

Luminescence-laser classification of heteroaromatic and aromatic compounds

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Abstract

The luminescent and laser properties of heteroaromatic and aromatic compounds are reviewed and discussed on the basis of all possible mutual arrangements of singlet and triplet states. All heteroaromatic compounds are divided into five classes. It is shown that a heteroaromatic compound can only be an effective laser dye if it belongs to class V (a situation where the $T_{n\pi^*}$ level lies at higher energy than the $S_{\pi\pi^*}^1$ level). Moreover, it is shown that the energy interval between the $T_{n\pi^*}$ and $S_{\pi\pi^*}^1$ states must be no less than 1000 cm^{-1} since the rate constant of the non-radiative process $S_{\pi\pi^*}^1 \rightarrow T_{n\pi^*} \rightarrow T_{\pi\pi}^1$ is usually 100 times greater than the fluorescence rate constant. The classification is extended to compounds with orbitals of $\pi l, \pi^*, \pi, v\pi^*$ and $\pi l, v\pi^*$ nature. Pure aromatic compounds, the spectral-luminescent properties of which are solely determined by transitions of π -electrons ($\pi \rightarrow \pi^*$), are also divided into five classes, depending on the mutual arrangement of the $S_p(^1L_a)$, $S_a(^1L_b)$, $T_p(^3L_a)$ and $T_b(^3B_b)$ states. It is found that only aromatic compounds of classes IV and V can be effective scintillators and laser dyes. It is also shown that the energy interval $S_a - S_p$ (for class IV) and $T_b - S_p$ (for class V) must be no less than 1000 cm^{-1} . To illustrate the classifications for heteroaromatic and aromatic compounds, 12 specifically chosen compounds were studied experimentally and quantum chemically. The quantum yields, γ and decay times, τ_f of fluorescence in aerated and non-deaerated ethanol or cyclohexane solutions were measured. The oscillator strength, f_o , fluorescence rate constant, k_f , natural lifetimes, τ_0^T and intersystem crossing rate constants, k_{ST} are calculated. The laser ability of each of the compounds studied is tested. The suggested classification schemes can be extremely useful in the quest for effective scintillators and laser dyes among hypothetical heteroaromatic and aromatic molecules, enabling evaluation of these properties for a particular compound using only quantum chemical simulations. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Laser dyes; Fluorescence; Classification of heteroaromatic and aromatic compounds

1. Introduction

To a large extent, the spectral-luminescent and laser properties of heteroaromatic and aromatic compounds are dependent upon the mutual ar-

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range of singlet and triplet levels and their orbital nature [1]. The majority of laser dyes are heteroaromatic compounds [2]. In most cases the fluorescence properties of a heteroaromatic molecule are determined by three types of electronic transitions: $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $\pi l \rightarrow \pi^*$ ($l \rightarrow a_\pi$). Depending on the arrangement of the singlet and triplet levels of $\pi\pi^*$, $n\pi^*$ and πl , π^* orbital nature, five different spectral-luminescent classes of heteroaromatic molecules can be identified [3,4]. It has been noted that a heteroaromatic compound is capable of laser action if it belongs to class V (according to the above classification): $S_{n\pi^*}$ and $T_{n\pi^*}$ levels must be situated above the $S_{\pi\pi^*}^1$ level [5]. However, not even all compounds of this type show effective laser action. The reason for this is that the quantum yield of fluorescence strongly depends upon the size of the energy gap between $T_{n\pi^*}$ and $S_{\pi\pi^*}^1$ levels. If this gap is less than 1000 cm^{-1} the non-radiative process $S_{\pi\pi^*}^1 \rightsquigarrow T_{n\pi^*} \rightsquigarrow T_{\pi\pi^*}^1$ channel of decay for the $S_{\pi\pi^*}^1$ state becomes very effective [5]. The rate of this process could be 100 times greater than the rate of fluorescence.

In the case of pure aromatic compounds the fluorescence and laser properties are entirely determined by $\pi \rightarrow \pi^*$ transitions. This class of aromatic compounds is also of great interest since some of them are excellent scintillators and give effective laser oscillation in the uv-region of the spectrum [2]. Unfortunately, to date there has been no spectral-luminescent and laser classification scheme for these compounds. The fluorescence properties of aromatic compounds are determined by the arrangement of the S_x and S_p levels. It is known that in a compound where the lowest singlet level is of S_x nature (and hence fluorescence is of ${}^1L_b \rightarrow {}^1A$ nature) there will be no laser action at room temperature [6]. It is also known that not all compounds with fluorescence of ${}^1L_a \rightarrow {}^1A$ nature are effective laser dyes or scintillators. The laser parameters of an aromatic compound are determined by many spectral factors such as the $S_0 \rightarrow S^1$ transition oscillator strength, fluorescence decay time and quantum yield [7]. Some publications also point out that the fluorescence properties of aromatic compounds are dependent on the position of the T_β

level [8–10]. All these factors need further investigation and systematization.

The objectives of this study are:

1. to review the spectral-luminescent classification of heteroaromatic compounds and to discuss the role of the $T_{n\pi^*} - S_{\pi\pi^*}^1$ energy gap;
2. to propose a spectral-luminescence and laser classification scheme for aromatic compounds and to discuss the role of the $S_x - S_p$ and $T_\beta - S_p$ energy gaps.

To illustrate the spectral-luminescent and laser classifications of heteroaromatic and aromatic compounds and to discuss related aspects the following compounds are studied: (1) acridine; (2) 1-azaanthracene; (3) 2-azaanthracene; (4) PPO; (5) PPD; (6) naphthalene; (7) anthracene; (8) tetracene; (9) *p*-quaterphenyl; (10) 3,3'-dimethyl-*p*-quaterphenyl; (11) β NPD and (12) β NND. The structural formulae of the compounds studied are shown in Fig. 1. The fluorescence properties of these compounds are presented in Table 1.

