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Irregular behaviour of fluorescence and laser properties of 9 and 9,10 derivatives of anthracene

N.Nijegorodov[1], V.Vasilenko[2], P.Monowe[1], D.P.Winkoun[1,*], J.G.King[1]
[1]Physics Department, University of Botswana, Private Bag UB 00704,
Gaborone, (BOTSWANA)
[2]Department of Environmental Science, Russian Friendship University,
Miklukho-Maklaya Street 6, 117198, Moscow, (RUSSIA)
E-mail: winkound@mopipi.ub.bw

Abstract

The absorption, fluorescence and laser properties of 9 specially selected 9,10-derivatives of anthracene are studied quantum-chemically and experimentally at room temperature (293 K). The quantum yield of fluorescence γ, fluorescence decay time τ_f, of dearated and non-dearated cyclohexane solutions are measured. The main laser parameters are determined. The oscillator strength f_e of the $S_0 \rightarrow S_p$ transition, fluorescence rate constant k_f, natural lifetime $\boldsymbol{\tau}_0^{\mathbf{T}}$, and intersystem crossing rate constant k_{ST}, are found for each compound. The orbital nature of the lowest excited state singlet S^1 state and direction of polarization of the $S_0 \rightarrow S^1$ transition are determined using the PPP-CI method. The investigation shows that the substitution of CH_3 group(s), phenyl ring(s) or Cl and Br atom(s) into position “9” or into position “9” and “10” causes the inversion of the S_p and $T_{\hat{a}}$ states. The inversion of these states suppresses the decisive $S_p \rightsquigarrow T_\beta$ channel of depopulation of S_p state, and improves the fluorescence and laser properties. It is found out that the k_{ST} of the decisive $S_p \rightsquigarrow T_\beta \left({}^1B_{1u} \rightsquigarrow {}^3B_{2u}^+\right)$ mixing process in anthracene is almost equal to 14.5×10^7 s^{-1}, that is almost 96% of the whole k_{ST} value. It is shown that the internal heavy atom effect depends not only upon the molecular symmetry, but also upon the position of the $T_{\hat{a}}$ level. It is found out that the compound 9,10-bis(phenyl-ethynyl)anthracene is not planar in the S_0 state due to specific interactions of π-electrons and that its laser ability, which was not studied before, is excellent, especially if XeCl laser is used for pumping.

Keywords

Fluorescence; Laser properties; 9,10-derivatives of anthracene.

Corresponding author’s name and address

D.P.Winkoun
Physics Department, University of Botswana, Private Bag UB 00704,
Gaborone, (BOTSWANA)

INTRODUCTION

It was reported in some monographs e.g.[1,2] and articles[3-6] that the introduction of any substituent onto position “9” or “10” or onto both of them causes dramatic changes in the fluorescence parameters of anthracene. For example, the introduction of a methyl group which is a very weak donor and does not affect the π-system of an aromatic molecule, onto position “9” of anthracene increases the quantum yield of fluorescence γ from 0.24 to 0.32. The introduction of another methyl group onto position “10” increase γ further up to 0.68. An even more dramatic increase in γ is observed when phenyl rings are substituted onto position “9” and then onto position “10”. Such substitutions increases γ from 0.24 to 0.47 and then up to 0.90. This case is extremely interesting since 9-phenylanthracene and 9,10-diphenylanthracene are not planar and rigid molecules[7,8]. And very surprising change in γ is observed when Cl or Br are substituted onto position “9” of anthracene and then onto position “10”.

In accordance with the effect of internal heavy atom introduction, a heavy atom like Cl or Br substituted into an aromatic molecule like anthracene should quench the fluorescence[1,9]. And this is the case when a heavy atom is introduced onto position “9” of anthracene. The introduction of a Cl atom in position “9” decreases γ from 0.24 to 0.13. The introduction of Br onto position “9” causes greater quenching as γ decreases from 0.24 to 0.025. It is logic to expect that the introduction of another heavy atom onto position “10” would cause further decrease of γ. However, surprisingly enough, the introduction of another Cl onto position “10” increases γ up to 0.51 and in the case of the introduction of another Br onto position “10” γ increases from 0.025 to 0.10. Such behaviour of chloro and bromo derivatives of anthracene was explained in[4] by the changes in the molecular symmetry and in[5] by the changes in the mutual arrangements of singlet and triplet levels. Anthracene itself does not show laser action at room temperatures under any conditions, but some of its 9,10 derivatives are excellent laser dyes and scintillators[10]. Such anomalous behaviour of the fluorescence and laser properties of 9 and 9,10 derivatives of anthracene were never properly investigated and explained. The objectives of this study is to investigate thoroughly the fluorescence and laser parameters of 9 and 9,10 derivatives of anthracene. For this purpose nine derivatives of anthracene were chosen. They are: (1) anthracene, (2) 9-methylanthracene, (3) 9,10-dimethylanthracene, (4) 9-chloroanthracene, (5) 9,10-dichloroanthracene, (6) 9-bromoanthracene, (7) 9,10-dibromoanthracene, (8) 9-phenylanthracene, (9) 9,10-diphenylanthracene, (10) 9,10-bis(phenylethynyl)anthracene. The structural formulae of the above compounds are given in Figure 1.

