	π_{-1}	64	−2.326	π_{-1}
60	−7.830	π_1	63	−7.755	π_1
59	− 8.660	π_2	62	−8.798	π_2
$APyTM_2$			*APyTCAn*		
71	−0.951	π_{-5}	79	−1.085	π_{-5}
70	−1.538	π_{-4}	78	−1.526	π_{-4}
69	−1.663	π_{-3} (Tr)	77	−1.728	π_{-3} (Tr)
68	−1.709	π_{-2} (Tr)	76	−1.850	π_{-2} (Tr)
67	−2.308	π_{-1}	75	−2.301	π_{-1}
66	−7.742	π_1	74	−7.735	π_1
65	−8.789	π_2	73	−8.775	π_2
$APyTAn_2$					
93	−1.027	π_{-5}	89	−2.252	π_{-1}
92	−1.463	π_{-4}	88	−7.684	π_1
91	−1.501	π_{-3}(Tr)	87	−8.732	π_2
90	−1.517	π_{-2} (Tr)			

Positive indices mark the occupied orbitals; negative indices mark the unoccupied orbitals; the HOMO orbital of a given molecule is indicated by 1, the LUMO orbital by −1; the symbol Tr refers to π orbitals localized on triazinyl ring.

Table 4 lists the characteristics of spectroscopically important CNDO/S singlet transitions of the studied compounds for their optimized geometry.

As the shape of MOs and the character of locally excited (LE) states for APy and its *N*-substituted derivatives are practically the same as they are for pyrene, we have used the Platt notation for the description of the substituted pyrene's LE states, though it is not exactly correct. The optical transitions of APy and APyAc are of the L_b type (π_1–π_{-2}, π_2–π_{-1}), L_a type (π_1–π_{-1}), and B_b types (π_2–π_{-1}, π_1–π_{-2}), i.e. of the same types as those for pyrene. Two new transitions appeared in the excited singlet state manifold for *N*-triazinyl derivatives. The new transitions are connected with a strong charge transfer (CT) from the pyrene-localized HOMO to the MO's π_{-2} and π_{-3} localized on the triazinyl ring. These transitions have a high dipole moment (D) and a low oscillator strength. The L_b and B_b states of *N*-triazinyl derivatives are formed, in contrast to APy and APyAc, by mixing of π_2–π_{-1} and π_1–π_{-4} transitions; MO π_{-4} has practically the same shape as π_{-2} for APy and APyAc. No mixing of the local pyrene L_b and L_a states mutually nor with CT states for the optimized geometry of the studied compounds was found. Our calculations predict mixing between both CT states for APyTCM and APyTCAn.

According to the presented theoretical data, the energy and the character of L_b, L_a and B_b states do not depend practically on the a type of *N*-substituent; this conclusion is further supported by the fact that experimental absorption spectra of all *N*-derivatives of APy are practically identical - see e.g. the spectrum of $APyTM_2$ [10,15,16] (Fig. 1). Furthermore, the observed and calculated absorption spectra are in a very good agreement. Contrary to the pyrene-type LE states, energy of the CT states dramatically raises with the