2. Experimental methods

The compounds studied were recrystallized, sublimized and purity controlled using chromatography. The absorption spectra of the substances were recorded using a SPECORD M40 spectrophotometer with spectroquality ethanol or cyclohexane as the solvent. A Hitachi MPF-4 spectrofluorimeter was used to record the fluorescence spectra. The quantum yields of fluorescence were measured using the method described in [11] and a highly diluted solution of 9,10-diphenylanthracene in cyclohexane served as a standard. The fluorescence quantum yield of 9,10-diphenylanthracene was measured using the method described in [12] and found to be 0.90.

In order to minimize reabsorption effects in cases where there is a large overlap between long-wavelength absorption and fluorescence bands, solutions for fluorescence quantum yield and lifetime measurements were prepared following the recommendations given in [13]. Since some of the substances investigated reveal a very structured long-wavelength absorption band, the spectral bandpass of the excitation monochromator was

Table 1
Experimental and calculated values for the main fluorescence parameters of diluted ethanol (1–3) and cyclohexane (4–12) solutions of the investigated aromatic and heteroaromatic compounds

No	S	ν_{00} (cm ⁻¹)	$\Delta\nu$ (cm ⁻¹)	γ	τ_f (ns)	τ_f^{Ex} (ns)	γ^*	τ_f^* (ns)	$\tau_f^{\text{Ex}*}$ (ns)	τ_0^{T} (ns)	$k_f \times 10^{-7}$ (s ⁻¹)	$k_{\text{ST}} \times 10^{-7}$ (s ⁻¹)	f_e	Nature of S ¹
1	C _{2v}	25 700	3040	0.015	0.80	53.33	0.015	0.80	53.33	–	1.88	123.13	0.115*	S _v ¹ (L _u)
2	C _s	25 380	3260	0.19	16.50	86.84	0.23	19.50	84.78	–	1.18	3.95	0.048*	S _v ¹ (L _u)
3	C _s	25 200	3460	0.53	15.40	29.06	0.62	18.00	29.03	33.80	3.44	2.11	0.158	S _v ¹ (L _u)
4	C ₁	29 760	6660	0.89	1.40	1.60	0.94	1.50	1.60	1.90	62.70	4.00	1.750	S _v ¹ (L _u)
5	C ₂	32 080	620	0.80	1.35	1.69	0.84	1.45	1.73	2.00	57.80	11.03	1.590	S _v ¹ (L _u)
6	D _{2h}	31 170	3140	0.23	96.40	417.40	0.42	175.00	418.00	–	0.24	0.33	0.006*	S _g ¹ (L _g)
7	D _{2h}	26 580	4100	0.24	.40	18.30	0.29	4.70	16.20	16.00	6.20	15.10	0.250	S _g ¹ (L _g)
8	D _{2h}	20 950	3700	0.21	6.00	28.57	0.29	8.30	28.60	28.60	3.49	8.55	0.190	S _g ¹ (L _g)
9	D ₂	30 100	7640	0.81	0.85	1.05	0.82	0.87	1.06	1.45	94.25	20.68	2.360	S _g ¹ (L _g)
10	C ₂	29 820	7840	0.88	0.90	1.02	0.90	0.92	1.02	1.38	97.83	10.87	2.580	S _g ¹ (L _g)
11	C ₁	29 400	3600	0.20	13.50	67.50	0.32	20.00	62.50	–	1.60	3.40	0.040*	S _g ¹ (L _g)
12	C ₂	29 180	5320	0.85	2.90	3.40	0.94	3.20	3.40	1.90	29.40	1.87	0.870	S _g ¹ (L _g)

Headings from left to right: No, compound number; S, symmetry group; ν_{00} , symmetry line wavenumber; $\Delta\nu_{\text{ST}}$, Stokes shift; γ , fluorescence quantum yield; τ_f , fluorescence decay time; τ_{00}^{Ex} , experimental natural fluorescence lifetime; τ_0^{T} , natural lifetime; k_f , fluorescence rate constant; k_{ST} , intersystem crossing rate constant; f_e , S₀ → S¹ transition oscillator strength. The nature of the S¹ state is given in Clar's notation with Platt's notation in parentheses.

* Parameters for deaerated solutions.

^a Values calculated using Eq. (4).

chosen to be not greater than 0.5 nm in each case. The emission slit width was chosen depending on the fluorescence intensity, but in each case it was not large enough to cause distortion in the fluorescence spectrum.

The decay times of fluorescence, τ_f , were measured using either a SLM-4800S phase fluorimeter or installations based on the stroboscopic principle combined with single photon counting measurements [14], depending on the value of τ_f . The natural lifetimes were calculated using the for-

mula presented in [14] and modified in [15]:

$$\frac{1}{\tau_0} = 2.88 \times 10^{-9} n^2 \langle \bar{\nu}_r^{-3} \rangle^{-1} \theta \int \frac{\epsilon(\bar{\nu}) d\bar{\nu}}{\bar{\nu}}, \quad (1)$$

where $\theta = 9n/(n^2 + 2)^2$ is the Lorentz–Lorenz factor [16], n is the refractive index of the solvent, $\bar{\nu}$ is the frequency in cm^{-1} and $\epsilon(\bar{\nu})$ is the molar extinction coefficient. Deaeration was carried out using the method described in [17]. The value of k_{ST} was calculated by taking into account the fact that the fluorescence quantum yield of highly

