Photonics and photochemical stability of aromatic molecules, family related in π-structure but different in planarity, rigidity and molecule symmetry

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Abstract

Intramolecular processes and fluorescence properties of 32 specially chosen aromatic molecules, different in degrees of planarity and rigidity, but family related in π-structure are experimentally and theoretically (using the PPP-method) studied at room temperature (293 K). The quantum yields of fluorescence γ, and decay times τ_f, of deaerated and non-deaerated cyclohexane solutions are measured. The oscillator strength f_e, the fluorescence rate constants k_f, the natural lifetimes τ_o^T, and the intersystem crossing rate constants k_{ST}, are calculated. The investigations showed the following differences in the behaviour of the fluorescence parameters in transition from the non-planar molecule to the planar and more rigid-type: the value of the symmetry line wave-number υ_{00} (the frequency of the $S_0 \rightarrow S^1 \pi\pi^*$ transition) and the Stokes shift $\Delta\upsilon_{ST}$, decrease. The oscillator strength and fluorescence constant, normally decrease. The change in the quantum yield of the fluorescence depends upon the changes in the k_f and k_{ST} values. Furthermore, the intersystem crossing rate constant generally decreases, sometimes very significantly. However, there are some interesting exceptions. For example, the k_{ST} value of the non-planar molecule of 9,10-diphenylanthracene is less than the k_{ST} value of the planar and very rigid molecule of anthracene. This important phenomenon is explained. The differences of the intramolecular processes of planar and non-planar molecules are discussed. The photochemical stability of planar and non-planar molecules is studied. The effect of planarity, rigidity and molecular symmetry upon laser properties is also traced.
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1. Introduction

Molecular structure plays a major role in determining the shape and wavelength position of the fluorescence spectra and fluorescence parameters of aromatic molecules. Non-planar molecules usually have structure-less absorption and fluorescence spectra, while planar and rigid molecules of the high-symmetry group show absorption and fluorescence spectra with well-resolved vibrational bands. Sometimes the absorption and fluorescence spectra of planar and rigid compounds show a similar structural pattern and display mirror symmetry. Very often, transition from a non-planar molecule to a similar but more planar and rigid molecule is accompanied by an increase in quantum yield of fluorescence. These conditions have been shown previously by numerous investigators and have been summarized in a number of monographs [1–5]. For instance, biphenyl in solution is non-planar [6] and has a very wide structure-less absorption band and a structural fluorescence spectrum. They do not show any mirror symmetry between them, but when phenyl rings of biphenyl are forced into a planar position by bridging with the introduction of a methylene group (fluorene), both the absorption and fluorescence spectra become very sharp. They also display mirror similarity, and the quantum yield values increase from 0.18 to 0.80 [4]. It has also been shown that, in addition to the quantum yield, some other fluorescence parameters such as Stokes shift and "full width at reciprocal 'e'" (FWRE) values can be correlated with the degrees of planarity and rigidity of a molecule. The values of Stokes shift and FWRE for planar and rigid molecules are generally small compared with the same parameters of non-planar molecules [4].

Prior to 1970 it was believed that the ability of some molecules to emit fluorescence radiation was totally attributable to molecular rigidity. Berlman [7], however, showed later that rigidity in the S_0 state was not as important factor as rigidity in the first excited S^1 state, that is, in maintaining a planar or near planar configuration. Currently there is no doubt that the planarity and rigidity of a molecule play important roles in determining the fluorescence parameters of a compound.

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Furthermore, it is obvious that not all the effects of these factors have been properly investigated. Specifically, the influence of planarity and rigidity on k_{ST} is little known. An approach to this problem requires the systematic analyses of a large quantity of experimental data. At present organic compounds are widely used in dye lasers. But for dye lasers, photochemical stability is extremely important. However, the dependence of photochemical stability on planarity and rigidity have never been properly investigated. The effect of molecular symmetry on fluorescence parameters and photochemical stability is also reviewed in this study.

This paper presents the results of such a study and a thorough analysis of the fluorescence properties of 32 specially chosen substances, different in degrees of planarity and rigidity but family related in π-structure. The type of compounds are as follows: (**1**) biphenyl; (**2**) 9,10-dihydrophenanthrene; (**3**) fluorene; (**4**) phenanthrene; (**5**) pyrene; (**6**) *p*-terphenyl (PPP); (**7**) 2,2′-ethylene-*p*-terphenyl; (**8**) 2,2′-methylene-*p*-terphenyl; (**9**) 2,2′-methylene-5′,6″-methylene-*p*-terphenyl; (**10**) dibenz[*a,h*]anthracene; (**11**) peropyrene; (**12**) 2-phenylindole; (**13**) 2-phenyl-3,2′-methyleneindole; (**14**) 2-phenyl-3,2′-ethyleneindole; (**15**) 2-phenyl-3,2′-trimethyleneindole; (**16**) 3,4-benzophenanthrene; (**17**) banzo[*g,h,i*]fluoranthene; (**18**) perylene; (**19**) 1,3,6,8-tetraphenylpyrene; (**20**) anthracene; (**21**) 9,10-diphenylanthracene; (**22**) 1,1′-binaphthyl; (**23**) chrysene; (**24**) sexiphenylbenzene; (**25**) carbazole; (**26**) *N*-methylcarbazole; (**27**) *N*-phenylcarbazole; (**28**) *N*-vinylcarbazole; (**29**) *p*-quaterphenyl; (**30**) 3,3″-dimethyl-*p*-quaterphenyl; (**31**) *p*-quinquephenyl; (**32**) coronene. The schematic molecular structures of the compounds studied are shown in Fig. 1. The objectives of this work are to investigate how the planarity and rigidity of the chosen organic molecules influence fluorescence parameters, k_{ST}-value and photochemical stability.