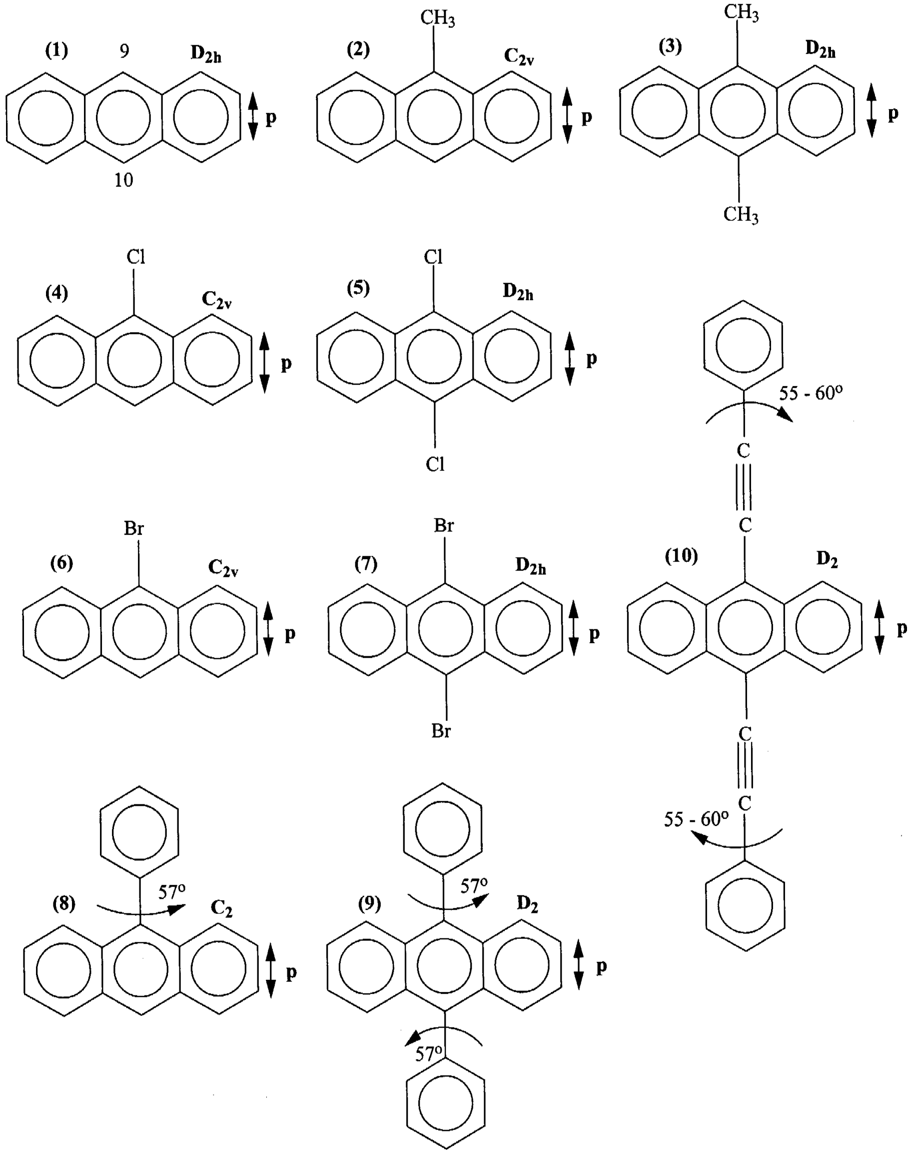

Figure 1 : Structural formulae of the investigated compounds. The symbol “↔” indicates the direction of polarisation of the $S_0 \rightarrow S^1$ *p*-band transition. The error limits for the simulated angles between adjacent fragments of molecules (8-10) are ± 5°.

EXPERIMENTAL METHODS

The compounds studied were recrystallized, sublimized and purity controlled using chromatography. The ultraviolet spectra of the substances were recorded using a SPECORD M40 spectrometer with spectroquality cyclohexane as 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 re-absorption effect in cases where there is a large amount of 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 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 formula presented in[14] and modified in[15].

$$\frac{1}{\tau_0^T} = 2.88\mathrm{x}10^{-9}\, n^2 \left\langle \tilde{\nu}_f^{-3} \right\rangle^{-1} \theta \int \frac{\varepsilon(\tilde{\nu})d\tilde{\nu}}{\tilde{\nu}} \qquad (1)$$

where $\theta = 9n / (n^2 + 2)^2$ is the Lorentz-Lorenz factor[16], n is the refractive index of the solvent, **$\tilde{\nu}$ is the frequency in cm^{-1}, and $\varepsilon(\tilde{\nu})$** 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 deaerated solutions of photostable compounds can be determined using the following equation, with only intramolecular quenching processes considered[16]:

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

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 the Ermolaev- Sveshnikova[18] molecules, k_S is very much less than $k_f + k_{ST}$ and in many cases $k_S << k_{ST}$, hence:

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

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

$\tilde{\nu}_a^{c.g}$ 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, $I(\tilde{\nu}_f)$ is the intensity of fluorescence. The oscillator strength of well resolved long wave absorption bands was determined using the formula:

$$f_e = 1.3\mathrm{x}10^{-8} \theta \int \varepsilon(\tilde{\nu})d\tilde{\nu} \qquad (3)$$

This formula, according to[16], is considered to be appropriate if the oscillator strength of free molecules is calculated from the absorption band of the solution. The oscillator strengths of low intensity or submerged long-wave bands were determined using the formula:

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

This was obtained by dividing Eq. (3) by a simplified version of Eq.(1), taking into account that

$$\left\langle \tilde{\nu}_f^{-3} \right\rangle^{-1} \approx \left(\tilde{\nu}_f^{c.g}\right)^3$$

The error limits determined for the various fluorescence parameters are as follows: quantum yield ± 10% for single measurement, decay time ± 5%, symmetry line frequencies ± 60 cm^{-1}, Stoke's shifts ± 200 cm^{-1}, k_{ST} and k_f values (if $\tau_f < 2$ ns) ± 15%. The angles between the adjacent benzene rings for compounds (8-10), dissolved in cyclohexane solution were simulated with the aid of the PPP-CI method. The direction of the $S_0 \rightarrow S^1$ transitions and the nature of the S^1 states were also found with the aid of the PPP-CI method with parameters taken from[19,20]

The cross section for absorption at the pumping frequency was calculated using Eq. (5):

$$\boldsymbol{\sigma}_{\mathbf{p}}(\tilde{\boldsymbol{\nu}}_{\mathbf{p}}) = 3.82\times10^{-21}\boldsymbol{\varepsilon}_{10}(\tilde{\boldsymbol{\nu}}_{\mathbf{p}}) \quad (5)$$

The spectral Einstein coefficient for the above frequency was found with the formula:

$$\mathbf{B}_{\mathbf{p}}(\tilde{\nu}_{\mathbf{p}}) = \frac{\sigma_{\mathbf{p}}(\tilde{\nu}_{\mathbf{p}})\mathbf{c}}{\mathbf{nh}\nu} \text{ or } \mathbf{B}_{\mathbf{p}}(\tilde{\nu}_{\mathbf{p}}) = \frac{\sigma_{\mathbf{p}}(\tilde{\nu}_{\mathbf{p}})\mathbf{c}\theta}{\mathbf{h}\nu} \quad (6)$$

where *c* is the speed of light in vacuum

The cross section for stimulated emission was calculated as:

$$\boldsymbol{\sigma}_{\mathbf{p}}(\tilde{\boldsymbol{\nu}}_{\mathbf{f}}^{\mathbf{max}}) = 3.82\times10^{-21}\boldsymbol{\varepsilon}_{10}(\tilde{\boldsymbol{\nu}}_{\mathbf{p}}) \quad (7)$$

assuming that $\boldsymbol{\sigma}_{\mathbf{e}}(\tilde{\boldsymbol{\nu}}_{\mathbf{f}}^{\mathbf{max}}) = \boldsymbol{\sigma}_{\mathbf{a}}(\tilde{\boldsymbol{\nu}}_{\mathbf{a}}^{\mathbf{max}})$

The threshold for the laser action was calculated using the equation from ref.[21]

$$\mathbf{U}_{\mathbf{f}}^{\mathbf{T}} = \left[\frac{\mathbf{A}}{\gamma\mathbf{B}_{\mathbf{p}}(\tilde{\boldsymbol{\nu}}_{\mathbf{p}})}\right]\left[\frac{\mathbf{K}_{\mathbf{loss}}}{\mathbf{N}\boldsymbol{\sigma}_{\mathbf{e}}(\tilde{\boldsymbol{\nu}}_{\mathbf{f}}^{\mathbf{max}}) - \mathbf{K}_{\mathbf{loss}}}\right] \quad (8)$$

where: $\mathbf{U}_{\mathbf{f}}^{\mathbf{T}}$ is the threshold density of radiation at the pumping frequency; K_{loss} is the loss coefficient, $K_{loss} = (1-R)/L$; *R* is the coefficient of reflection of the mirror (which is not blind); *L* is the length of the active medium; *N* is the molecular concentration in the active medium, $\mathbf{N} = \frac{\mathbf{CN_A}}{\mathbf{1000}}$; C is the molar concentration; N_A is the Avogadro number. For the meaning of *A* and $\mathbf{B}_{\mathbf{p}}(\tilde{\boldsymbol{\nu}}_{\mathbf{p}})$ see TABLE 2.