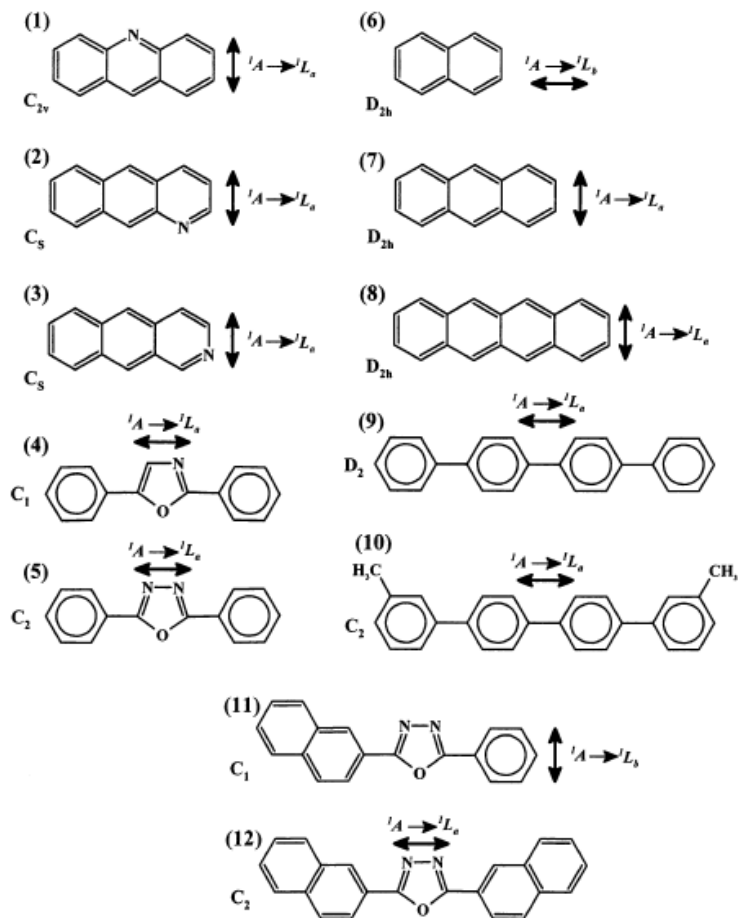


Fig. 1. Structural formulae of the investigated compounds. The symbol \leftrightarrow indicates the direction of polarization of the $S_0 \rightarrow S^1$ transition (the nature of the $S_0 \rightarrow S^1$ transition is given in Platt's notation).

deaerated solutions of photostable compounds can be determined using Eq. (2), with only the intramolecular quenching processes considered [16],

$$\gamma^* = \frac{k_f}{(k_f + k_s + k_{ST})} \quad (2)$$

where γ^* is the fluorescence quantum yield of the deaerated solution and k_s is the internal conversion rate coefficient. From Eq. (2) one obtains:

$$k_s + k_{ST} = \frac{(1 - \gamma^*)}{\tau_f^*},$$

where τ_f^* is the fluorescence decay time for the deaerated solution. For Ermolaev–Sveshnikova [18] molecules, k_s is very much less than $k_f + k_{ST}$ and in many cases $k_s \ll k_{ST}$. Hence:

$$k_{ST} = \frac{(1 - \gamma^*)}{\tau_f^*}.$$

The Stoke's shift values were determined using the formulae:

$$\Delta\tilde{\nu}_{ST} = \tilde{\nu}_a^{c.g.} - \tilde{\nu}_f^{c.g.},$$

where,

$$\tilde{\nu}_a^{c.g.} = \int \tilde{\nu}_a \varepsilon(\tilde{\nu}_a) d\tilde{\nu}_a \quad \text{and} \quad \tilde{\nu}_f^{c.g.} = \int \tilde{\nu}_f I(\tilde{\nu}_f) d\tilde{\nu}_f.$$

$\tilde{\nu}_a^{c.g.}$ and $\tilde{\nu}_f^{c.g.}$ are the 'centre of gravity' or 'first moment' of the long-wave absorption band and fluorescence spectrum, respectively. $\tilde{\nu}_a$ and $\tilde{\nu}_f$ are the frequencies in the range of the absorption and fluorescence spectra and $I(\tilde{\nu}_f)$ is the quantum intensity of fluorescence. The oscillator strengths of well resolved long-wave absorption bands were determined using the formula [16]:

$$f_e = 1.3 \times 10^{-8} \theta \int \varepsilon(\tilde{\nu}) d\tilde{\nu}. \quad (3)$$

The oscillator strengths of low intensity or sub-merged bands were determined using the formula:

$$f_e = \frac{4.514 \tilde{\nu}_a^{c.g.} \gamma}{n^2 (\tilde{\nu}_f^{c.g.})^3 \tau_f^*}. \quad (4)$$

This was obtained by dividing Eq. (3) by a simplified version of Eq. (1), essentially, $\langle \tilde{\nu}^{-3} \rangle^{-1} \approx (\tilde{\nu}_f^{c.g.})^3$.

The error limits determined for the various fluorescence parameters are as follows: quantum yield, $\pm 10\%$, decay time, $\pm 5\%$, symmetry line frequencies, $\pm 60 \text{ cm}^{-1}$, Stokes shift, $\pm 200 \text{ cm}^{-1}$, k_{ST} and k_f values (if $\tau_f < 2 \text{ ns}$) $\pm 15\%$. The error limits for experimental values of the oscillator strength, f_e of the $S_0 \rightarrow S^1$ transitions are within $\pm 15\%$.

Quantum-chemical simulations were performed using the CNDO/S or PPP-CI methods with parameters taken from [19–21].

A routine transverse scheme of pumping was used to test the laser ability of the compounds studied [7]. In testing the laser ability of compounds (4), (5) and (9–12), a XeCl (308 nm) laser was used for pumping, while for the other compounds a N_2 (337 nm) laser was employed.

3. Discussion

3.1. Luminescence-laser classification of heteroaromatic compounds

It is well known that the value of $S-T$ separation of $n\pi^*$ states ($2000-4000 \text{ cm}^{-1}$) is always less than the $S-T$ separation of $\pi\pi^*$ states ($7000-10000 \text{ cm}^{-1}$) [22]. It is also known that, with increasing π conjugation, the energy of $\pi \rightarrow \pi^*$ transitions decreases faster than the energy of $n \rightarrow \pi^*$ transitions [1,3,22]. This is why only five cases of mutual arrangement of $S_{n\pi^*}$, $T_{n\pi^*}$, $S_{\pi\pi^*}$ and $T_{\pi\pi^*}$ states are possible:

- Case I $S_{\pi\pi^*} > T_{\pi\pi^*} > S_{n\pi^*} > T_{n\pi^*}$
- Case II $S_{\pi\pi^*} > S_{n\pi^*} > T_{\pi\pi^*} > T_{n\pi^*}$
- Case III $S_{n\pi^*} > S_{\pi\pi^*} > T_{n\pi^*} > T_{\pi\pi^*}$
- Case IV $S_{n\pi^*} > S_{\pi\pi^*} > T_{n\pi^*} > T_{\pi\pi^*}$
- Case V $S_{n\pi^*} > T_{n\pi^*} > S_{\pi\pi^*} > T_{\pi\pi^*}$

