Photonics and photochemical stability of aromatic molecules, family related in \(\pi\)-structure but different in planarity, rigidity and molecule symmetry

N. Nijegorodov\(^a\), V. Zvolinsky\(^b\), P.V.C. Luhanga\(^{a,*}\)

\(^a\) Physics Department, University of Botswana, Private Bag UB00704, Gaborone, Botswana
\(^b\) Department of Environmental Sciences, Russian Friendship University, Mokhoto-Makalapa Street 6, 117998 Moscow, Russia

Abstract

Intramolecular processes and fluorescence properties of 32 specially chosen aromatic molecules, different in degrees of planarity and rigidity, but family related in \(\pi\)-structure are experimentally and theoretically (using the PFP-method) studied at room temperature (293 K). The quantum yields of fluorescence \(\gamma\) and decay times \(\tau\) of deoxygenated and non-deoxygenated cyclohexane solutions are measured. The oscillator strength \(f\), the fluorescence rate constants \(k_f\), the natural lifetimes \(\tau^\ast\), and the intersystem crossing rate constants \(k_{ISC}\) 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 \(\nu_0\) (the frequency of the \(S_0 \rightarrow S_0^\ast\) transition) and the Stokes shift \(\Delta\lambda_{ST}\) 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 \(k_{ISC}\) values. Furthermore, the intersystem crossing rate constant generally decreases, sometimes very significantly. However, there are some interesting exceptions. For example, the \(k_{ISC}\) value of the non-planar molecule of 9,10-diphenylanthracene is less than the \(k_{ISC}\) 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.

Keywords: Planarity, Rigidity, Fluorescence and laser properties

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 structureless 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 minor 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 structureless 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. Berhman [7], however, showed later that rigidity in the \(S_0\) state was not an 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.
Furthermore, it is obvious that not all the effects of these factors have been properly investigated. Specifically, the influence of planarity and rigidity on molar extinction coefficients is little known. An approach to this problem requires the systematic analyses of a large quantity of experimental data. As 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 compounds, different in degrees of planarity and rigidity but family related in structure. The type of compounds are as follows: (1) biphenyl; (2) 9,10-dihydrophenanthrene; (3) fluorene; (4) phenanthrene; (5) pyrene; (6) naphthalene; (7) 2,2'-ethylenyl-2,2'-terphenyl; (8) 2,2'-methylene-naphthalene; (9) 2,2'-methylene-5,5'-terphenyl; (10) dibenz[a]anthracene; (11) pyrene; (12) 2,2-bisphenyl; (13) 2-phenyl-3,3'-methyleneindoles; (14) 2-phenyl-3,3'-benzophenone; (15) 2,2',2'-trimethyleneindoles; (16,17,18) benzophenone; (18) benzophenone-pyrene; (19) benzophenone-terphenyl; (20) anthracene; (21) 9,10-diphenylanthracene; (22) 1,1'-biphenyl; (23) chrysene; (24) naphthalene-carbazole; (25) carbazole; (26) N-methylcarbazole; (27) N-phenylcarbazole; (28) N-vinylcarbazole; (29) p-quinophenyl; (30) 3,3'-dimethyl-2,2'-terphenyl; (31) p-quinophenyl; (32) carbazole. 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, kST value and photochemical stability.

2. Experimental methods

The compounds studied were re-cristallized, sublimated and purity-controlled by using high-sensitivity thin-layer chromatography. The ultraviolet spectra of the compounds were recorded using a SPECORD M40 spectrophotometer with spectrophotometry cyclohexane or benzene as solvent. Compounds (6, 11, 29, 31), which are low solubility, were dissolved using a 9:1 cyclohexane-benzene mixture in an ultrasonic USL-61.25 bath. A Hitachi MPS-4 spectrophotometer 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-diphenylanthracene 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-diphenylanthracene 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 bandwidth 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, τF, was measured using either an SLM-4800S pulse fluorimeter or installation based on the spectroscopic principle combined with single photon counting measurements [12], depending on the value of τF. The natural lifetimes were calculated using the formula presented in [12] and modified in [13]:

\[
\frac{1}{\tau_F} = 2.28 \times 10^{-6} \eta^2 \left( \frac{v}{\nu} \right)^{-1} \int \frac{x(\tilde{v})}{\tilde{v}} d\tilde{v}
\]

where \( \eta = \frac{9}{4\pi} \left( 2 \nu^2 + 2 \nu^2 \right) \) (Lorentz factor), \( \nu \) is the refractive index of the solvent, \( \nu \) is the frequency in cm\(^{-1} \) and \( x(\tilde{v}) \) is the molecular extinction coefficient. Decoloration 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 unfrozen. For deep de-coloration, the procedure could be repeated. The value of \( k_{ST} \) was calculated by taking into account the fact that the fluorescence quantum yields of highly decelerated solutions of photo-stable compounds can be determined using Eq. (2), with only intramolecular quenching processes considered:

\[
y_k = \frac{k_S}{k_S + k_{ST}}
\]

where \( y_k \) is the fluorescence quantum yield of the de-colorated solution and \( k_S \) is the internal conversion rate coefficient. From Eq. (2) one obtains:

\[
k_S + k_{ST} = \frac{1 - y_k}{y_k}
\]

where \( \tau_F \) is the fluorescence decay time for the de-colorated solution. For the Ermolaev-Svetlikova [15] molecules, \( k_S \) is very much less than \( k_B + k_{ST} \) and in many cases \( k_S \ll k_{ST} \), hence \( k_S \approx \frac{1 - y_k}{\tau_F} \).

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

\[
\Delta \omega_{ST} = \omega_k - \omega_0
\]

where

\[
\omega_k = \frac{\int \sigma(\nu) x(\nu) d\nu}{\int \sigma(\nu) x(\nu) d\nu}
\]

and

\[
\omega_0 = \frac{\int \sigma(\nu) x(\nu) d\nu}{\int \sigma(\nu) x(\nu) d\nu}
\]

\( \Delta \omega_{ST} \) and \( \omega_k \) are the center of gravity” or first moment of the long-wave absorption band and fluorescence spectrum, respectively, \( \nu_0 \) and \( \nu_k \) are the frequencies in the range of the absorption and fluorescence spectra, \( \sigma(\nu) \) is the intensity of fluorescence. The oscillator strength of well-resolved long-wave absorption bands was determined using the formula:

\[
f_\alpha = 1.3 \times 10^{-8} \int f(\nu) d\nu
\]
Fig. 1. Structural formula of the investigated compounds.
Table 1

Experimental and calculated values for the main fluorescence parameters of diluted ethylene solutions of the investigated compounds

<table>
<thead>
<tr>
<th>No.</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>10400</td>
<td>616</td>
<td>2400</td>
<td>750</td>
<td>616</td>
<td>2400</td>
<td>750</td>
<td>616</td>
<td>2400</td>
</tr>
<tr>
<td>V</td>
<td>2500</td>
<td>2500</td>
<td>2500</td>
<td>2500</td>
<td>2500</td>
<td>2500</td>
<td>2500</td>
<td>2500</td>
<td>2500</td>
</tr>
<tr>
<td>T</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>L</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>R</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>S</td>
<td>10400</td>
<td>616</td>
<td>2400</td>
<td>750</td>
<td>616</td>
<td>2400</td>
<td>750</td>
<td>616</td>
<td>2400</td>
</tr>
<tr>
<td>V</td>
<td>2500</td>
<td>2500</td>
<td>2500</td>
<td>2500</td>
<td>2500</td>
<td>2500</td>
<td>2500</td>
<td>2500</td>
<td>2500</td>
</tr>
<tr>
<td>T</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>L</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>R</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

1. Heads: left to right: No. = compound number; S = symmetry group; V = symmetry point group; T = point group; L = point group; R = point group; S = symmetry point group; V = symmetry point group; T = point group; L = point group; R = point group. 2. Values in the | 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:

\[ f_0 = \frac{4.51 \times 10^6 \gamma}{\beta^4 \gamma \gamma} \]  

(4)