For pumping, either a XeCl (308 nm; 32466 cm^{-1}) or a N_2 (337 nm; 29679 cm^{-1}) laser was used.

In all cases, the transverse method of pumping was used. A Bethune cell[22] with a bore diameter of 2 mm and of 2 cm length was used in combination with transverse pumping. The concentration of the dye solution was calculated using the formula:

$$\mathbf{N}\boldsymbol{\sigma}_{\mathbf{p}}(\tilde{\boldsymbol{\nu}}_{\mathbf{p}})\mathbf{r} = \mathbf{1} \quad (9)$$

where *N* is the molecular concentration in cm^3 and *r* is the radius of the bore in cm. The condition in Eq. (9) provides maximum fluorescence intensity on the axis of the bore[23]. The density of the radiation thresholds shown in TABLE 2 were calculated for transverse pumping[24]. The threshold values in TABLE 2 are for R_1 = 100% and R_2 = 50% (R_1 and R_2 are the mirrors of the resonator)

BRIEF THEORY

Concerning the effect of internal heavy atom, since compounds (4 – 7) contain internal heavy atom, one have to take into account the related theory.

If there are *n* triplet levels below the S^1 state, then k_{ST} can be expressed as

$$k_{ST} = \sum_{i=1}^{n} k_{ST}^{i}\left(S^1 \rightsquigarrow T_i\right)$$

where $\mathbf{E}_{\mathbf{T_n}} \leq \mathbf{E}_{\mathbf{S^1}}$

According to ref.[25] $k_{ST}^{i}\left(S^1 \rightsquigarrow T_i\right)$ can be estimated very accurately using the formula:

$$k_{ST}^{i}\left(S^1 \rightsquigarrow T_i\right) = \frac{2\pi}{h}\left|\left\langle \Psi_{S^1}\middle|\hat{H}_{SO}\middle|\Psi'_{T_i}\right\rangle\right|^2 \Pi_k\left\langle \nu_0\middle|\nu_k\right\rangle^2 \rho_k \quad (10)$$

where $\left\langle \boldsymbol{\Psi}_{\mathbf{S^1}}\middle|\hat{\mathbf{H}}_{\mathbf{SO}}\middle|\boldsymbol{\Psi}'_{\mathbf{T_i}}\right\rangle$ are the matrix elements for the spin-orbit coupling of S^1 and T_i. According to the first order perturbation theory, considering the S^1 excited state as the perturbing singlet state, the mixed wave function, $\boldsymbol{\Psi}'_{\mathbf{T_i}}$ of the state T_i is given by[9]

$$\boldsymbol{\Psi}'_{\mathbf{T_i}} = \boldsymbol{\Psi}_{\mathbf{T_i}} + \frac{\left\langle \boldsymbol{\Psi}_{\mathbf{S^1}}\middle|\hat{\mathbf{H}}_{\mathbf{SO}}\middle|\boldsymbol{\Psi}_{\mathbf{T_i}}\right\rangle}{\mathbf{E}_{\mathbf{T_i}} - \mathbf{E}_{\mathbf{S^1}}}\boldsymbol{\Psi}_{\mathbf{S^1}} \quad (11)$$

where $\boldsymbol{\Psi}_{\mathbf{T_i}}$ is the pure triplet wave function of the T_i state, H_{SO} is the operator of the spin-orbit coupling and $\boldsymbol{\Psi}_{\mathbf{S^1}}$ is the wave function of the S^1 state.

$\boldsymbol{\Pi}_{\mathbf{k}}\left\langle \boldsymbol{\nu}_{\mathbf{0}}\middle|\boldsymbol{\nu}_{\mathbf{k}}\right\rangle^2$ is the Franck-Condon factor which is determined by overlapping the zeroth vibrational function ν_o, of the S^1 state with the k^{th} active vibrational function of the T_i state. ρ_k is the average density of active vibrational levels of the T_i state in the vicinity of the S^1 state. Accurate determination of $\boldsymbol{\Pi}_{\mathbf{k}}\left\langle \boldsymbol{\nu}_{\mathbf{0}}\middle|\boldsymbol{\nu}_{\mathbf{k}}\right\rangle^2$ and the value of ρ_k (in Eq. (10)) are difficult tasks since they require accurate knowledge about the active vibrational modes. Instead the empirical Robinson-Frosch formula[26] is used to estimate $k_{ST}^{i}\left(S^1 \rightsquigarrow T_i\right)$, that is,

$$k_{ST}^{i}\left(S^1 \rightsquigarrow T_i\right) \approx 10^{12}\left|\beta_{S^1T_i}\right|^2 e^{\left(-0.25E^{0.4}S^1T_i\right)} \quad (12)$$

where $\boldsymbol{\beta}_{\mathbf{S^1T_i}} = \left\langle \boldsymbol{\Psi}_{\mathbf{S^1}}\middle|\hat{\mathbf{H}}_{\mathbf{SO}}\middle|\boldsymbol{\Psi}'_{\mathbf{T_i}}\right\rangle$ are the matrix elements of the spin-orbit coupling of S^1 and T_i, $\mathbf{E}_{\mathbf{S^1T_1}}$ is the energy gap between the S^1 and T_i levels in cm^{-1}. The exponential term in Eq. (12) approximates the Franck-Condon factor.

$$\hat{\mathbf{H}}_{\mathbf{SO}} = \hat{\mathbf{H}}_{\mathbf{SO}}^{\mathbf{x}} + \hat{\mathbf{H}}_{\mathbf{SO}}^{\mathbf{y}} + \hat{\mathbf{H}}_{\mathbf{SO}}^{\mathbf{z}}$$

In the one electron approximation, the component of H_{SO} are given by:

$$\mathbf{\hat{H}^{j}_{SO}} = \frac{\mathbf{he^2}}{\mathbf{4m^2c^2}}\sum_{\mathbf{k}}^{\mathbf{N}}\frac{\mathbf{Z_k L^k_j \hat{S}_j}}{\mathbf{r^3}} \tag{13}$$

where $j = x, y$ or z, e and m are the charge and mass of the electron, c the speed of light, Z_k the effective charge on the k^{th} nucleus, $\mathbf{L^k_j}$ the j component of the angular momentum operator of the ith electron, $\mathbf{\hat{S}_j}$ is the j component of the spin operator of the ith electron and r is the distance of the electron to the k^{th} nucleus. For simplicity, the summation over all i electrons of a molecule is omitted in Eq. (13).

In the LCAO MO approximation, the problem of determination of the integrals $\left\langle \Psi_{S^1} \middle| \hat{H}_{SO} \middle| \Psi'_{T_i} \right\rangle$ is reduced to the determination of the integrals $\left\langle \mathbf{b} \middle| \hat{\mathbf{H}}_{SO} \middle| \mathbf{c}_i \right\rangle$, where b and c_i are the molecular orbitals of the S^1 and T_i states.