2. Experimental methods

The compounds studied were re-crystallized, sublimized and purity-controlled using chromatography. The ultraviolet spectra of the substances were recorded using a SPECORD M40 spectrometer with spectroquality cyclohexane or benzene as solvent. Compounds (**6**, **11**, **29**, **31**), which are of low solubility, were dissolved using a 9:1 cyclohexane/benzene mixture in an ultrasonic USU-0.25 bath. A Hitachi MPF-4 spectrofluorimeter was used to record the fluorescence spectra. The quantum yields of fluorescence were measured using the method described in [8] and a highly diluted solution of 9,10-diphenylanthrancene in cyclohexane served as a standard.

The essence of this method to determine the quantum yield of fluorescence is given in [9]. The fluorescence quantum yield of 9,10-diphenylanthrancene was measured using the method described in [10] 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 yields and lifetime measurements were prepared following the recommendations given in [11]. Since some of the substances investigated reveal a very large structured long-wavelength absorption band, the

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

The decay times of fluorescence, τ_f, was measured using either an SLM-4800S phase fluorimeter or installations based on the stroboscopic principle combined with single photon counting measurements [12], depending on the value of τ_f. The natural lifetimes were calculated using the formula presented in [12] and modified in [13].

$$\frac{1}{\tau_0^T} = 2.88 \times 10^{-9} n^2 \left\langle \tilde{v}_f^{-3} \right\rangle^{-1} \theta \int \frac{\varepsilon(\tilde{v})}{\tilde{v}} d\tilde{v} \tag{1}$$

where $\theta = 9n/(n^2 + 2)^2$ (Lorentz-Lorenz factor), n is the refractive index of the solvent, $\tilde{v}$ is the frequency in cm^{-1} and $\varepsilon(\tilde{v})$ is the molecular extinction coefficient. Deaeration was carried out using the method described in [14]. According to this method, a solution of the sample in a cell is frozen. The air is evacuated from the cell and replaced by nitrogen gas before the sample is un-frozen. For deep deaeration, the procedure could be repeated. 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 Eq. (2), with only intramolecular quenching processes considered:

$$\gamma* = \frac{k_f}{k_f + k_S + k_{ST}} \tag{2}$$

where $\gamma*$ 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 [15] molecules, k_S is very much less than $k_f + k_{ST}$ and in many cases $k_S \ll k_{ST}$, hence

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

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

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

where

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

$\tilde{v}_a^{c.g.}$ and $\tilde{v}_f^{c.g.}$ are the "center of gravity" or first moment of the long-wave absorption band and fluorescence spectrum, respectively. $\tilde{v}_a$ and $\tilde{v}_f$ are the frequencies in the range of the absorption and fluorescence spectra, $I(\tilde{v}_f)$ is the intensity of fluorescence. The oscillator strength of well-resolved long-wave absorption bands was determined using the formula:

$$f_e = 1.3 \times 10^{-8} \theta \int \varepsilon(\tilde{v}) d\tilde{v} \tag{3}$$
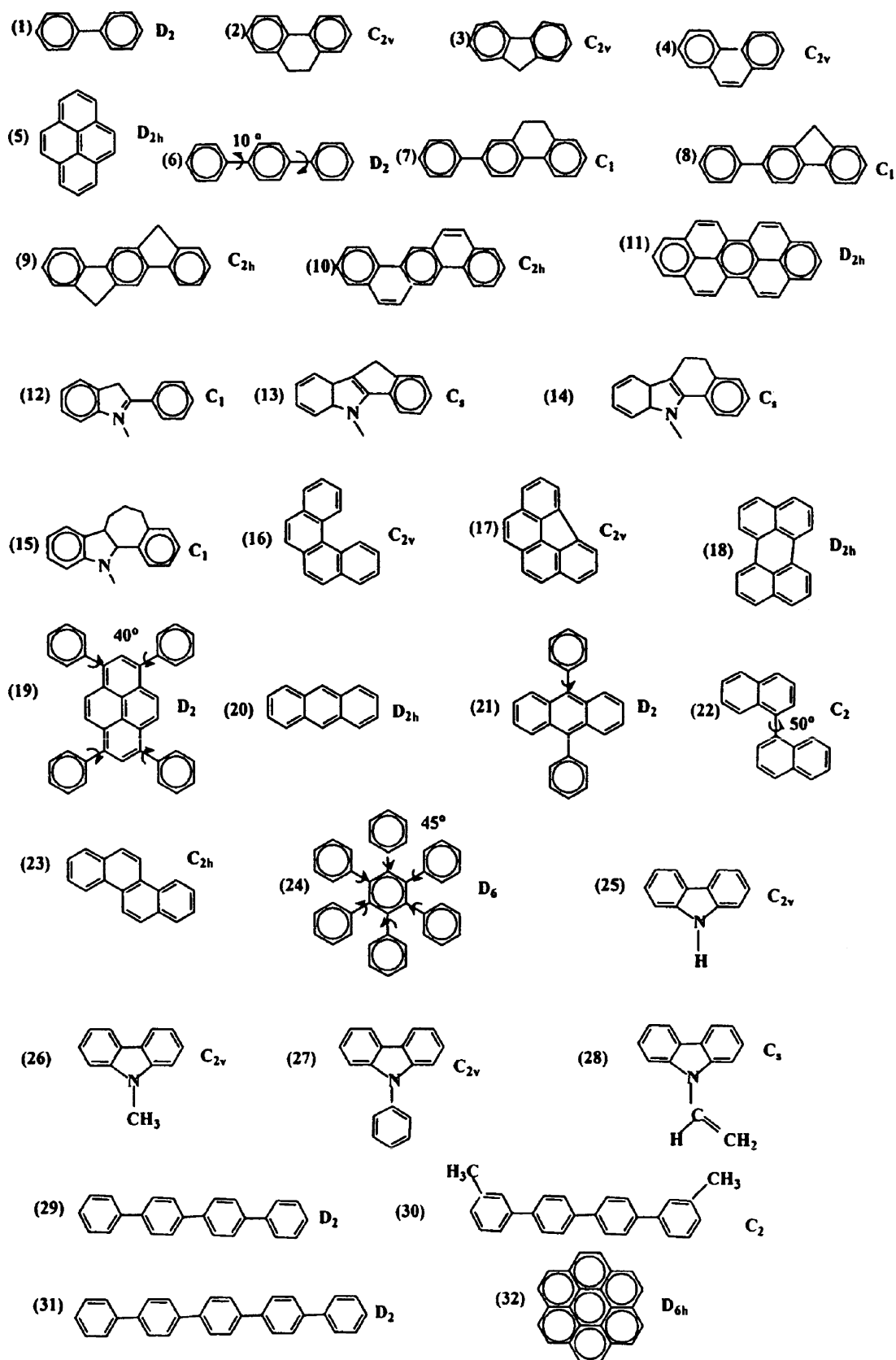
Fig. 1. Structural formula of the investigated compounds.