This was obtained by dividing Eq. (3) by a simplified version of Eq. (3), taking into account that \( (\gamma^2)^{1/2} = f_0^{1/2} \). The error limits determined for the various fluorescence parameters are as follows: quantum yield \( \pm 10% \), decay time \( \pm 5% \), symmetric line frequencies \( \pm 600 \text{cm}^{-1} \), Stokes shifts \( \pm 200 \text{cm}^{-1} \), and \( \beta \) values \( \pm 15% \). The error limits for experimental values of the oscillator strength, \( f_0 \), of the \( S_0 \rightarrow S_1 \) transitions are within \( \pm 10% \). The direction of polarization of the \( S_0 \rightarrow S_1 \) transitions and the nature of the \( S_1 \) states were found with the aid of the PPP-Cl method. The photophysical stability of the compounds was investigated using either an XeCl-laser (308 nm) or a N\(_2\)-laser (337 nm). A solution of the compound in question was exposed to laser impulles until noticeable changes in the absorption spectrum were observed. The number of impulles 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 centered at p-band \( (1A \rightarrow 1B_1) \) with \( \lambda_{max} = 250 \text{ nm} \) and forbidden \( (1A \rightarrow 1A) \) and \( (1A \rightarrow 1B_2) \) 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 bond which joins the phenyl rings. The lowest electronic transition in a biphenyl molecule is the \( 1A \rightarrow 1A \) transition, which 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
hydrogen atoms on adjacent rings. To explain the structure in the fluorescence spectrum of biphenyl, it is assumed that, in the S1 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 S0 → S1 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 D2h symmetry group (compound 1) to C2v 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 C2v symmetry group it goes along the C2v-axis [19]. That is why the 1A → 1Eg (1A → 1B1) transition of the biphenyl molecule which forms the p-band is associated with the M2-component of the dipole moment operator M, while 1A → 1A1 (1B1 → 1B2) transition of the fluorescence molecule is associated with the M1-component. Examining the results (Table 1) reveals that changes within the fluorescence parameters of compounds (1–4) are unsystematic with the notable exception of kν. Also note the diminished value of the quantum yield of phenanthrene (compound 4), relative to fluorene (compound 5). 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, kν, 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 π 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 kν (90 ms) and τ0 (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 π band while the value of t0 was determined (Bp (1)) by integrating over the whole of the π band. Fluorescence parameters concerning compounds (1–4) have been previously noted in [21]. The decrease in the value of kν in the row of compounds (1–4) can be explained by the decrease in the σ σ interaction, which plays an important role in the spin–orbit interaction between S2π and T2π 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 D2h symmetry group. It is extremely rigid and planar. The lowest absorption band of pyrene is the forbidden α band. The kν value for this compound is 0.16 × 107 s−1. The kν value in the row of compounds (1–5) steadily decreases from 3.38 × 107 to 0.16 × 107 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 S0 → S1 transition (low value of fluorescence rate constant, kν).

Now consider compounds (6–11). These can be regarded as π-terphenyl-based molecules with different degrees of planarity and rigidity, although dimeric[6–9] anthracene and perpyrene 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 (S0 non-planar, S1 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, $r_0$ and $r_0^*$ increase, and $\Delta \nu$ and $f_0$ decrease with $k_{ST}$, decreasing dramatically from a value of $1.14 \times 10^7 s^{-1}$ to $0.63 \times 10^7 s^{-1}$, 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 $1^{1}L_0 \rightarrow 1A$ transition, whereas in the case of compound 10 it is formed by $1^{1}L_0 \rightarrow 1A$ transition. The decrease in $\gamma$ in compound 10 can be explained by the dramatic decrease in $k_{ST}$ that is, for compounds (6–10), $k_{ST}$ decreases from a value of $3.50 \times 10^7 s^{-1}$ to $0.44 \times 10^7 s^{-1}$, i.e., by over 100 times. Compound (11) is extremely planar and rigid. Its absorption and fluorescence spectra are highly structural. The quantum yield, $\gamma$, 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, $S_1^{fluoro}$, of compound (11) is allowed, but allowed states mix with triplet states more readily [18]. However, all the triplet states in compound (11) 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 $\gamma$, $\Delta \nu$, $r_0$, and $f_0$ change by only a small amount but $k_{ST}$ changes significantly. As planarity and rigidity increase in compounds (12–14), the values of $\nu_0$, $\Delta \nu$, $f_0$, 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 $\gamma$ 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 $k_{ST}$

Compounds 16 and 17 belong to the same symmetry group, $C_{2v}$, but compound 18 is more planar and rigid. From compounds 16 and 17 the value of $\nu_0$ decreases with $\gamma$ and $k_{ST}$ increases, which at first inspection appears to be unusual. However, this is explained by the fact that compound 17, benzof[4,5]fluoranthene, does not belong to the Enckel-Svechkarev-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 $\gamma$ is due to the increase in the value of $f_0$ and consequently also of $k_{ST}$.