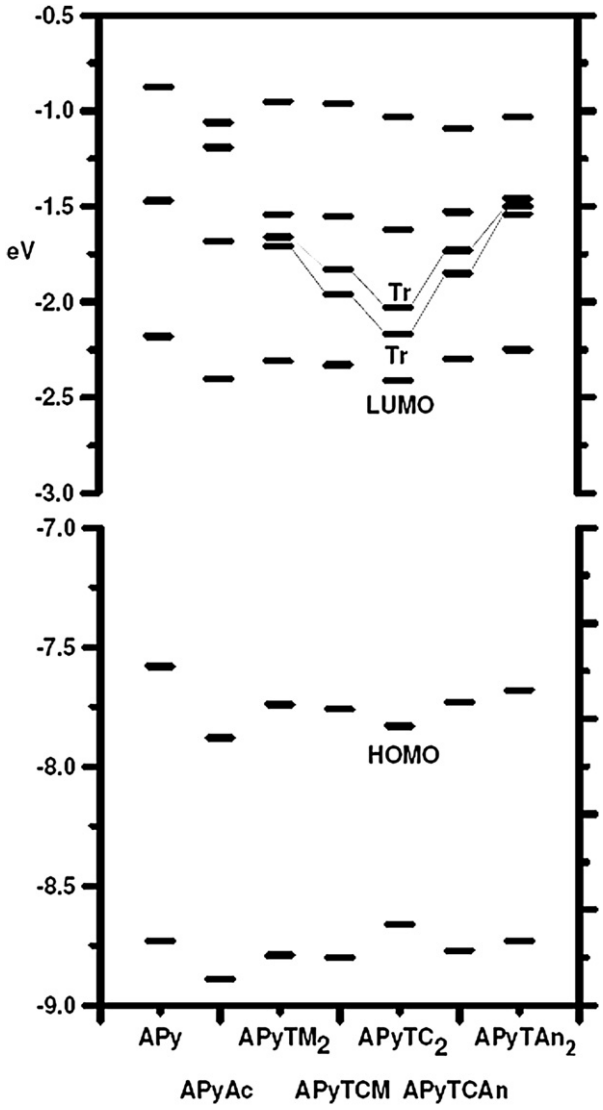


Fig. 2. MO energies of studied compounds.

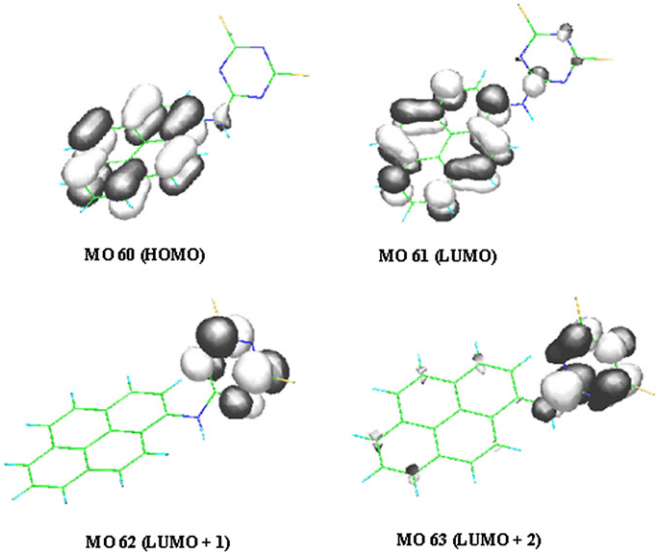


Fig. 3. The shape of spectroscopically important MOs of $APyTC_2$.

Table 4
CNDO/S transitions of studied compounds; (* denotes experimental absorption maxima in dibutyl ether).