Table 1
Experimental and calculated values for the main fluorescence parameters of diluted cyclohexane solutions of the investigated compounds[a]

No.	S	υ_{00} (cm^{-1})	$\Delta\upsilon_{ST}$ (cm^{-1})	γ	τ_f (ns)	τ_0^{ex} (ns)	γ^*	τ_f^* (ns)	τ_0^{ex*} (ns)	τ_0^T (ns)	k_f ($\times 10^{-7}$ s^{-1})	k_{ST} ($\times 10^{-7}$ s^{-1})	f_e S$_0 \to$ S^1	Nature of S^1
1	D_2	34600	9260	0.17	16.0	94.10	0.25	22.2	89.00	2.90	1.12	3.38	0.025	S$_\alpha$(^{1}L$_b$)
2	C_{2V}	32760	3480	0.50	7.6	15.20	0.70	11.2	16.00	20.50	6.25	2.68	0.100	S$_\alpha$(^{1}L$_b$)
3	C_{2V}	33140	2740	0.72	10.0	13.90	0.89	12.7	14.30	15.30	7.00	0.87	0.135	S$_\alpha$(^{1}L$_b$)
4	C_{2V}	28900	3260	0.13	55.0	423.00	0.31	130.2	420.00	–	0.24	0.53	0.007[b]	S$_\alpha$(^{1}L$_b$)
5	D_{2h}	26900	3360	0.29	117.0	403.50	0.60	243.0	405.00	–	0.25	0.16	0.007[b]	S$_\alpha$(^{1}L$_b$)
6	D_2	31960	7860	0.84	1.0	1.19	0.88	1.05	1.19	1.50	83.80	11.40	2.060	S$_p$(^{1}L$_a$)
7	C_1	30780	6640	0.80	1.4	1.75	0.88	1.5	1.70	1.70	58.80	8.00	1.710	S$_p$(^{1}L$_a$)
8	C_1	31080	5940	0.83	1.5	1.81	0.92	1.65	1.80	1.90	55.50	4.85	1.510	S$_p$(^{1}L$_a$)
9	C_{2h}	29860	2900	0.86	2.4	2.79	0.95	2.7	2.84	2.90	35.20	1.85	0.920	S$_p$(^{1}L$_a$)
10	C_{2h}	25300	2600	0.18	40.0	222.20	0.41	93.0	226.80	–	0.44	0.63	0.018[b]	S$_\alpha$(^{1}L$_b$)
11	D_{2h}	22500	2600	0.90	2.2	2.44	0.95	2.5	2.63	2.50	38.00	2.00	2.200	S$_p$(^{1}L$_a$)
12	C_1	30000	5920	0.81	1.9	2.35	0.88	2.1	2.39	2.50	41.80	5.71	1.370	S$_p$(^{1}L$_a$)
13	C_S	29600	4980	0.81	2.3	2.84	0.90	2.6	2.92	2.98	34.30	3.85	1.180	S$_p$(^{1}L$_a$)
14	C_S	28760	5340	0.82	2.7	3.29	0.93	3.1	3.30	3.34	30.30	2.26	1.110	S$_p$(^{1}L$_a$)
15	C_1	29640	5840	0.71	2.3	3.24	0.78	2.5	3.21	3.22	31.20	8.80	1.190	S$_p$(^{1}L$_a$)
16	C_{2V}	26880	4040	0.12	75.0	625.00	0.29	174.0	600.00	–	0.16	0.41	0.006[b]	S$_\alpha$(^{1}L$_b$)
17	C_{2V}	23820	4240	0.28	45.0	161.00	0.40	67.0	167.50	–	0.59	0.89	0.031[b]	S$_\alpha$(^{1}L$_b$)
18	D_{2h}	22860	3200	0.93	6.4	6.88	0.98	6.7	6.84	6.84	14.62	0.30	0.810	S$_p$(^{1}L$_a$)
19	D_2	25500	3220	0.84	2.6	3.01	0.90	2.7	3.00	2.89	33.30	3.70	1.520	S$_p$(^{1}L$_a$)
20	D_{2h}	26580	4100	0.24	4.4	18.30	0.29	4.7	16.20	16.00	6.20	15.10	0.250	S$_p$(^{1}L$_a$)
21	D_2	25000	4320	0.90	8.4	9.33	0.97	9.1	9.40	10.60	10.60	0.33	0.440	S$_p$(^{1}L$_a$)
22	C_2	30600	8360	0.72	3.0	4.17	0.82	3.4	4.15	4.34	24.10	5.29	0.820	S$_p$(^{1}L$_a$)
23	C_{2h}	27720	3230	0.16	44.0	275.00	0.36	95.0	263.90	257.20	0.38	0.67	0.014[b]	S$_\alpha$(^{1}L$_b$)
24	D_6	32400	7640	0.01	1.4	140.00	0.01	1.4	140.00	–	0.71	70.70	0.018[b]	S$_\alpha$(^{1}L$_b$)
25	C_{2V}	30060	3000	0.42	16.1	38.00	0.64	21.1	33.10	25.00	3.00	1.70	0.120	S$_\alpha$(^{1}L$_b$)
26	C_{2V}	29080	2940	0.46	17.0	36.90	0.64	19.2	30.00	19.00	3.33	1.87	0.130	S$_\alpha$(^{1}L$_b$)
27	C_{2V}	29260	2920	0.33	10.3	31.20	0.43	13.7	32.00	24.00	3.40	4.16	0.140	S$_\alpha$(^{1}L$_b$)
28	C_S	29320	3000	0.32	9.0	28.10	0.42	10.2	24.30	18.00	4.12	5.69	0.150	S$_\alpha$(^{1}L$_b$)
29	D_2	30100	7640	0.81	0.85	1.05	0.82	0.85	1.04	1.45	94.25	21.18	2.360	S$_p$(^{1}L$_a$)
30	C_2	29820	7840	0.88	0.9	1.02	0.90	0.9	1.02	1.38	97.83	11.10	2.580	S$_p$(^{1}L$_a$)
31	D_2	29060	7460	0.89	0.8	0.90	0.89	0.8	0.90	1.15	111.10	13.75	2.600	S$_p$(^{1}L$_a$)
32	D_{6h}	23390	2780	0.29	200.0	689.65	0.60	400.0	666.67	680.00	0.15	0.10	0.008	S$_\alpha$(^{1}L$_b$)