Experimental [22,23] and theoretical [24,25] studies show that the rate constants for intersystem crossing between states of the same orbital nature are of different orders of magnitude to the rate constants for intersystem crossing between states of different orbital natures:

$$k_{ST}(S_{n\pi^*} \rightarrow T_{n\pi^*}; S_{n\pi^*} \rightarrow T_{\pi\pi^*}) \cong 10^6 - 10^9 \text{ s}^{-1}$$

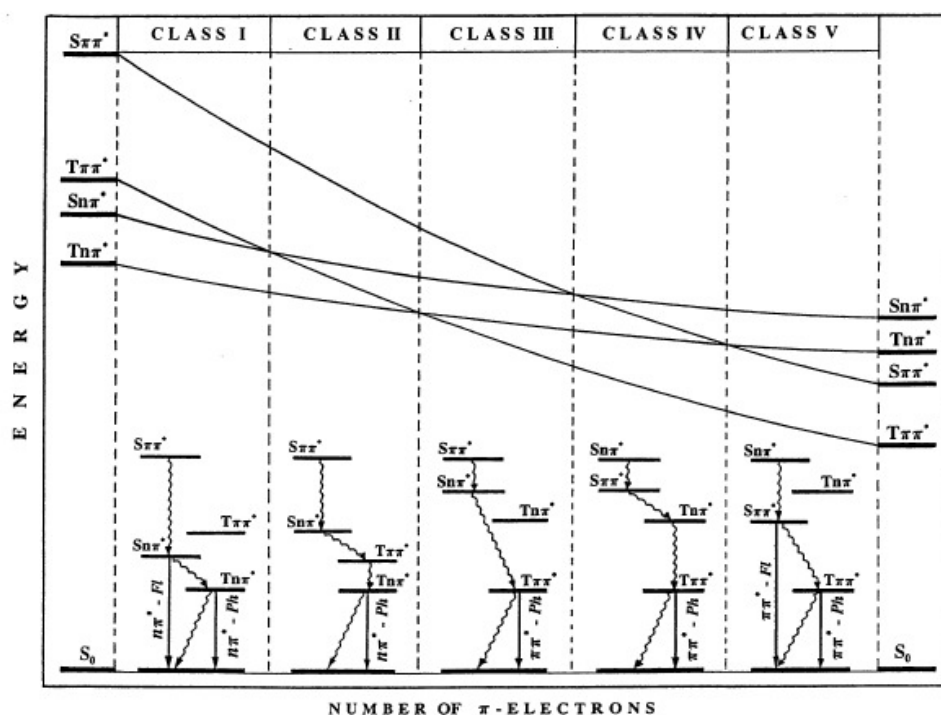


Fig. 2. Five classes of mutual arrangement of $S_{n\pi^*}$, $T_{n\pi^*}$, $S_{\pi\pi^*}$ and $T_{\pi\pi^*}$ states, dominant non-radiative processes and the nature of the resultant radiative processes.

$$k_{ST}(S_{n\pi^*} \rightarrow T_{n\pi^*}; S_{\pi\pi^*} \rightarrow T_{n\pi^*}) \cong 10^{10} - 10^{11} \text{ s}^{-1}$$

Knowing the rate constants for internal conversion between states of different orbital nature $S_{\pi\pi^*} \rightarrow S_{n\pi^*}$, $S_{n\pi^*} \rightarrow S_{\pi\pi^*}$, $T_{n\pi^*} \rightarrow T_{\pi\pi^*}$ and $T_{\pi\pi^*} \rightarrow T_{n\pi^*} \cong 10^{12} - 10^{13} \text{ s}^{-1}$ and the rate constants of radiative transitions (fluorescence and phosphorescence)

$$S_{n\pi^*} \rightarrow S_0 \cong 10^6 - 10^7 \text{ s}^{-1}; S_{\pi\pi^*} \rightarrow S_0 \\ \cong 10^7 - 10^9 \text{ s}^{-1}$$

$$T_{n\pi^*} \rightarrow S_0 \cong 10^2 - 10^4 \text{ s}^{-1}; T_{\pi\pi^*} \rightarrow S_0 \\ \cong 10^{-1} - 10 \text{ s}^{-1}$$

it is not difficult to reach the conclusion that in each class of heteroaromatic compounds there are dominant non-radiative transitions that determine the nature of the final radiative process. Substances of class I can only show fluorescence and

phosphorescence of $n\pi^*$ nature. Substances belonging to class II can show only $n\pi^*$ phosphorescence (the $S_{n\pi^*} \rightarrow S_0$ radiative process cannot compete with the non-radiative $S_{n\pi^*} \rightarrow T_{n\pi^*}$ process). Substances of class III and IV can only show $\pi\pi^*$ phosphorescence due to the fact that the non-radiative processes $S_{n\pi^*} \rightarrow T_{n\pi^*}$ and $S_{\pi\pi^*} \rightarrow T_{n\pi^*}$ are at least 100 times faster than the radiative processes $S_{n\pi^*} \rightarrow S_0$ and $S_{\pi\pi^*} \rightarrow S_0$. Substances from class V usually show $\pi\pi^*$ fluorescence of high quantum yield, although $\pi\pi^*$ phosphorescence is also possible. The mutual arrangement of $\pi\pi^*$ and $n\pi^*$ orbital nature states, the dominant non-radiative transitions and the possible radiative transitions for all five classes are shown in Fig. 2.