State	Energy (10^3 cm^{-1})	Osc. St. (f)	Main CI configuration	Dipole moment (D)	Character of transition	
APy						
1	26.72	0.062	40–42 (0.80) 39–41 (0.54)	1.8	L_b	
2	28.60	0.810	40–41 (0.95)	2.3	L_a	27.71*
3	32.00	0.005	40–43 (0.96)	2.6		
4	35.70	0.813	39–41 (0.81) 40–42 (0.53)	1.6	B_b	
APyAc						
1	27.05	0.031	48–50 (0.78) 47–49 (0.58)	7.2	L_b	
2	29.15	0.835	48–49 (0.96)	7.8	L_a	29.33*
3	32.85	0.002	48–52 (0.92)			
4	34.33	0.072	48–51 (0.71)	15.2	CT	
5	35.84	0.793	47–49 (0.76) 48–50 (0.55)	7.9	B_b	
$APyTC_2$						
1	27.06	0.013	60–64 (0.77) 59–61 (0.59)	4.8	L_b	
2	28.76	0.878	60–61 (0.96)	9.0	L_a	29.32*
3	30.91	0.086	60–63 (0.93)	24.5	CT	
4	31.27	0.005	60–62 (0.96)	32.9	CT	
5	33.02	0.001	60–65 (0.94)			
6	35.92	0.867	59–61 (0.77) 60–64 (0.59)	6.8	B_b	
APyTCM						
1	27.02	0.016	63–67 (0.78) 62–64 (0.59)	1.9	L_b	
2	28.86	0.917	63–64 (0.97)	3.6	L_a	29.31*
3	31.55	0.038	63–66 (0.76) 63–65 (0.59)	23.7	CT	
4	32.57	0.004	63–65 (0.77) 63–66 (0.57)	27.0	CT	
5	32.97	0.001	63–68 (0.93)			
6	35.88	0.870	62–64 (0.77) 63–67 (0.59)	2.2	B_b	
$ApyTM_2$						
1	27.01	0.020	66–70 (0.77) 65–67 (0.59)	2.6	L_b	
2	28.95	0.929	66–67 (0.97)	3.6	L_a	29.31*
3	32.81	0.026	66–69 (0.85)	21.0	CT	
4	32.94	0.006	66–71 (0.85)			
5	34.31	0.001	66–68 (0.96)	30.7	CT	
6	35.91	0.864	65–67 (0.77) 66–70 (0.59)	3.6	B_b	
APyTCAn						
1	27.31	0.022	74–78 (0.77) 73–75 (0.60)	4.4	L_b	
2	28.97	0.955	74–75 (0.97)	4.6	L_a	29.31*
3	32.17	0.030	74–77 (0.72) 74–76 (0.64)	24.6	CT	
4	33.00	0.001	74–81 (0.94)			
5	33.53	0.007	74–76 (0.73) 74–77 (0.62)	28.8	CT	
6	36.05	0.922	73–75 (0.77) 74–78 (0.60)	4.1	B_b	
$APyTAn_2$						
1	27.68	0.033	87–89 (0.59) 88–92 (0.49)	1.3	L_b	
2	29.03	0.948	88–89 (0.96)	1.2	L_a	29.24*
3	33.19	0.001	88–97 (0.98)			
4	34.18	0.045	88–91 (0.77) 88–92 (0.62)	23.9	CT	
5	35.72	0.049	88–90 (0.88)	26.4	CT	
6	36.12	0.772	87–89 (0.75) 88–92 (0.51)	2.2	B_b	

successive substitution of chlorine atoms by the methoxy or the anilino groups (Table 4, Fig. 4).

From these theoretical results it is obvious that the dependence of q_F of the studied compounds on their chemical structure may be connected with energy and polarity of the CT states. As the number of Cl atoms increases, an electron-withdrawing character of the triazinyl ring is enhanced. At the same time, the energy of CT states decreases. It may be assumed that the energy of the highly polar CT states could decrease in polar solvents even more significantly than the energy of LE states, it could fall to the vicinity or even below the LE fluorescent state and participate in the deactivation process of the excited state.

Our ZINDO calculations, took into account the solvent, and clearly illustrate the dramatic influence of the solvent polarity on the energy of CT states. We have calculated the $APyTC_2$ (Fig. 5), APyTCM and $APyTM_2$ singlet excited states energy for the optimized geometry of those compounds in three differently polar solvents: dibutyl ether ($F = 0.096$), ethyl acetate ($F = 0.200$) and acetonitrile ($F = 0.305$). According the results, the L_b state energy and its dipole moment do not depend on the solvent polarity while the L_a state shifts somewhat bathochromically and its dipole moment slightly increases with increasing solvent polarity. On the contrary, the CT states of those compounds show high dipole moments and, depending on solvent polarity, their energy decreases toward the L_a state. No mixing of the local pyrene L_b and L_a states with CT states for optimized geometry of the studied compounds was found. This combination of molecular states and their polarity shifts offer a possible explanation of the fluorescence quenching of the $APyTC_2$ and APyTCM already in non-polar DBE. The $APyTM_2$ and $APyTAn_2$ compounds show a large L_a-CT gap, so the CT states can play no role here, not even in the strongly polar solvents. The very low q_F for $APyTM_2$ in methanol – in comparison with the high q_F in polar aprotic acetonitrile – may be caused by H-bonding of methanol to the *N*-atoms of the triazine resulting in an increase of electronegativity of the trizinyl ring.