^a Headings from left to right: No. = compound number; S = symmetry group; υ_{00} = symmetry line wave number; $\Delta\upsilon$ = Stokes shift; γ = fluorescence quantum yield; τ_f = fluorescence decay time; τ_f^{ex} = experimental natural fluorescence lifetime; τ_0^T = natural lifetime; k_f = fluorescence rate constant; k_{ST} = intersystem crossing rate constant; f_e = S$_0 \to$ S^1 transition oscillator strength. The nature of the S^1 state is given in Clar's notation with Platt's notation in parentheses. *Denotes parameters for deaerated solutions.

^b Values in the f_e column (right) were calculated using Eq. (4).

This formula, according to [2], 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 bands were determined using the formula:

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

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

The error limits determined for the various fluorescence parameters are as follows: quantum yield ±10%, decay time ±5%, symmetry line frequencies ±60 cm^{-1}, Stokes shifts ±200 cm^{-1}, k_{ST} and k_f values ±15%. The error limits for experimental values of the oscillator strength, f_e, of the S$_0 \to$ S^1 transitions are within ±10%. The direction of polarization of the S$_0 \to$ S^1 transitions and the nature of the S^1 states were found with the aid of the PPP-CI method. The photochemical stability of the compounds was investigated using either an XeCl-laser (308 nm) or an N$_2$-laser (337 nm). A solution of the compound in question was exposed to laser impulses until noticeable changes in the absorption spectrum were observed. The number of impulses was counted. The ability of the compound for laser action was tested by employing the above lasers, and the transverse method of pumping was used.