Analyses of laser dyes, the most popular of which are presented in [2], show that the majority

are heteroaromatic compounds. Moreover, all heteroaromatic laser dyes belong to class V. However, not all heteroaromatic compounds of this class show effective laser action. It was shown in [5] that the quantum yield of fluorescence and laser ability depend upon the $T_{n\pi^*} - S_{\pi\pi^*}$ energy separation. If the separation is less than 1000 cm^{-1} then the $S_{\pi\pi^*}^1 \rightarrow T_{n\pi^*} \rightarrow T_{n\pi^*}^1$ non-radiative channel of decay becomes very effective. To illustrate this, consider the fluorescence and laser properties of compounds (1)–(3), presented in Table 1. Acridine, when dissolved in inert solvents, belongs to class IV and does not show any fluorescence. However, when acridine is dissolved in ethanol it shows fluorescence (albeit very weakly, $\gamma = 0.015$). Thus, in ethanol acridine belongs to class V but the $T_{n\pi^*} - S_{\pi\pi^*}$ energy gap is slightly less than $200\text{--}300 \text{ cm}^{-1}$. Inversion of the $S_{\pi\pi^*}$ and $T_{n\pi^*}$ levels occurs due to the fact that H-bonding decreases the energy of the $S_{\pi\pi^*}$ state and increases the energy of the $T_{n\pi^*}$ state [22]. 1-azaanthracene belongs to class V in inert and polar solvents but the $T_{n\pi^*} - S_{\pi\pi^*}$ energy gap is slightly less than 1000 cm^{-1} . For example, in heptane $\gamma = 0.06$ for this compound. In 2-azaanthracene however, the $T_{n\pi^*} - S_{\pi\pi^*}$ separation is much greater than 1000 cm^{-1} and hence, $\gamma = 0.53$. The influence of the $T_{n\pi^*} - S_{\pi\pi^*}$ separation is illustrated by the values of k_{ST} (123.13×10^7 , 3.95×10^7 and $2.11 \times 10^7 \text{ s}^{-1}$, respectively). None of these three compounds shows laser action at room temperature, but compound (3) shows good laser oscillation at low temperatures. The reason for the lack of laser action for compound (3) at room temperature is the low value of k_f ($3.44 \times 10^7 \text{ s}^{-1}$).

The role of the $T_{n\pi^*} - S_{\pi\pi^*}$ interval is well illustrated by compounds (4) and (5). Both belong to class V but the $T_{n\pi^*} - S_{\pi\pi^*}$ interval for compound (4) is greater than 3000 cm^{-1} while for compound (5) this gap is slightly less than 1000 cm^{-1} . The decrease in the $T_{n\pi^*} - S_{\pi\pi^*}$ gap is due to the introduction of a second *N*-heteroatom which leads to a reduction in the donor properties of the diazole fragment and hampers the π -electron density transfer onto the peripheral benzene cycles which accompanies the $S_0 \rightarrow S^1$ transition in both PPO and PPD [26]. As a result the *p*-band under-

goes a hypsochromic shift and the value of $f_s(S_0 \rightarrow S_p)$ decreases. The $T_{n\pi^*} - S_{\pi\pi^*}$ gap also decreases due to the proximity of the two *N*-atoms which causes the separation of the $S_{n\pi^*}$ and $T_{n\pi^*}$ levels and hence, a bathochromic shift of the $T_{n\pi^*}$ level occurs. Both (4) and (5) are good laser dyes but the threshold of PPO is twice as low as that of PPD.

Classification of heteroaromatic compounds is regarded for cases where $n\pi^*$ states are associated with $\pi\pi^*$ states but heteroaromatic molecules may also have *l*-pairs and vacant, *v*, orbitals. Hence, singlet and triplet states can be of $\pi l, \pi^*$, $\pi, v\pi^*$ or $\pi l, v\pi^*$ orbital nature. These states can be treated as states mixed with $\pi\pi^*$ states and hence, can be regarded as analogous to $\pi\pi^*$ states. Hence, the above classification can be extended to $\pi l, \pi^*$, $\pi, v\pi^*$ or $\pi l, v\pi^*$ orbital cases. This extended classification for heteroaromatic compounds is shown in Fig. 3 (adapted from [4]). The most effective laser dyes belong to class V, are of $\pi l, \pi^*$ orbital nature and have a large $T_{n\pi^*} - S_{\pi\pi^*}$ energy gap.

3.2. Luminescence-laser classification of aromatic compounds

Spectral-luminescent and hence, laser properties of pure aromatic compounds are, to a large extent, determined by the mutual arrangement of $S_\beta(^1B_b)$, $S_\alpha(^1L_b)$, $S_\beta(^1L_a)$ and the corresponding $T_\beta(^3B_b)$, $T_\alpha(^3L_b)$ and $T_\beta(^3L_a)$ states. The S_β state is biconfigurational, symmetric with respect to the electron coordinates and antisymmetric with respect to the spin coordinates ($\psi_e^+ \psi_s^-$). The S_α state is also biconfigurational but is antisymmetric with respect to both the electron and spin coordinates ($\psi_e^- \psi_s^-$). The corresponding triplet states, T_β and T_α , are of the opposite nature: $\psi_e^- \psi_s^+$ and $\psi_e^+ \psi_s^+$ (see Fig. 4). The energy separation between S_β and S_α states and between T_β and T_α states are determined by double values of the so called electrostatic exchange integrals for singlet and triplet states (K_{nk}^S, K_{nk}^T). The quantity $2K_{nk}$ is known as the Fermi correlation energy. This is much smaller for triplet states due to there being better correlation of the electron orbits [27]. Thus, the mutual arrangement of S_β , S_α , T_β and T_α levels is determined by the Coulomb integral, J_{nk}

★	CLASS I	CLASS II	CLASS III	CLASS IV	CLASS V
n					
π					
σ					
l					
v					
n					
π					
σ					

Fig. 3. Five classes of heteroaromatic compounds for different orbital natures, dominant non-radiative processes and the nature of the resultant radiative processes. Adapted from [4]. The '★' marked column shows orbital nature.