We have previously shown [15] that whereas $APyTC_2$ and APyTCM in 2-methyltetrahydrofuran (2-MTHF) do not fluoresce at room temperature, they show a relatively intense fluorescence in the frozen state at −190 °C but their q_F still depends on the number

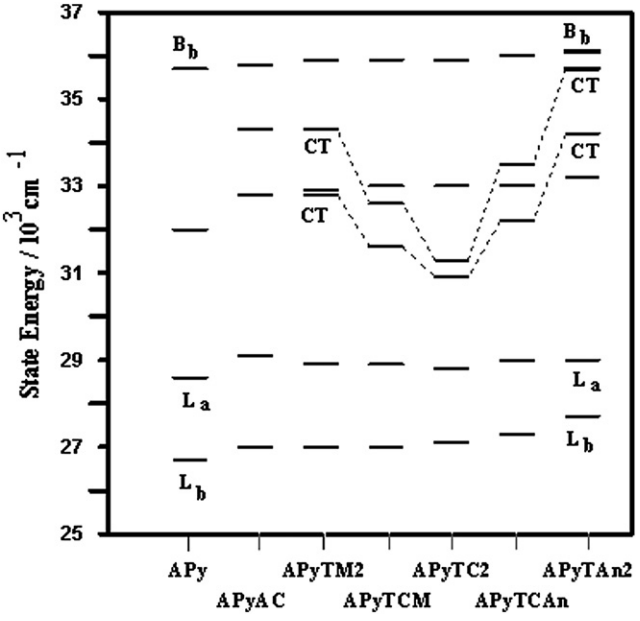


Fig. 4. CNDO/S excited state energies of studied compounds.

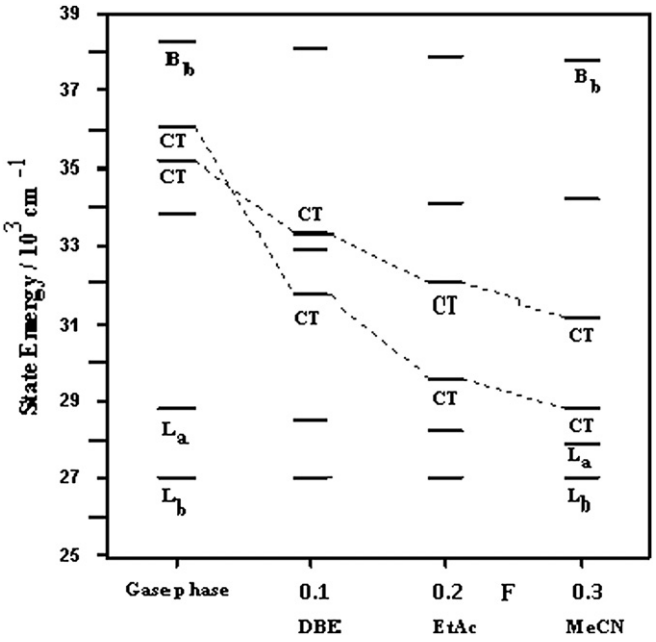


Fig. 5. ZINDO excited state energies of $APyTC_2$ in dependence on solvent polarity function $F = (\varepsilon - 1/2\varepsilon + 1) - (n^2 - 1/2n^2 + 1)$; ε, dielectric constant; n, refractive index.

of chlorine atoms on the triazinyl ring (Table 1). The shape of their low temperature fluorescence spectra is practically identical with those of $APyTM_2$ in 2-MTHF at room temperature. The fluorescence maxima of $APyTM_2$ in 2-MTHF are hypsochromically shifted by 8 nm at low temperature compared with that at room temperature; the Stokes shift is 3670 cm^{-1} at room temperature and is 2880 cm^{-1} at −190 °C. As no changes of molecular geometry can be expected at low temperature in the solid state in comparison with the solution at room temperature, the dramatic q_F dependence on temperature could result from geometry changes during the lifetime of the emitting excited state.

As the geometry of the molecules in their electronic excited states was not optimized in our calculations, we have investigated the character of the vertical electronic transitions for different geometries of the ground state. Though the structure of the molecules discussed here is characterized by two dihedral angles α and β only, the choice of their mutual combination is rather complicated. We calculated the characteristics of the singlet excited states of $APyTC_2$, APyTCM and $APyTM_2$ for angle β fixed to the value corresponding to the optimized geometry, angle α was chosen as 0°, 30°, 60° and 90°. From the resulting data we can draw the following facts and conclusions for the $APyTC_2$ molecule:

- no mixing of electronic states occurs for α equals 0° and 30°; all excited states retain their character;
- for α equals 60° and 90°, a significant mixing of L_a and CT states occurs; this results in the L_a state dipole moment increase and in the decrease of that of the CT state; simultaneously, the oscillator strength of L_a state drops while that of the CT state dramatically rises;
- the L_a state energy decreases somewhat with increasing α.