3. Results and discussion

The main experimental fluorescence parameters of compounds studied are presented in Table 1. The UV absorption spectrum of biphenyl contains broad and structure-less p-band (^{1}A $\to$ ^{1}B$_1$) with ($\lambda_{max} = 250$ nm) and forbidden α(^{1}A $\to$ ^{1}A) and α^*(^{1}A $\to$ ^{1}B$_2$) bands which are submerged in the long-wavelength end of the p-band [16]. The shape of the biphenyl p-band can be explained by the rotational vibrations of the phenyl rings about the essential band which joins the phenyl rings. The lowest electronic transition in a biphenyl molecule is the ^{1}A $\to$ ^{1}L$_b$ (^{1}A $\to$ ^{1}A) transition. It has been shown in [6] that, in solution, the preferred angle between the phenyl rings is about 23°, caused by small amounts of steric hindrance between
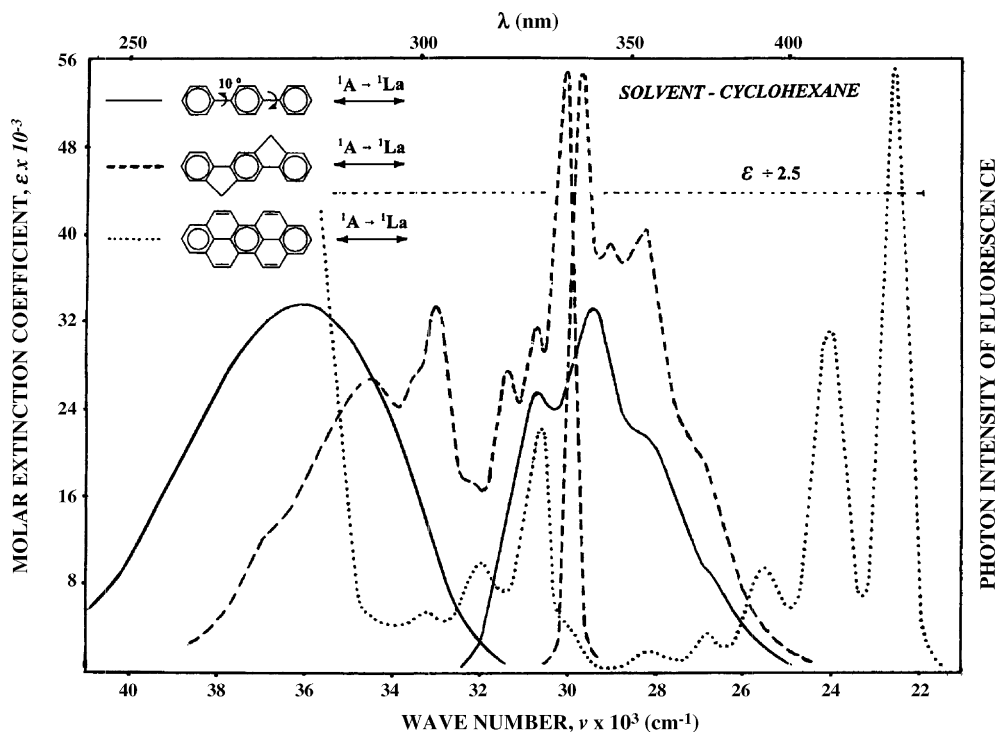
Fig. 2. Absorption and fluorescence spectra of compound **6** (*p*-terphenyl), compound **9** (2,2′-methylene-5′,6″-methylene-*p*-terphenyl), and absorption spectrum of compound **11** (peropyrene). The molar extinction coefficient of compound **11** was divided by 2.5. The ↔ mark shows the direction of polarization of the $S_0 \rightarrow S^1$ transition.

hydrogen atoms on adjacent rings. To explain the structure in the fluorescence spectrum of biphenyl, it is assumed that, in the S^1 excited state, the essential bond joining the phenyl rings acquires a certain amount of double-bond character and that the rings are coerced into a more planar configuration. In the $S_0 \rightarrow S^1$ transition, the bond order of the essential bond increases from 0.280 to 0.371 [17]. Considering the compounds (**1**–**4**), it is clear that the molecules in this row are becoming increasingly more planar and rigid, and change from D_2 symmetry group (compound **1**) to C_{2V} symmetry group (compounds **2**–**4**). It is important that the symmetry of compounds (**2**–**4**) is the same since this parameter greatly influences the fluorescence characteristics [18]. It is also necessary to point out that in the molecule of biphenyl the principal *z*-axis goes along the essential bond joining the phenyl rings, while in molecules of C_{2V} symmetry group it goes along the C_{2V}-axis [19]. That is why the $^1A \rightarrow {}^1L_a$ ($^1A \rightarrow {}^1B_1$) transition of the biphenyl molecule which forms the p-band is associated with the M^z-component of the dipole moment operator $\hat{M}$, while $^1A \rightarrow {}^1L_a$ ($^1A \rightarrow {}^1B_1$) transition of the fluorene molecule is associated with the M^y-component. Examining the results (Table 1) reveals that changes within the fluorescence parameters of compounds (**1**–**4**) are unsystematic with the notable exception of k_{ST}. Also note the diminished value of the quantum yield of phenanthrene (compound **4**), relative to fluorene (compound **3**). This is the case, even though phenanthrene has a more rigid and planar structure than fluorene. This is explained by the substantial decrease in the fluorescence rate constant, k_f, of phenanthrene in comparison with fluorene. The long-wave absorption band of fluorene is the α* band, while the long-wave absorption band of phenanthrene is the forbidden α band. This

contention is supported by modeling simulation using the PPP and INDO/S methods [20]. However, it should be noted that phenanthrene is not an iso-π-electron molecule, as is the case with compounds (**1**–**3**). It is also necessary to compare the value for τ_0^T (2.90 ns) and τ_0^* (89.00 μs) of biphenyl (Table 1). These values indicate that, in this compound, fluorescence is formed by the low intensity α band which is submerged in the more intense p-band while the value of τ_0^T was determined (Eq. (1)) by integrating over the whole of the p-band. Fluorescence parameters concerning compounds (**1**–**4**) have been previously noted in [21]. The decrease in the value of k_{ST} in the row of compounds (**1**–**4**) can be explained by the decrease in the σπ-interaction, which plays an important role in spin–orbit interaction between $S^1_{\pi\pi}$ and $T^1_{\pi\pi}$ states. Compound (**5**), pyrene, can also be regarded as a molecule with the biphenyl basis, though it is not an iso-π-electron molecule, like compounds (**1**–**3**) and belongs to the D_{2h} symmetry group. It is extremely rigid and planar. The lowest absorption band of pyrene is the forbidden α band. The k_{ST}-value for this compound is $0.16 \times 10^7 \text{ s}^{-1}$. The k_{ST}-value in the row of compounds (**1**–**5**) steadily decreases from 3.38×10^7 to $0.16 \times 10^7 \text{ s}^{-1}$, i.e. changes in the ratio 21:1. None of compounds (**1**–**5**) show laser action under any conditions. This is because of the forbidden nature of the $S_0 \rightarrow S^1$ transition (low value of fluorescence rate constant, k_f).

Now consider compounds (**6**–**11**). These can be regarded as *p*-terphenyl-based molecules with different degrees of planarity and rigidity, although dibenz[*a,h*]anthrancene and peropyrene are not iso-π-electron structures as are compounds (**6**–**9**).