Examination of Eq. (12) leads to the conclusion that substitution of a heavy atom into an aromatic molecule may produce four different effects. Firstly, the value of H_{SO} may increase if the π-electron of a C atom bonded with the heavy atom or the π-electrons of a heavy atom itself (e.g. $\ddot{O}$ or $\ddot{S}$) contribute greatly to the MO of the perturbing S^1 state. Secondly, it may change the symmetry of a molecule and hence the values of the $\beta_{S^1T_i}$ matrix elements would change because, in a molecule of high symmetry, not all T_i states are able to mix with the S^1 state[9]. Thirdly, the energy arrangement of the T_i states may be affected and consequently, the Franck-Condon factors may change[4]. These three effects can change the k_{ST} value of an aromatic molecule dramatically. Fourthly, the introduction of a heavy atom can change the degree of a π-electron conjugation and hence, f_e and consequently, k_f may change. A combination of all four effects would determine the final changes in all fluorescence parameters.

RESULTS AND DISCUSSION

The lowest singlet state of all compounds studied is of $S_p(^1L_a)$ nature. All compounds are planar in the S_0 and S^1 states, except compounds (8) and (9) which are non planar in the ground, S_0 and S^1 state. The main fluorescence parameters including the intersystem crossing rate constants are given in TABLE 1. The main laser parameters are presented in TABLE 2.

According to Berlmann[27], compounds (1–3) belong to Class I: the molecules of this class are planar in S_0 and S^1 states. At first glance, the introduction of a CH_3 group(s) onto position "9" and "10" does not change the spectral properties of anthracene, except the bathochromic shift of ν_{00}. But in reality compounds (1–3) represent a very interesting case whereby substitution of methyl group(s) causes not only an increase in the γ value, but also a significant decrease in k_{ST}.

In these compounds the value of γ increases from 0.24 to 0.68, while k_{ST} decreases from 15.1 × 10^{-7} S^{-1} to 1.30 × 10^{-7} S^{-1}. A qualitative attempt to explain this phenomenon was made in[3]. The substitution of CH_3 onto position "9" and then onto position "10" affect the symmetry of the compound. However, in this case k_f undergoes very little change from 6.20 × 10^{-7} S^{-1} to 6.50 × 10^{-7} S^{-1}.

TABLE 1 : Experimental and calculated values for the main fluorescence parameters of diluted cyclohexane solutions of the investigated aromatic and heteroaromatic compounds.

No.	S	ν_{00} (cm^{-1})	$\Delta\nu_{ST}$ (cm^{-1})	Non-deaerated			Deaerated			τ_0^T (ns)	k_f (s^{-1}) (x 10^{-7})	k_{ST} (s^{-1}) (x 10^{-7})	f_e $S_0 \rightarrow S^1$	Nature of S^1 state
				γ	τ_f (ns)	τ_f^{Ex} (ns)	γ^*	τ_f^* (ns)	τ_f^{Ex*} (ns)					
1	D_{2h}	26580	4100	0.24	4.4	18.30	0.29	4.7	16.20	16.00	6.20	15.10	0.25	$S_p(^1L_a)$
2	C_{2v}	25660	4120	0.32	5.0	15.60	0.38	6.0	15.80	16.80	6.30	10.30	0.26	$S_p(^1L_a)$
3	D_{2h}	25080	4240	0.68	10.7	15.70	0.83	12.9	15.40	16.30	6.50	1.30	0.28	$S_p(^1L_a)$
4	C_{2v}	25480	3900	0.13	2.4	18.46	0.15	2.8	18.60	18.50	5.40	30.40	0.19	$S_p(^1L_a)$
5	D_{2h}	24760	3850	0.51	7.3	14.30	0.57	8.0	14.00	13.70	7.12	5.37	0.29	$S_p(^1L_a)$
6	C_{2v}	25300	4000	0.025	0.45	18.00	0.025	0.45	18.00	17.00	5.60	220.00	0.21	$S_p(^1L_a)$
7	D_{2h}	24500	3900	0.10	1.5	15.00	0.11	1.65	15.00	15.80	7.00	54.00	0.26	$S_p(^1L_a)$
8	C_2	25580	4220	0.47	5.5	11.70	0.57	6.7	11.75	13.43	8.50	6.42	0.35	$S_p(^1L_a)$
9	D_2	25000	4320	0.90	7.9	8.78	0.97	8.6	8.87	8.80	11.30	0.35	0.44	$S_p(^1L_a)$
10	D_2	21400	3500	0.96	5.4	5.62	0.98	5.5	5.61	4.70	20.80	0.36	1.33	$S_p(^1L_a)$

Headings from left to right: No. - compound number, S - symmetry group, ν_{00} - symmetry line wave number, $\Delta\nu_{ST}$ - Stokes shift, γ - fluorescence quantum yield, τ_f - fluorescence decay time, τ_0^{Ex} - experimental natural fluorescence lifetime, τ_0^T - natural lifetime, k_f - fluorescence rate constant, k_{ST} - intersystem crossing rate constant, $f_e(S_0 \rightarrow S^1)$ transition oscillator strength. The nature of the S^1 state is given in Clar's notation with Platt's notation in parentheses.

*** Parameters for dearated solutions.**

TABLE 2 : Main laser parameters of the investigated aromatic and heteoaromatic compounds.

No.	Lp	Main Laser Properties						
		C (mol l-1) (x103)	A (s-1) (x10-7)	p (cm2) (x1017)	p (cm3 . erg -1 l-1) (x10-4)	e (cm2) (x1017)	Ut T (erg. cm-3)	L max (nm)
2	N2	1.97	6.30	0.84	3.20	3.90	16.60	-
3	N2	1.55	6.50	1.07	4.10	4.10	7.60*	432
4	N2	1.35	5.40	1.23	4.68	3.70	37.00	-
5	N2	1.89	7.12	0.88	3.35	5.35	8.60*	434
8	N2	1.66	8.50	1.00	3.81	4.40	13.50	-
9	N2	1.14	11.30	1.45	5.52	5.40	7.60	433
10	N2	0.44	20.80	0.38	1.52	11.08	52.50	510
10	XeCl	0.44	20.80	13.00	52.00	11.08	1.54	510

Headings from left to right: No. - compound number; L_P - pumping laser; C - molar concentration; A - Einstein coefficient for spontaneous emission which is equal to k_f, σ_P - absorption cross section of a molecule at the pumping frequency; B_P - Einstein absorption coefficient at the pumping frequency; σ^e - emission cross section at λ_f^{max}; U_t^T - theoretical threshold of laser action; λ_f^{max} - wavelength of the laser beam at blackbody conditions; * Experimental values are higher than the theoretical ones