For APyTCM, partial mixing of L_a with the first CT states for α equal to 60° and 90° causes a decrease of the dipole moment, simultaneously with a strong rise of the oscillator strength of this CT state. In the case of $APyTM_2$, the energy gap between the L_a and CT states is large and no mixing of the excited states occurs at any geometry.

We calculated the characteristics of the singlet excited states for $APyTC_2$, APyTCM and $APyTM_2$ also for angle β fixed to 0° (i.e. strong conjugation of $2p_z$ amino nitrogen electrons with π-electrons of the pyrene ring); angle α was chosen as 0° (planar geometry), 30°, 60°, and 90°. The following facts are evident from the data obtained:

- for $APyTC_2$, mixing of L_a with one of the CT states occurs for $\alpha = 60°$; the L_a state gains the character of CT state, its dipole moment increases, and, at the same time, an originally "pure" CT state loses its CT character by mixing with L_a state leading to a decrease of its dipole moment and a strong increase of the oscillator strength. Furthermore, the "pure" CT state appears in between L_b and L_a states for $\alpha = 90°$ geometry;
- mixing of L_a and CT states is also noticeable for APyTCM and it brings about some features of both APyTCM and $APyTC_2$ molecules;
- no mixing of the excited states was found for $APyTM_2$; the energy of its CT state drops with increasing α but the character of individual excited states remains the same.

It should be emphasized that neither the energy of the L_b and B_b states nor their character were influenced by assumed geometry changes in the case of *N*-derivatives of 1-aminopyrene, according to our calculations.

As for the influence of the temperature on q_F of some studied compounds in 2-MTHF (Table 1), the ratio of L_a and CT states in a mixed emitting state determines the deactivation rate and hence the fluorescence quantum yield. In any case, the energy gap between L_a and CT states that depend on electronegativity of the triazinyl ring is the dominant structural mechanism determining the q_F of *N*-triazinyl derivatives of 1-aminopyrene.

According to the semiempirical methods we used (CNDO/S, ZINDO), the first excited singlet state of 1-APy and its *N*-derivatives in their optimized structures, is the L_b state. But, the fluorescence decay of all fluorescent derivatives show a single-exponential character with τ_F equal $4.0–7.0 \times 10^{-9}$ s and $k_F \sim 10^7\ s^{-1}$ [10]. Most probably the data suggest that L_b and L_a (L_a/*CT*) inversion takes place in the relaxed excited state. It should be noted that the L_b and L_a states are mutually well separated for 2-derivatives of pyrene, without their inversion; these compounds exhibit – similarly to pyrene -fluorescence from the first excited L_b state with $\tau_F \sim 10^{-7}$ s [10].

3. Conclusions

The geometry and the characteristics of electronic excited states of five *N*-triazinyl derivatives of 1-aminopyrene were calculated using semiempirical AM1, CNDO/S and ZINDO/S methods. It was found that the first six electronic transitions are of ππ* type. Besides the L_b, L_a and B_b transitions localized on the amino pyrene moiety, there are other transitions with a strong charge transfer to the π*MO localized on triazinyl ring. These CT transitions are characterized by very low oscillator strength and a very high dipole moment. In agreement with experimental absorption spectra, the energy of local transitions does not depend on a substituent on the triazinyl ring and on solvent polarity. On the contrary, the energy of the CT state decreases dramatically with electronegativity of the triazinyl ring (which is influenced by the type of the substituent), and decreases with the solvent polarity. Experimental fluorescence quantum yields of the corresponding compounds show the same falling trends. We therefore conclude that the fluorescence quenching is caused by participation of the CT state in an excited state deactivation mechanism due to their downward shift to the vicinity or even below the emitting state and by their mixing. Obviously, the energy gap between the CT and the emitting state determines the fluorescence quantum yield of *N*-triazinyl derivatives of 1-aminopyrene.

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