The different degrees of planarity and rigidity are achieved by bridging between adjacent phenyl rings. It is believed that

in solution the terminal rings of *p*-terphenyl make an angle of about $10°$ with the plane containing the central ring [22]. Due to vibrational freedom of the phenyl rings in *p*-terphenyl, the absorption p-band of this compound is structure-less, wide and "bell-like" with $\lambda_{max} = 276$ nm. The structure of the fluorescence spectra is interpreted as being produced by a relatively planar configuration in the S^1 excited state. According to the classification suggested in [7], *p*-terphenyl as well as biphenyl belongs to the class III (S_0 non-planar, S^1 planar configurations). Within compounds (**6–10**), there is evidence of systematic changes within the various parameters from one compound to another; i.e. absorption and fluorescence become more structural, τ_f and τ_0^T increase, and $\Delta\upsilon_{st}$ and f_e decrease with k_{ST}, decreasing dramatically from a value of 11.40×10^7 s^{-1} to 0.63×10^7 s^{-1}, i.e. by more than 18 times. This decrease in k_{ST} from compounds (**6–9**) was first reported in [23]. Examples of the influence of "bridging" in *p*-terphenyl-based molecules on absorption and fluorescence spectra is shown in Fig. 2. In the case of compounds (**6–9**), the fluorescence is formed by a $^1L_a \rightarrow {}^1A$ transition, while in the case of compound **10** it is formed by a $^1L_b \rightarrow {}^1A$ transition. The decrease in γ in compound **10** can be explained by the dramatic decrease in k_f; that is, for compounds (**6–10**), k_f decreases from a value of 83.80×10^7 s^{-1} to 0.44×10^7 s^{-1}, i.e. by over 190 times. Compound (**11**) is extremely planar and rigid. Its absorption and fluorescence spectra are highly structural. The quantum yield, γ, is high and the k_{ST} value is low, although it is higher than the k_{ST} value of compounds (**9**) and (**10**). This is because the lowest fluorescent state, $S^1_{\pi\pi*}$, of compound (**11**) is allowed, but allowed states mix with triplet states more readily [18]. All the compounds under consideration, except compound (**10**) show good laser action, although the threshold of pumping in the row of compounds (**6–9, 11**) is increasing by a factor of 5.

Now consider the compounds in the group (**12–15**), chosen for their low-symmetry characteristics. These are also good examples of the influence of the degrees of planarity and rigidity on fluorescence parameters and the k_{ST} value. Through compounds (**12–15**), the values of γ, υ_{00}, $\Delta\upsilon_{st}$, and f_e change by only a small amount but k_{ST} changes significantly. As planarity and rigidity increase in compounds **12–14**, the values of υ_{00}, $\Delta\upsilon_{st}$, f_e and k_{ST} are decreasing, but when planarity and rigidity are affected by the tri-methylene group (compound **15**), all of the above parameters increase with the value of γ decreasing by about 13%. These compounds show laser action, but again the pumping threshold for the row of compounds (**12–15**) is slightly increasing. This fact could be explained by the decrease in the k_f value.

Compounds **16** and **17** belong to the same symmetry group, C_{2V}, but compound **15** is more planar and rigid. From compounds **16** and **17** the value of υ_{00} decreases with γ and k_{ST} increases, which at first inspection appears to be unusual. However, this is explained by the fact that compound **17**, benzo[*g,h,i*]fluoranthene, does not belong to the Ermolaev-Sveshnikova-type molecules, and the obtained value of k_{ST} is, in reality, the sum of k_{ST} and k_S. The increase in the value of γ is due to the increase in the value of f_e and consequently also of k_f. Compounds (**16** and **17**) do not show laser action because of the

forbidden nature of the S^1 state (S_α). Compound (**18**) is planar and rigid. As a result it has a high quantum yield and a low k_{ST} value. Its lowest transition ($^1A \rightarrow {}^1L_a$) is allowed and it displays laser action at room temperature, though the threshold is quite high. Compound (**19**) can be regarded as a derivative of compound (**5**). The transition from compound (**5**) to compound (**19**) is accompanied by the inversion of ^1L_b and ^1L_a states. But compound (**19**) is non-planar and non-rigid and hence the k_{ST} value has increased from 0.16×10^7 s^{-1} to 3.7×10^7 s^{-1}. Nevertheless, γ also has increased from 0.29 to 0.84. This is because the k_f value has increased from 0.25×10^7 s^{-1} to 33.3×10^7 s^{-1}, i.e. by a factor of 133. Compound (**19**) shows good laser action.