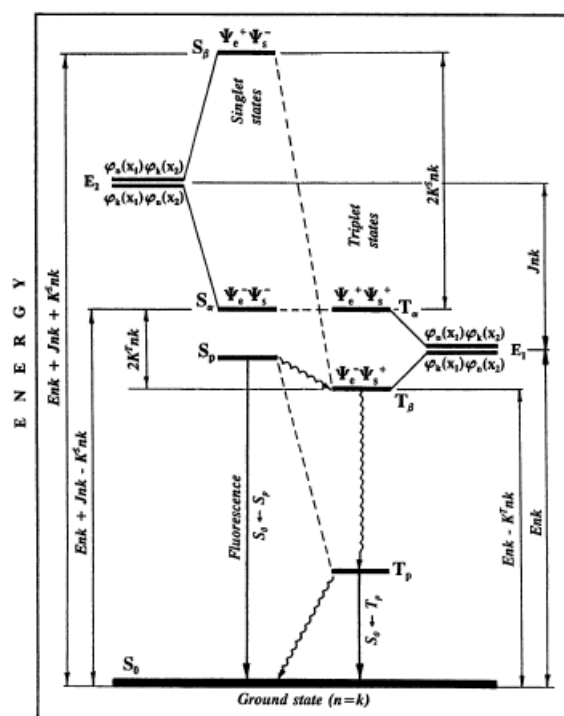


Fig. 4. Quantum mechanical interpretation of the $\pi\pi^*$ orbital nature of $S_\beta(^1B_b)$, $S_\alpha(^1L_b)$, $T_\alpha(^3L_b)$ and $T_\beta(^3B_b)$ states and of the energy separation between them.

and the exchange integrals K_{nk}^S and K_{nk}^T . As one can see from Fig. 4, the T_β level is always situated below the S_α and T_α states.

It was shown in [9] that the S_p state, which is a monoconfigurational singlet state, mixes with the T_β state several times more efficiently than with monoconfigurational triplet states. This means that direct spin-orbit coupling $S_{\pi\pi^*} \leftrightarrow T_{\pi\pi^*}$ occurs through the channels $S_{\pi\pi^*}^+ \leftrightarrow T_{\pi\pi^*}^-$ and $S_{\pi\pi^*}^- \leftrightarrow T_{\pi\pi^*}^+$ (the notation is taken from [9]). In other words, spin-orbit coupling is more effective when the singlet and triplet states are of a different orbital nature (symmetric and antisymmetric or vice versa). Taking this fact into account one can assume that the luminescent-laser properties of an aromatic compound are mostly determined by the mutual arrangement of S_p , S_α , T_p and T_β levels.

With the knowledge that increasing conjugation in the π -system decreases the energy of the S_p and T_p levels more rapidly than the energy of the S_β and S_α (and hence, T_β) states, one can conclude that five different cases of mutual arrangement of S_p , S_α , T_p and T_β states are possible (see Fig. 5). This idea was introduced for the first time in [9].

Analysis of the dominant non-radiative processes shows that compounds of the first two classes may show fluorescence of $^1L_b \rightarrow ^1A$ and phosphorescence of $^3B_b \rightarrow ^1A$ nature. Compounds of class III would show fluorescence of $^1L_b \rightarrow ^1A$ and phosphorescence of $^3L_a \rightarrow ^1A$ nature. Compounds of classes IV and V would show $^1L_a \rightarrow ^1A$ fluorescence and $^3L_a \rightarrow ^1A$ phosphorescence. Since $S_\alpha(^1L_b)$ is a forbidden state, it is only possible for compounds of class IV and V to have high fluorescence rate constants and high fluorescence quantum yields.

However, not necessarily all compounds of class V have high quantum yields. Considering compounds (6)–(8), naphthalene, anthracene, tetracene. According to this suggested classification scheme, naphthalene belongs to class III: the lowest singlet state is $S_2(^1L_b)$ and $T_\beta(^3B_b)$ is situated between the S_x and T_p states. k_f of naphthalene is low ($0.24 \times 10^7 \text{ s}^{-1}$) but k_{ST} is also very low ($0.33 \times 10^7 \text{ s}^{-1}$) due to the forbidden nature of the S_x state. γ of naphthalene is 0.23. The change from naphthalene to anthracene is accompanied by an inversion of the S_p and S_x states, hence, anthracene belongs to class IV. S_p is an allowed state and due to this fact k_f for anthracene ($6.20 \times 10^7 \text{ s}^{-1}$) is 25.8 times greater than that for naphthalene. Nevertheless, γ for anthracene (0.24) is almost equal to that of naphthalene. The explanation of this striking fact is that the T_β level in anthracene is situated just below the

S_p level with which it mixes readily. As a result of this k_{ST} for anthracene is greater than k_{ST} for naphthalene by a factor of 45. The change from anthracene to tetracene is accompanied by a decrease of k_f to almost half the value. Surprisingly however, the quantum yield for tetracene (8) is almost the same ($\gamma = 0.21$) as that of anthracene. This can be explained by the inversion of the S_p and T_β levels, hence, tetracene belongs to class V. k_{ST} for tetracene ($8.55 \times 10^7 \text{ s}^{-1}$) is less than that for anthracene ($15.10 \times 10^7 \text{ s}^{-1}$). However, the energy barrier between the T_β and S_p states is not more than 400 cm^{-1} , hence mixing of these states can still occur. Changing from tetracene to pentacene leads to an increase in the $T_\beta - S_p$ barrier and so k_{ST} decreases further to $2.13 \times 10^7 \text{ s}^{-1}$ although the rate of internal conversion, k_s increases sharply and becomes the predominant non-radiative process