Therefore, the whole growth of γ can be attributed to the decrease in the k_{ST} value. To explain this phenomenon, the lowest singlet and triplet levels of all three compounds were simulated using the PPP-CI method. The results of the simulation were published in ref.[28]. The type of symmetry of each state (irreducible representation) are determined and shown. According to the first order perturbation theory[9], in molecules of high symmetry groups (C_{2v}, D_2, D_{2h}) only states of different orbital symmetry are able to mix. If an inversion centre exists in the molecule, the number of mixing states is reduced because only states of the same parity are allowed to mix. In anthracene, the $S^1(^1B_{1u})$ state cannot mix with the $^3B_{1u}$ state because they have the same type of orbital symmetry and it cannot effectively mix with the $^3B_{3g}$ state because of different parities. Strictly speaking, it mixes effectively only with a $^3\mathbf{B}_{2u}^+$ state. Substitution of a CH_3 group onto position "9" or "10" or onto both of them affects only those singlet (and corresponding triplet) states which are formed by transitions polarized along the *z* axis[29]. As a result of this, the $^1B_{1u}$ and $^1B_{3g}$ states go down and the corresponding triplet states slightly move up. The $^1\mathbf{B}_{2u}^-$, **$^1\mathbf{B}_{2u}^+$, $^3\mathbf{B}_{2u}^-$ and $^3\mathbf{B}_{2u}^+$ states remain almost unaffected because the corresponding transitions are polarised along the *y*-axis. Hence the only change in the range of the molecules (1-3) is the change of the position of the $^3\mathbf{B}_{2u}^+$ state relative to the position of the $^1\mathbf{B}_{1u}$ state. In anthracene, the** $^3\mathbf{B}_{2u}^+(\mathbf{T}_\beta)$ state is lower than $^1B_{1u}$. In molecules (2) and (3) the $^3\mathbf{B}_{2u}^+(\mathbf{T}_\beta)$ state is higher than $^1B_{1u}$. The locations of $^1B_{1u}$ states of these compounds are known and the $^3\mathbf{B}_{2u}^+(\mathbf{T}_\beta)$ state of anthracene was found to be at 26050 cm^{-1}[30]. Since the substitution of CH_3 group(s) onto position "9" and "10" almost do not affect the $^1\mathbf{B}_{2u}^+$ and $^3\mathbf{B}_{2u}^+$ states, we may consider that the energy of the T_β state is the same (or almost) the same for all compounds (1–3). The population distribution of the S^1 state in the multi-atom molecule can be approximated by the following Boltzmann formula: $\frac{\mathbf{dN}}{\mathbf{N}} = \mathbf{Ag(E_v)e^{-E_v/kT}dE}$, where $g(E_v)$ is the degeneracy of the E_v vibrational level and *A* the normalisation coefficient. If $g(E_v)$ is proportional to E_v and the above formula is normalised to 1, then A = $1 / g(kT)^2$. Figure 2 clearly shows that in anthracene the T_β level is 530 cm^{-1} lower than the S^1 level. Hence, in this molecule there is no energy barrier for $^1B_{1u} \rightsquigarrow {}^3B_{2u}^+$ intersystem crossing. In the 9-methylanthracene molecule, due to the inversion of the S^1 and T_β levels, the energy barrier become equal to 390 cm^{-1}. Thus only 42% of the molecules can undergo the $^1A_1 \rightsquigarrow {}^3B_{2u}^+$ intersystem crossing process. In 9,10-dimethylanthracene, the energy barrier further increases to 970 cm^{-1} so that only 5% of the molecules can undergo the $^1B_{1u} \rightsquigarrow {}^3B_{2u}^+$ process. Thus Figure 2 clearly explains why k_{ST} decreases in compounds (1–3). Taking into account the fact that in compounds (1) and (3), which have the same D_{2h} molecular symmetry, there are only two effective mixing channels, that is $^1B_{1u} \rightsquigarrow {}^3B_{2u}^+$ and $^1B_{1u} \rightsquigarrow {}^3B_{3g}$, and assuming that $k_{ST}\left(^1B_{1u} \rightsquigarrow {}^3B_{3g}\right)$ value is almost the same for both compounds, one can easily find that

$$k_{ST}\left({}^{1}B_{1u}\rightsquigarrow{}^{3}B_{2u}^{+}\right)\approx 14.5\times10^{7}\,s^{-1}$$ and

$$k_{ST}\left({}^{1}B_{1u}\rightsquigarrow{}^{3}B_{3g}\right)\approx 0.6\times10^{7}\,s^{-1}\ .$$

According to the luminescence-laser classification for aromatic compounds given in[31], anthracene belongs to Class IV, while compounds (2) and (3) belong to Class V. Anthracene does not show any laser action under any pumping conditions, but compound (2) gives laser oscillations at low temperature, while compound (3) displays laser action at room temperature[10]. Hence compounds (1–3) are examples whereby substitution of methyl group(s) can improve fluorescence and laser parameters due to change in the relative location of S^1 and T_β levels.

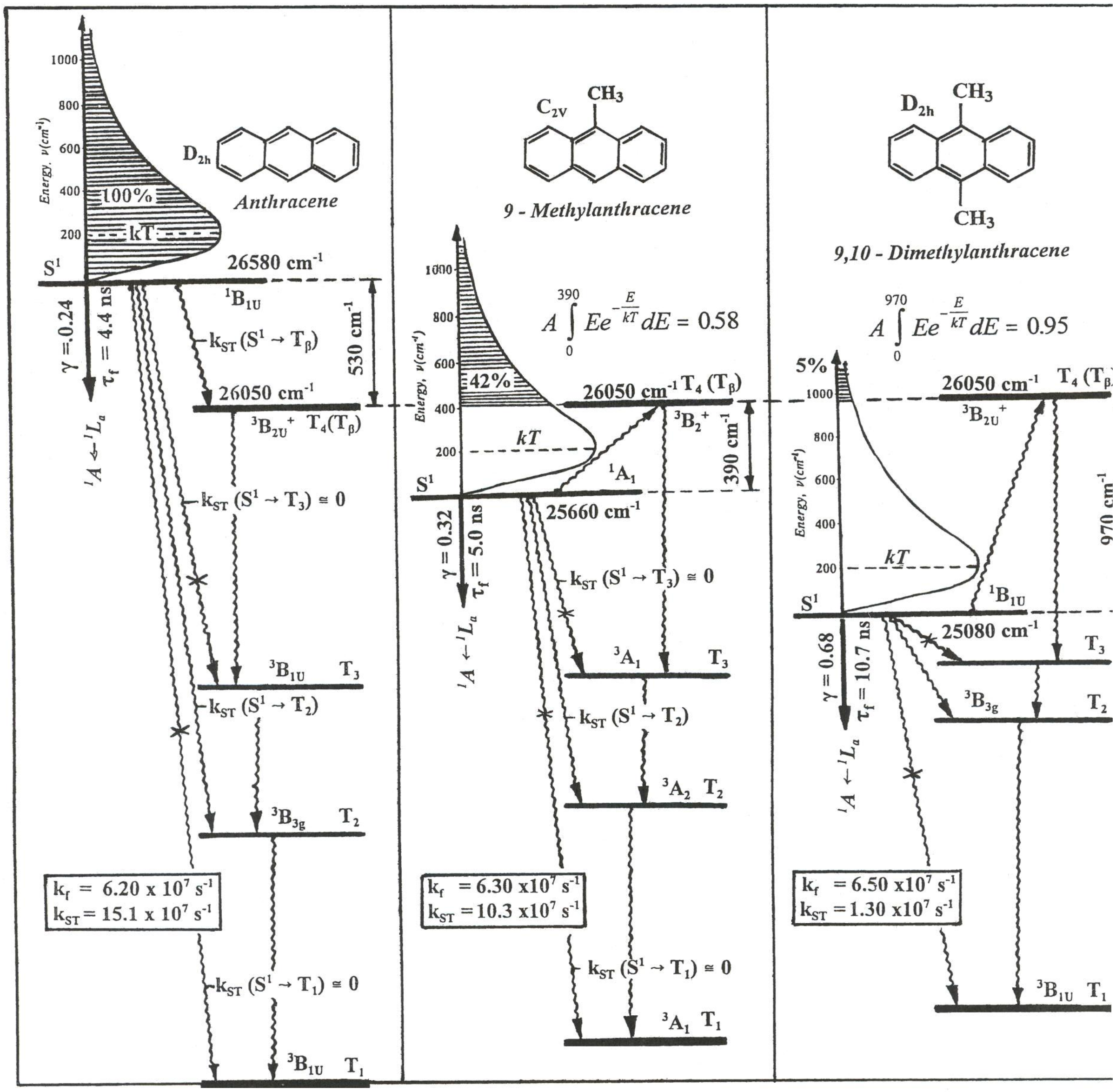

Figure 2 : Mutual locations of experimentally found S^1 (^1L_a) and T_β states of anthracene (1), 9-methylanthracene (2) and 9,10-dimethylanthracene (3). Distribution of population of S^1 states and percentages of molecules which can undergo $S_p \rightsquigarrow T_\beta$ mixing.