From the compounds considered up to this point, it is evident that when we investigate the non-planar to planar and non-rigid to rigid-type molecular structures, the values of k_{ST} generally decrease. There are however, important exceptions, an example of which can be demonstrated by the comparison of compounds (**20**) and (**23**). These compounds differ by their π-electron systems and by their symmetry groups D_{2h} and D_2, respectively. Nevertheless they can be justifiably and effectively compared, since most of the electron excitation in the S^1 excited state, about 90% according to estimates made using the PPP method in [24] of 9,10-diphenylanthracene, is localized in the anthracene fragment. With a comparison of compounds **20** and **21**, it is clear that the shape of the absorption and fluorescence curves remains unchanged while the values of υ_{00}, and k_{ST} decrease, the latter, steeply. Notably, however, the value of γ, contrary to expectations, increases from 0.24 (compound **20**) to 0.90 (compound **21**), by a factor of 3.75, even though the phenyl rings of compound **21** (9,10-diphenylanthracene) are turned through $57°$ relative to anthracene fragment [25]. The reason for this striking phenomenon is that the system of singlet and triplet levels in anthracene (compound **20**) is extremely sensitive to any substitution in positions 9 and 10. Calculations made using the PPP method show that, with the introduction of phenyl rings into the 9,10-anthracene positions, the system of singlet levels drops, while that of triplet levels rises, especially those which lie above the $T^1_{\pi\pi*}$ level (Fig. 3). The level of displacement as described above brings about a situation where only the T^1 level lies below the $S^1_{\pi\pi*}$ level in the 9,10-diphenylanthracene, which is a rare case. This accounts for the abrupt decrease in the value of k_{ST} (from 15.10×10^7 to 0.33×10^7 s^{-1}), which, in combination with the growth in the value of f_e of the long-wave p-band to $f_e = 0.25$–0.44 (for compounds **20** and **21**, respectively), results in a sharp increase in the value of γ. The long-wave absorption bands of compounds **20** and **21** are p-bands, and the fluorescence is formed in both cases by the $^1L_a \rightarrow {}^1A$ transition. It should be noted that the simulation (using the INDO/S method) of the systems of singlet and triplet levels of anthracene and of 9,10-diphenylanthracene levels gives the same qualitative results as those obtained by the PPP method. Anthracene does not display laser action under any pumping, while 9,10-diphenylanthracene is a good compound for dye laser, although the threshold is a bit high. The only reason for the high threshold is low k_f (10.6×10^7 s^{-1}).
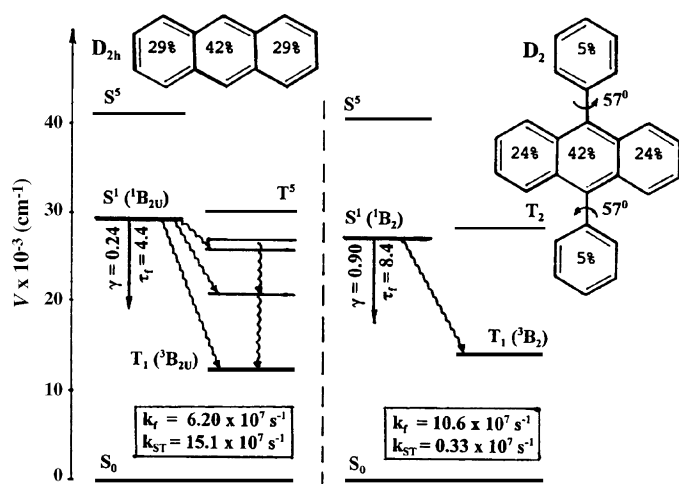
Fig. 3. Systems of singlet and triplet levels of anthracene and 9,10-diphenylanthracene, simulated by the PPP-CI method. The distribution of the electronic excitation in the $S^1_{\pi\pi*}$ state is shown in percentage. The distribution of the electronic excitation was simulated using the method described in [31].

If we now compare the behaviour of compounds (**22**) and (**23**), the degrees of planarity and rigidity increase and as a consequence the values of υ_{00}, $\Delta\upsilon_{ST}$ and k_{ST} decrease, with the latter one dramatically decreasing from a value of $5.29 \times 10^7 \, s^{-1}$ to $0.67 \times 10^7 \, s^{-1}$, i.e. by a factor of approximately 8. The value of γ decreases also because of the inversion of the S_p and S_α levels, and consequently, the value of k_f decreases dramatically by a factor of approximately 6.3. The absorption and fluorescence spectra of compound **23** are very structured and sharp, as opposed to those of compound **22**, which are almost structure-less. Only compound **22** shows laser action, because the lowest singlet state of compound **23** is forbidden. The values of the fluorescence parameters for compound **24** are those typical of a non-planar and non-rigid molecule with $\Delta\upsilon_{ST} = 7.64 \times 10^3 \, cm^{-1}$ and $k_{ST} = 70.70 \times 10^7 \, s^{-1}$ (Table 1).

Now consider compounds (**25–28**). Compounds (**26–28**) are produced by replacing the H-atom of carbozole (compound **25**). The oscillator strength of the $S_0 \rightarrow S_1$ transition in the row of compounds (**25–28**) is slightly increasing: 0.120, 0.130, 0.140, 0.150 and consequently the value of k_f is also increasing: 3.0×10^7, 3.33×10^7, 3.40×10^7 and $4.12 \times 10^7 \, s^{-1}$. This is explained by the fact that the extension of the carbazole molecule is happening in the direction of the polarization of the $S_0 \rightarrow S_1$ ($^1A \rightarrow {}^1L_b$) transition. The value of k_{ST} in the row of compounds (**25–28**) is also increasing: 1.70×10^7, 1.87×10^7, 4.16×10^7 and $5.69 \times 10^7 \, s^{-1}$. The only one explanation to this fact is the increase in the degree of disturbance of the π-system by the torsional vibrations of the substituted group of the molecule, because any out-of-plane vibrations of the π-system increase the $\sigma\pi$-interaction and consequently the spin–orbit coupling. None of the compounds (**25–28**) display laser action.

Compounds (**29, 31**) have the same symmetry group as compound (**6**) PPP. In the row of compounds (**6, 29, 31**) k_f is increasing: 83.90×10^7; 94.25×10^7; $97.83 \times 10^7 \, s^{-1}$, respectively, but the k_{ST} values of these compounds behave in a strange way. In transition from compound (**6**) to compound (**29**)

it increases from $11.40 \times 10^7 \, s^{-1}$ to $21.18 \times 10^7 \, s^{-1}$ and then it drops to $13.75 \times 10^7 \, s^{-1}$ (compound **31**). Such behaviour can be explained by the position of T_β (^3B_b) level relative to the S_p (^1L_a) level. According to the luminescence-laser classification of aromatic molecules given in [26], compounds (**6, 29**) belong to class IV, while compounds (**30**) and (**31**) belong to class V. Detailed study of compounds (**6, 29, 31**) is given in [17]. Compounds (**29–31**) display very good laser action.