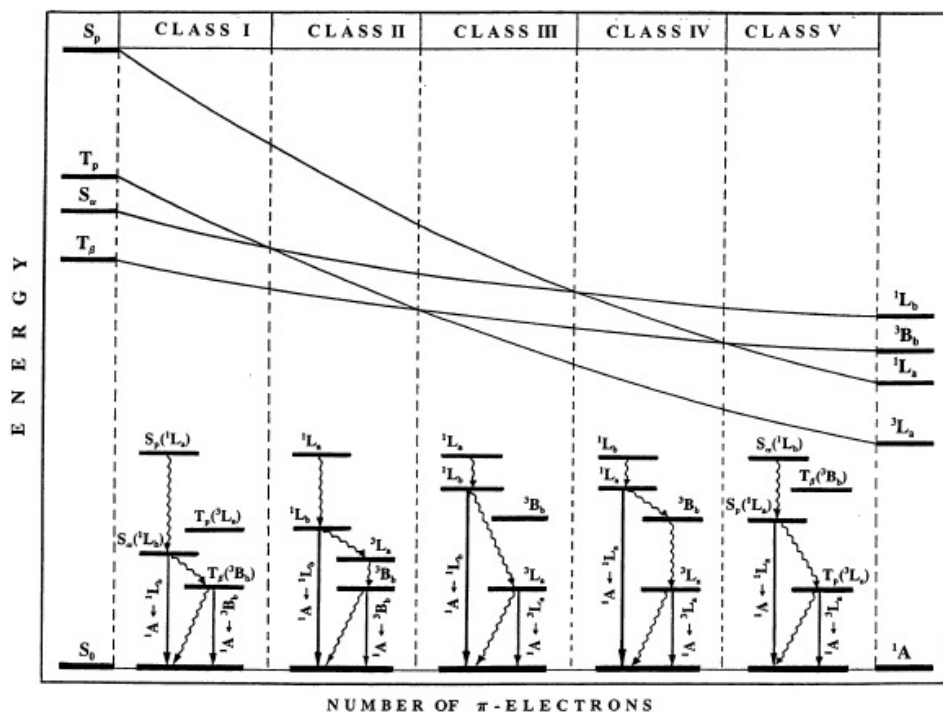


Fig. 5. Five classes of mutual arrangement of $S_p(^1B_b)$, $S_x(^1L_b)$, $T_x(^1L_b)$ and $T_\beta(^3B_b)$ states, dominant non-radiative processes and the nature of the resultant radiative processes.

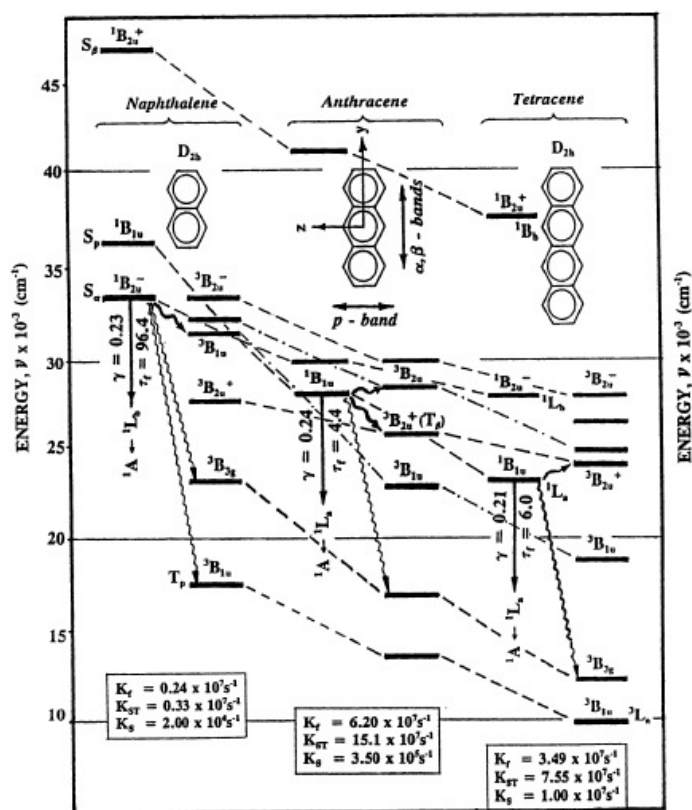


Fig. 6. Simulated (PPP method) singlet and triplet states of naphthalene, anthracene and tetracene. States which mix by spin-coupling are shown joined by wavy arrows. Axes y and z are according to Mulliken [27]. The '+' and '-' signs denote the symmetric and antisymmetric wave functions, respectively. States of the same symmetry are shown joined by dashed lines.

[10]. The detailed arrangement of the singlet and triplet levels in compounds (6)–(8) is shown in Fig. 6. These compounds illustrate the situation where moving from class III through class IV to V leaves γ virtually unchanged (there is a very slight decrease) because k_f and k_{ST} change accordingly. k_{ST} changes due to the change in the position of the T_β level.

Analysis shows that only compounds belonging to classes IV and V can be used as laser dyes. However, it is clear that the best aromatic laser dyes should belong to class V. To illustrate this,

consider compounds (9) and (10). Usually the introduction of methyl groups into an aromatic molecule is accompanied by an increase in k_{ST} [28] (this is due to torsional vibrations of methyl groups) and by a decrease in γ . In the case of compounds (9) and (10) introduction of the two methyl groups actually leads to a decrease in k_{ST} (compare 20.68×10^7 and $10.87 \times 10^7 \text{ s}^{-1}$) and to an increase in γ from 0.81 to 0.88. Analysis of results simulated using the PPP method shows that the introduction of the two methyl groups onto compound (9) leads to the inversion of S_p

and T_β levels. Consequently, compound (9) belongs to class IV while compound (10) belongs to class V. It is obvious that to eliminate the $S_p \rightsquigarrow T_\beta \rightsquigarrow T_p$ channel completely the $T_\beta - S_p$ energy gap must be no less than 1000 cm^{-1} .

The above deals with the classification of pure aromatic compounds but this classification is also applicable to heteroaromatic compounds and in many cases becomes extremely helpful. According to the solely heteroaromatic classification scheme, molecules (11) and (12) belong to class V. However, compound (11) does not show laser action under any conditions [29,30], while compound (12) shows laser oscillation but with a high threshold. The explanation is that compound (11) would belong to class III and compound (12) would belong to class V under the pure aromatic classification scheme. The high threshold of compound (12) can be explained by the fact that the energy gap between the S_x and S_p states is less than 1000 cm^{-1} and hence, under intensive excitation (pumping) the S_p state acquires the forbidden character of the S_x state through mixing.

4. Conclusion

On the basis of the quantum chemical and experimental analyses of the spectral-luminescent and laser properties of heteroaromatic and aromatic compounds the following conclusions may be drawn.