The next group of compounds (4-7) in comparison with anthracene represent an extremely interesting case. In these compounds γ, k_{ST}, f_e and other parameters behave in an irregular way. Moving through these compounds beginning from (1) γ first decreases, then increases sharply, then decreses and finally increases again: 0.24, 0.13, 0.51, 0.025, 0.10. k_{ST} undergoes the following changes: 15.10×10^{-7} S^{-1}, 30.4×10^{-7} S^{-1}, 5.37×10^{-7} S^{-1}, 220.00×10^{-7} S^{-1}, 54.0×10^{-7} S^{-1}. The oscillator strength f_e of the $^1A \rightarrow {}^1L_a$ transition also changes irregularly 0.25, 0.19, 0.29, 0.21, 0.26. An astonishing fact is clearly seen: two heavy atoms (introduced in position "9" and "10") produce less effect than a single heavy atom introduced into either of these positions. It is clear that this phenomenon is related to the molecular symmetry and to the change in the mutual arrangement of the singlet and triplet levels. Introduction of one heavy atom at the position “9” or “10” position of anthracene reduces the symmetry group from D_{2h} to C_{2v} and the introduction of the second heavy atom restores the original D_{2h} symmetry. It has previously been observed in this study that the introduction of a methyl group into position”9” or into position “9” and “10” shifts the $S^1(^1L_a)$ level bathochromatically and the T_i levels hypsochromically and hence changes the arrangement of the S^1 and T_i levels. Such changes could be crucial for the k_{ST}value, especially if the positions of the S^1 and T_β levels undergo an inversion. The introduction of chlorine atom(s) into position “9” and “10” affect the T_i levels differently. In this case almost all levels undergo a bathochromic shift, though the S^1 level shift is much bigger than the T_i shifts, hence the inversion of the S^1 and T_β levels is also possible. The oscillator strength f_e of the $S_0 \rightarrow S^1$ transition in the series of compounds (1-3) consistently increases (0.25, 0.26, 0.28) while in compounds (1), (4) and (5), f_e of the $S_0 \rightarrow S^1$ transition changes irregularly (0.25, 0.19, 0.29). This difference in the change of f_e can be explained by the fact that the CH_3 group is a weak donor but Cl is an acceptor and they affect the LUMO, HOMO, and the M^z component of the dipole moment of the $S_0 \rightarrow S^1$ transition differently. In the case of CH_3 group(s), the M^z component consistently increases, while one Cl atom causes the M^z component to decrease, and the symmetrical introduction Cl atoms increases the value of M^z. The changes caused by one or two Br atoms are qualitatively similar to those produced by Cl atoms. The differences in γ, $k_{ST,}$ and f_e of the $^1A \rightarrow {}^1L_a$ transition of compounds (4) and (5) and compounds (6) and (7) can be explained by the greater mass of bromine. The changes in the fluorescence parameters caused by the introduction of a heavy atom(s) in positions “9” and “10” of anthracene are explained not only by the changes in the M^z component, but also by the changes in H_{SO} value caused by a heavy atom(s) (see Eq. (13)), by the changes in the molecular symmetry, and the changes in the arrangement of $S^1(^1L_a)$ the and T_i levels. The arrangements of the S^1 and T_i levels for compounds (1) and compounds (4) and (5) are shown in Figure 3. From this figure it is clear that in compounds (1) and (4) the $k_{ST}^4\left(S^1 \rightsquigarrow T_4\right)$ component contribute greatly to the total $k_{ST,}$. This is because the matrix element $\left\langle \Psi_{S^1} \middle| \hat{H}_{SO} \middle| \Psi'_{T\beta} \right\rangle$ is large since S^1 readily mixes with $T_4(T_\beta)$.

Therefore in compounds (1) and (4) $S^1 \rightsquigarrow T_\beta \rightsquigarrow T_1$ is a decisive channel in the depopulation of the S^1 state, while in compound (5) this channel is suppressed by the energy barrier between the S^1 and T_β levels. Thus, in compounds (4-7) all aspects of the heavy atom effect can be explained by a combination of the changes in the arrangement of the singlet and the triplet levels (see Eq. (11)), in the values of the M^z component, H_{SO}, $\left\langle \Psi_{S^1} \middle| \hat{H}_{SO} \middle| \Psi'_{T_i} \right\rangle$ matrix elements and by the changes in the Franck-Condon factors (see Eq. (12)). However, there is one more factor which explains why two heavy atoms cause less quenching effect than one. In the case of symmetrical introduction of two heavy atoms, the electron

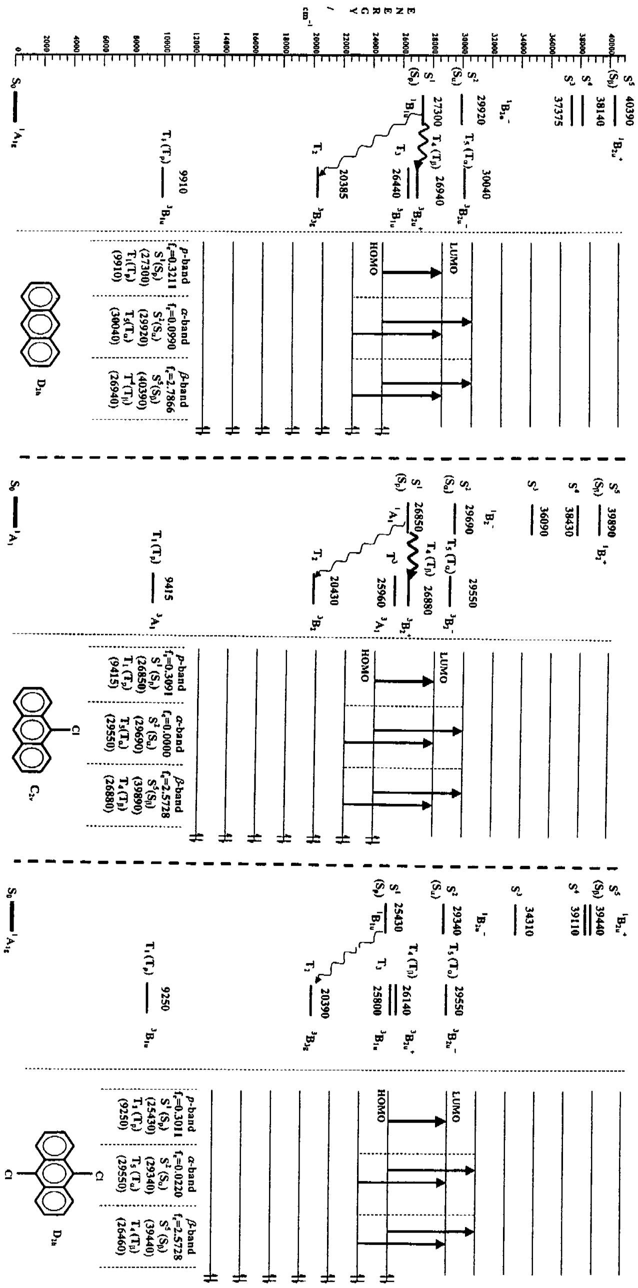

Figure 3 : Simulated singlet and triplet levels of anthracene (1), 9-chloroanthracene (4) and 9,10-dichloroanthracene (5). The thick wavy arrows indicate the decisive component of spin-orbit coupling. The nature of *p*-, α-and β-bands are shown by Cl vectors. Forbidden mixing states are not shown.