Compound (**32**) is extremely planar and rigid, and belongs to D_{6h} symmetry group. That is why it has the lowest possible value of k_{ST} ($0.10 \times 10^7 \, s^{-1}$) among aromatic molecules. It also has the lowest possible value of k_f ($0.15 \times 10^7 \, s^{-1}$). Compounds (**32**) and (**18**) are studied in detail in [27].

3.1. The effect of planarity and rigidity on photochemical stability of aromatic compounds

The dependence of photochemical stability of aromatic compounds on planarity and rigidity was investigated in the rows of compounds (**1–5**), (**6–11**), (**12–15**) and (**20, 21**). The experiments conducted showed that photochemical stability decreases with increasing planarity and rigidity. For example, compound (**1**) is much more stable than compounds (**4**) and (**5**). In the row of compounds (**6–11**) the photochemical stability is declining steadily. Compound (**21**) is considerably more stable than compound (**20**). The quantum yield of fluorescence of compounds (**1**), (**6**) and (**21**) does not depends on the concentration of the solution, while the quantum yield of fluorescence of compounds (**5**), (**11**) and (**20**) is strongly affected by the concentration of the solution. The authors observed that concentration quenching of fluorescence is a common phenomenon for planar and rigid aromatic molecules. However, if the coefficient of absorption of a dye on the frequency of pumping is low then the concentration of solution must be high enough, otherwise the laser action would not be achieved. The concentration quenching becomes a great deal of concern if the transverse scheme of pumping is used [28]. May be because of this reason, among popular dyes there are no planar and rigid aromatic compounds [29]. There are two possible reasons which may explain why planar and rigid molecules are less photochemically stable than non-planar ones. First, planar and rigid molecules like pyrene, peropyrene and anthracene (compounds **5**, **11** and **20**) tend to dimerize with increasing concentration, while non-planar molecules are not converted to dimmers [4]. Secondly, it is well known that triplet states, being bi-radical in nature, are photochemically more active. But it is clear that non-planar and non-rigid molecules, due to different non-planar vibrational modes, degrade from the triplet T^1 level much easier than planar ones. Hence, the probability that non-planar molecules may undergo some photochemical process, while in the T_1 state is less than those for planar and rigid molecules. Finally, it should be pointed out that the values of γ for some compounds studied in this study are generally somewhat a bit lower than those presented in the monograph of [4]. However, the values of decay times τ_f are in good agreement with [4,30]. To determine the values of γ, Berlman [4] used 9,10-diphenylanthracene as a standard, considering its quan-

tum yield value to be equal to unity, which is now regarded as too high. According to our measurements, the γ value of dilute cyclohexane solution of 9,10-diphenylanthracene is 0.90.

4. Conclusions

The investigations showed differences in the behaviour of fluorescence parameters from the non-planar molecule to the planar and more rigid-type molecule in the following ways: the values of the symmetry line wave-number, υ_{00} (the frequency of the $S_0 \rightarrow S^1_{\pi\pi*}$ transition) and Stokes shift, $\Delta\upsilon_{ST}$, decrease. The oscillator strength, with consequences for the fluorescence rate constant, normally decreases. The changes in the quantum yield of fluorescence depend upon the changes in the k_f and k_{ST} values. Furthermore, the intersystem crossing rate constant generally decreases, sometimes very significantly, but there are some important exceptions. For example, the k_{ST} value of the non-planar molecule 9,10-diphenylanthracene is much lower than the k_{ST} value of the planar and more rigid molecule, anthracene. This phenomenon is explained. Planar and rigid aromatic molecules display very structural absorption and fluorescence spectra, while non-planar and non-rigid molecules do not exhibit any vibrational structure. If a molecule is more planar in excited state S^1 than in the ground S_0 state, then its absorption spectrum is non-structural and the fluorescence spectrum can show some structure. An example is *p*-terphenyl (PPP), i.e. compound (**6**). Compound (**24**) has the highest k_{ST} value known to the authors among aromatic molecules, because it is not planar and not rigid at all. Compound (**32**), coronene, has the lowest known k_{ST} value because it is planar, very rigid, and belongs to the high D_{6h} symmetry group. It is also found that the k_{ST} value depends strongly on the symmetry group of a molecule; the higher the symmetry the lower the k_{ST} value. It is also observed that the photochemical stability of a compound is also affected by planarity and rigidity: non-planar and non-rigid molecules are more stable. For example, 9,10-diphenylanthracene is much more stable than anthracene. Biphenyl is more stable than phenanthrene. *p*-Terphenyl (PPP) is more stable than compounds (**10**) or (**11**). The difference in stability is explained by the fact that in non-planar and non-rigid molecules torsional vibrations of some fragments of a molecule increase the probability of deactivation of triplet level T_1, which is chemically very active. Dimerisation is also much less possible between non-planar and non-rigid molecules. The observation of the dependence of pho-

tochemical stability upon planarity and rigidity is very important for the quest for new effective laser dyes. Although compound (**11**) has a high oscillator strength and very high quantum yield it practically cannot be used as an active medium in dye lasers because of the low photochemical stability. The laser abilities of the investigated compounds have been tested.

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