1. Depending on the mutual arrangement of the $S_{\pi\pi^*}$, $T_{\pi\pi^*}$, $S_{n\pi^*}$ and $T_{n\pi^*}$ states, all heteroaromatic compounds may be divided into five classes. Only those heteroaromatic compounds belonging to class V, with the $T_{n\pi^*} - S_{\pi\pi^*}^1$ energy gap exceeding 1000 cm^{-1} can have high fluorescence quantum yields and be used as effective laser dyes. The classification can be extended to compounds with orbitals of $\pi l, \pi^*$, $\pi, v\pi^*$ or $\pi l, v\pi^*$ nature. Heteroaromatic compounds with $\pi l, \pi^*$ orbital nature belonging to class V are extremely effective laser dyes since $\pi l \rightarrow \pi^*$ transitions, accompanied by internal charge transfer (ICT), usually provide large $f_d(S_0 \rightarrow S^1)$ and hence, high fluorescence rate constants.
2. All aromatic compounds may also be divided into five classes depending on the mutual arrangement of $S_p(^1L_a)$, $S_x(^1L_b)$, $T_p(^3L_a)$ and $T_\beta(^3B_b)$ states. It is only possible for aromatic compounds of classes IV and V to be effective scintillators and laser dyes. However, aromatic compounds of class IV can only be effective if the $S_x(^1L_b) - S_p(^1L_a)$ energy gap exceeds 1000 cm^{-1} . Otherwise the S_p state would mix with the S_x state and acquire partly forbidden character. It is also desirable that aromatic compounds of class V have a $T_\beta - S_p$ interval larger than 1000 cm^{-1} otherwise the $S_p \rightsquigarrow T_\beta \rightsquigarrow T_p$ non-radiative channel will depopulate the S_p state quite effectively.
3. These classification schemes for heteroaromatic and aromatic compounds will be useful in the search for effective scintillators and laser dyes. This requires analysis of the singlet and triplet states. Heteroaromatic compounds can be effective if they belong to class V according to the scheme for heteroaromatic compounds or to classes IV and V according to the scheme for aromatic compounds. The $T_{n\pi^*} - S_{\pi\pi^*}^1$, $S_x - S_p$ and $T_\beta - S_p$ energy intervals should be no less than 1000 cm^{-1} . Prediction as to the effectiveness of a particular compound could be made using only PPP-CI and CNDO/S simulation methods.

References

- [1] R.S. Becker, Theory and Interpretation of Fluorescence and Phosphorescence, John Wiley, New York, London, Sydney, Toronto, 1969.
- [2] M. Maede, Laser Dyes, Academic Press, Tokyo, 1984.
- [3] R.N. Nurmuhametov, V.G. Plotnikov, D.N. Shigorin, J. Phys. Chem. (USSR) 40 (1966) 1154.
- [4] D.N. Shigorin, V.G. Plotnikov, Rep. Acad. Sci. (USSR) 234 (1) (1977) 121.
- [5] N.I. Nijegorodov, Ph.D. Dissertation, Russian Friendship University, Moscow, 1979.
- [6] N.I. Nijegorodov, W.S. Downey, M.B. Danailov, Spectrochim. Acta Part A 56 (2000) 783.
- [7] K.H. Drexhage, in: F.R. Schafer (Ed.), Dye lasers, Springer, Berlin, 1990.
- [8] R.E. Kellog, J. Chem. Phys. 44 (1966) 411.
- [9] G.B. Maier, D. Sc. Dissertation, University of Tomsk, Russia, 1987.
- [10] N.I. Nijegorodov, V. Ramachandran, D.P. Winkoun, Spectrochim. Acta Part A 53 (1997) 1813.

- [11] A.S. Cherkasov, *J. Phys. Chem. USSR* 29 (1955) 2209.
- [12] J.N. Demas, G.A. Crosby, *J. Phys. Chem.* 75 (1971) 991.
- [13] J.V. Morris, M.A. Mahaney, J.R. Huber, *J. Phys. Chem.* 80 (1976) 969.
- [14] J. Birks, I. Munro, *J. Achievements Phys. Sci. Moscow* 105 (1971) 251.
- [15] N.I. Nijegorodov, *J. Appl. Spectrosc. (Eng. Trans.)* 56 (1992) 84.
- [16] A.N. Terenin, *Photonics of Dyes and Related Organic Compounds*, Science, Leningrad, 1967.
- [17] A.V. Aristov, V.A. Kusun, A.S. Cherkasov, *Opt. Spectrosc. (Eng. Trans.)* 33 (1973) 230.
- [18] V.L. Ermolaev, E.B. Sveshnikova, *Acta Phys. Pol.* 34 (1968) 771.
- [19] V. Minkin, B. Simkin, V. Minjaev, *Theory of Composition of Molecules*, High School, Moscow, 1979, p. 269.
- [20] J. Griffiths, *Dyes Pigments* 3 (1982) 211.
- [21] J. Griffiths, *Chem. Br.* November (1986) 997.
- [22] R.N. Nurmuhametov, *Absorption and Fluorescence of Aromatic Compounds*, Chemistry, Moscow, 1971.
- [23] K.A. Rogojin, V.M. Komarov, A.N. Rodionov, V.G. Plotnikov, D.N. Shigorin, *J. Phys. Chem. (USSR)* 23 (1976) 343.
- [24] V.G. Plotnikov, B.A. Dolgikh, V.M. Komarov, *Opt. Spectrosc. (USSR) (English Trans.)* 43 (1977) 1072.
- [25] V.G. Plotnikov, B.A. Dolgikh, *Opt. Spectrosc. (USSR) (English trans)* 44 (1978) 450.
- [26] N.I. Nijegorodov, W.S. Downey, *Spectrochim. Acta Part A* 51 (1995) 2335.
- [27] S.P. McGlynn, T. Azumi, M. Kinoshita, *Molecular Spectroscopy of the Triplet State*, Science, Moscow, 1972.
- [28] V.P. Zvolinsky, N.I. Nijegorodov, *J. Phys. Chem. (Moscow)* 68 (1994) 709.
- [29] C. Rulliere, J.-C. Rayes, *Appl. Phys.* 11 (1976) 377.
- [30] N.I. Nijegorodov, R. Mabbs, *Spectrochim. Acta Part A* 56 (2000) 2157.