localization of the excitation of the $S_0 \rightarrow S^1$ transition on each heavy atom is decreasing and, hence, H_{SO} is decreasing too. A careful analysis of the results of the simulations for the compounds (4) and (5) and for compounds (6) and (7) allows one to estimate the contribution of the heavy atom(s) to the total value of the k_{ST} of these compounds. The contribution to the k_{ST} of one chlorine atom in compound (4) is about 15.3×10^7 S^{-1}, while two chlorine atoms in compound (5) contribute only for about 4.8×10^7 S^{-1}. The contribution to the k_{ST} of one bromine atom in compound (6) is about 205.0×10^7 S^{-1}, while two bromine atoms in compound (7) contribute only for about 53.0×10^7 S^{-1}. The result is amazing: two heavy atoms substituted symmetrically produce less quenching of fluorescence than one. Among compounds (4-7) only compound (5) show laser action at room temperature.

Compounds (8) and (9) also represent a very interesting case. The absorption and fluorescence spectra of these compounds are as structural as the spectra of anthracene, hence according to Berlman's classification[27] they belong to Class I, molecules are planar in S_0 and S^1 state. However, compounds (8) and (9) are not planar at all. The phenyl rings of these molecules are turned through 57° relative to the anthracene fragment[7]. Phenyl rings could be quite effective donors, but since in compounds (8)

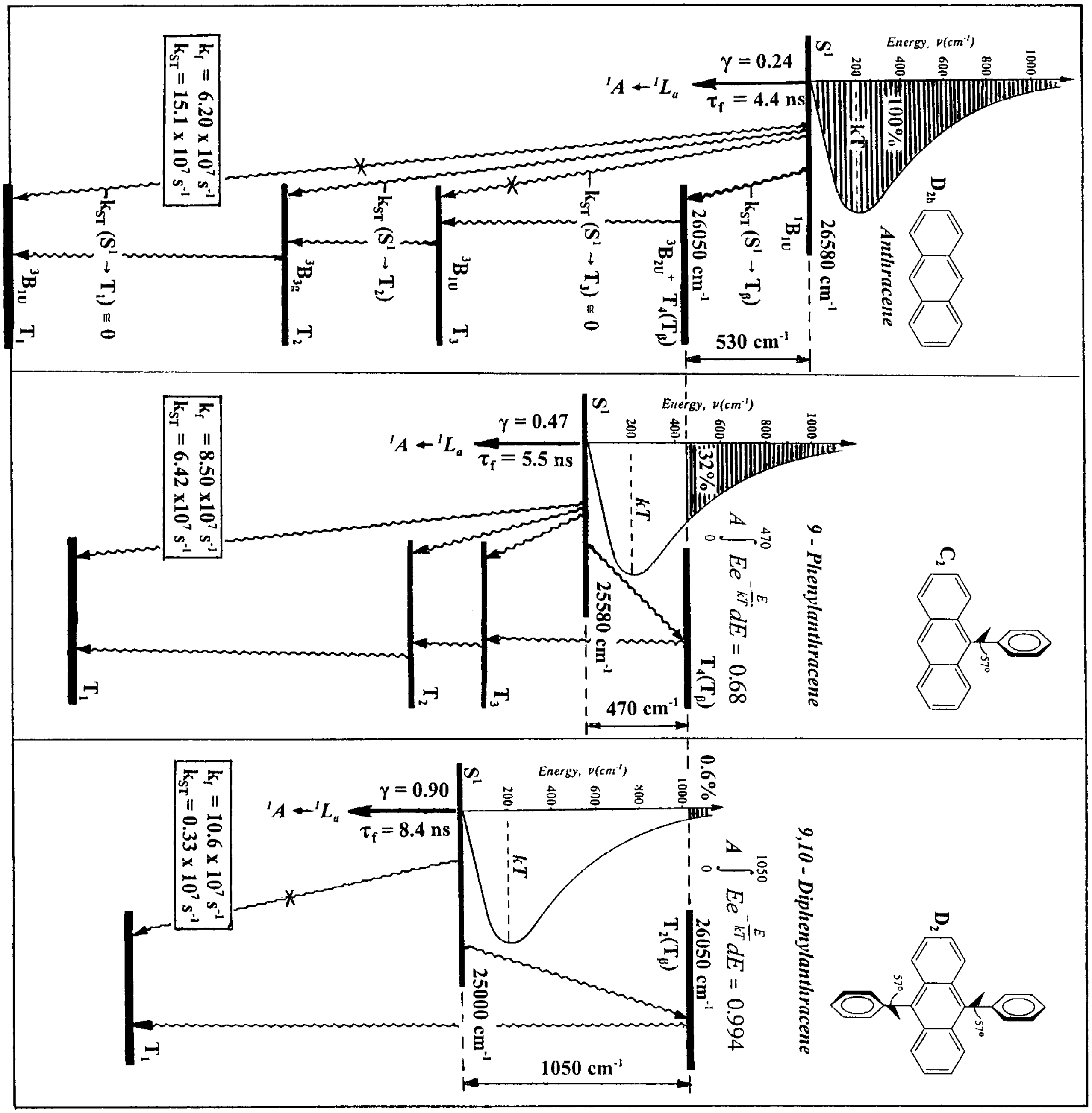

Figure 4 : Mutual locations of experimentally found S^1 (^1L_a) and T_β states of anthracene (1), 9-phenylanthracene (8) and 9,10-dimethylanthracene (9). Distribution of population of S^1 state and percentages of molecules which can mix with the T_β state.

and (9) they are not coplanar with the anthracene fragment, they behave like weak donors, slightly stronger than methyl group(s). In ref.[7] it was shown that the contribution of the phenyl rings to the electron excitation of the S^1 state of compound (9) is only 10%, that is why the fluorescence properties of this compound are almost determined by the anthracene fragment. However, like CH_3 groups in compounds (2) and (3), phenyl rings in compound (8) and (9) cause dramatic changes in the fluorescence parameters of anthracene. The substitution of phenyl ring(s) into position "9" or into positions "9" and "10" changes the molecular symmetry and arrangement of the S^1 and T_i levels. The simulation (PPP-CI) shows that like in the case of compounds (2) and (3) the phenyl group(s) shift the S^1 level bathochromically and the three T_i levels hypsochromically. At the same time the S_β and T_β levels remain almost unaffected. That is because $\mathbf{S_0 \rightarrow S_\beta\left({}^1A_{1g} \rightarrow {}^1B_{2u}^+\right)}$ transition is polarized along the *y*-axis, and the substitution of phenyl group(s) occur in the direction of the *z*-axis. Due to this, the introduction of phenyl ring(s) into position "9" or into position "9" and "10" cause the inversion of the $S_p({}^1B_{1u})$ and $\mathbf{T_\beta\left({}^3B_{2u}^+\right)}$ levels. The results of the simulation are presented. In anthracene the $S_p({}^1B_{1u})$ state is effectively mixing only with the $T_2({}^3B_{3g})$ and $\mathbf{T_\beta\left({}^3B_{2u}^+\right)}$ triplet levels. In anthracene the T_β level is located below the S_p level (see Figure 4). Due to its low symmetry group (C_2), the S_p state of 9-phenylanthracene is allowed to mix with all triplet states. Nevertheless, k_{ST} of 9-phenylanthracene is less than k_{ST} of anthracene. This striking effect can be explained only by the position of the $T_\beta({}^3B^+)$ level. As it is shown in Figure 4, the $T_\beta({}^3B^+)$ level of compound (8) is located higher than the $S_p({}^1A)$ level. The energy barrier (470 cm^{-1}) partly suppresses the mixing of the S_p and T_β states. Due to this barrier, only one third of the molecules which are populating the S_p state can effectively mix with the T_β state. More dramatic changes in the k_{ST} and, hence, in the γ values occur when two phenyl groups are introduced into position "9" and "10". In 9,10-diphenylanthracene, below the $S_p({}^1B_1)$ level there is only one $T_p({}^3B_1)$ level, but due to the same orbital symmetry they cannot mix. The energy barrier between the S_p and T_β states has increased up to 1050 cm^{-1}, hence less than 1% of the molecules which are populating the S_p state can mix with the $\mathbf{T_\beta\left({}^3B_2^+\right)}$ state.

Thus, the $S_p \rightsquigarrow T_\beta \rightsquigarrow T_p$ channel of depopulation is suppressed almost completely. However, due to collisions of molecules, which may decrease the molecular symmetry mixing of the S_p and T_p states is partly allowed. This explains why γ of 9,10-diphenylanthracene is less than 1.0.

Finally, consider compound (10). To the authors knowledge the quantum-chemical and laser properties of this compound were never studied. Compound (10) represents an extremely rare case where non planarity is caused not by steric hindrance, but by the interaction of π-electrons. At first glance the molecule of this compound should be planar because there is no any steric hindrance in the compound, but that is not true. The long-wave absorption band of this compound is not structural[2], though the fluorescence spectrum is very structural. Each ethynyl group of compound (10) contributes to the π-system of the molecule four π-electrons: the orbits of two of them are perpendicular to the plane of the anthracene fragment, and hence effectively conjugated with it. The orbits of the other two π-electrons are situated in the plane of the anthracene fragment and because of that they cannot conjugate with its π-system. The peripheral phenyl rings tend to conjugate with either pair of the ethynyl group, since the phenyl rings are free to rotate around the essential bond between a phenyl ring and an ethynyl group. And it seems that the phenyl rings are conjugating more with the pairs of π-electrons which are in the plane of the anthracene fragment, because the other π-pair are strongly involved into conjugation with the π-system of the anthracene fragment. The PPP-CI simulation shows that the long-wave absorption band of the compound (10) is formed by one $S_0 \rightarrow S^1$ (${}^1A \rightarrow {}^1L_a$) transition which is polarized along the *z*-axis. Actually, the p(${}^1L_a$) absorption band is formed by the manifold of the $S_0 \rightarrow S^1$ transition which corresponds with the particular position of the phenyl rings relatively to the anthracene fragment. The bigger the angle between the phenyl rings and the anthracene fragment, the bigger the hypsochromic shift of the $S_0 \rightarrow S^1$ transition. Hence, the torsional vibrations of the phenyl rings explain the erosion of the *p*-band. The oscillator strength of the $S_0 \rightarrow S^1$ transition calculated using Eq. (3) gives $f_e \approx 1.33$ and the calculation of fluorescence parameter using Eq. (4) gives $f_e \approx 1.15$. According to the simulation conducted, the most probable angle between the phenyl ring and the anthracene fragment is 55-60°. In the excited S^1 state, the molecule becomes more planar and rigid, and that explains the structural character of the fluorescence spectrum. The difference in the S_0 and S^1 configuration explains the difference between $\boldsymbol{\tau_0^{Ex}}$ and $\boldsymbol{\tau_0^{T}}$ (see TABLE 1). Low temperature investigations of the absorption spectrum of compound (10) are necessary for the detailed interpretation of its absorption spectrum since different parts of it are formed by transitions related to different positions of the peripheral phenyl rings. For example, the transition which corresponds to the $S_0 \rightarrow S_\beta$ transition of anthracene fully reveals itself when the angle between the phenyl rings and the anthracene fragment exceeds 60°. The quantum yield of fluorescence of compound (10) is high because, as in compound (9), the T_β triplet state of compound (10) is much higher than the S^1 state, and below the S^1 state there is only one $T_1(T_p)$ state. The investigation of the laser properties of the compound (10) showed that it is an excellent laser dye. It is especially effective if a XeCl laser is used for the pumping, because B_p on the frequency of this laser is high.

CONCLUSIONS

From the fluorescence and laser data presented and discussed in the paper, the following conclusions may be drawn. The position of the T_β state exerts great influence upon the fluorescence and laser properties of 9,10-derivatives of anthracene. If the T_β level is situated below the S_p level, it mixes with the S_p level readily and the $S_p \rightsquigarrow T_\beta$ mixing process becomes a decisive channel of depopulation of the S_p state. This fact was predicted theoretically[32] and in this paper it is proved experimentally. The value of $k_{ST}\left({}^1B_{1u} \rightsquigarrow {}^3B_{2u}^{+}\right)$ in anthracene is found to be equal to 14.5 × 10^7 S^{-1} while $k_{ST}\left({}^1B_{1u} \rightsquigarrow {}^3B_{3g}\right) \approx 0.6\times 10^7 s^{-1}$. Due to the substitution of CH_3 or phenyl rings or even Cl and Br atoms into position "9" and "10", the inversion of the S_p and T_β levels occurs, and the T_β level is found to be above the S_p level. This suppresses the $S_p \rightsquigarrow T_\beta$ mixing and, hence, k_{ST} decreases and γ increases. Because of this, 9,10-derivatives of anthracene are able to show laser action, while anthracene itself is not able to produce laser action under any conditions. The inversion of the S_p and T_β levels in 9,10-derivatives of anthracene, and the change in the symmetry group explains why two heavy atoms (Cl or Br) produces less quenching effect than one. It is shown in this study that the compound (10), 9,10-bis(phenylethynyl)anthracene is not planar in the S_0 state because of specific interaction of π-electrons, but not because of steric hindrance. The laser action of this compound, which was not studied earlier, is found to be excellent, especially, if a XeCl laser is used for pumping. Further investigations, including at low temperature are needed to explain all particularities of the absorption properties of compound (10). The results achieved in this study show that the effect of internal heavy atom(s) depends not only upon the symmetry group of a molecule, but also upon the mutual positions of the S_p and T_β states.

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