Compounds 16 and 17 do not show laser action because of the forbidding nature of the $S_1$ state ($S_1$). Compound (18) is planar and rigid. As a result it has a high quantum yield and a low $k_{ST}$ value. Its lowest transition ($1^{1}A \rightarrow 1^{1}L_0$) 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 (8). The transition from compound (5) to compound (19) is accomplished by the inversion of $1^{1}L_0$ and $1^{1}L_2$ states. But compound (19) is non-planar and non-rigid and hence the $k_{ST}$ value has increased from $0.16 \times 10^7 s^{-1}$ to $3.7 \times 10^7 s^{-1}$. Nevertheless, the $k_{ST}$ value has increased from $0.25 \times 10^7 s^{-1}$ to $3.3 \times 10^7 s^{-1}$, i.e., by a factor of 13. 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 transition rigid to rigid type more, the value of $\gamma$ generally decrease. There are however important exceptions, an example of which can be demonstrated by the comparison of compounds (20) and (21). These compounds differ by their $\pi$-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 $\nu_0$, $\Delta \nu$, and $k_{ST}$ decrease, the latter, steeply. Notably, however, the value of $r_0$, contrary to expectations, increases from 0.24 (compound (20)) to 0.50 (compound (21)), by a factor of 3.75, even though the phenyl rings of compound (21) show laser action, whereas the long-wave absorption bands of compounds (20) and (21) are p-bands, and the fluorescence is formed in both cases by the $1^{1}L_0 \rightarrow 1A$ transition. It should be noted that the simulation (using the INDO method) of the systems of singlet and triplet levels of anthracene and of 9,10-diphenylanthracene 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 $k_{ST}$ ($10.6 \times 10^6 s^{-1}$).
it increases from $1.14 \times 10^{7}$ 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 behavior can be explained by the position of $T_{0}$ ($^{1}B_{g}$) level relative to the $S_{u}$ ($^{1}L_{a}$) 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 $D_{3h}$ 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 $k_{T}$ ($0.15 \times 10^{7}$ 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 depend 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, perylene 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 state level much easier than planar ones. Hence, the probability that non-planar molecules may undergo some photochemical process, while in the $T_{0}$ state is less than those for planar and rigid molecules. Finally, it should be pointed out that the values of $\nu$ for some compounds studied in this study are generally somewhat lower than those presented in the monograph [4]. However, the values of decay times $\tau_{P}$ are in good agreement with [4,29]. To determine the values of $\nu$, Bertman [4] used 9,10-diphenylanthracene as a standard, considering its quan-
4. Conclusions

The investigations showed differences in the behaviour of fluorescence parameters from the non-planar molecule to the planar and more rigid-type molecules in the following ways: the values of the symmetry line wave-number, \( \nu_{98} \) (the frequency of the \( S_0 \rightarrow S_{98} \) transition) and Stokes shift, \( \Delta \nu_{98} \), 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 \( k_{98} \) values. Furthermore, the intersystem crossing rate constant generally decreases, sometimes very significantly, but there are some important exceptions. For example, the \( k_{98} \) value of the non-planar molecule \( 9,10 \text{-diphenylanthracene} \) is much lower than the \( k_{98} \) 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-structured and the fluorescence spectrum can show some structure. An example is \( p \)-terphenyl (PPP), i.e., compound (6). Compound (24) has the highest \( k_{98} \) value known to the authors among aromatic molecules, because it is not planar and not rigid at all. Compound (24), coronene, has the lowest known \( k_{98} \) value because it is planar, very rigid, and belongs to the high \( D_{4h} \) symmetry group. It is also found that the \( k_{98} \) value depends strongly on the symmetry group of a molecule; the higher the symmetry the lower the \( k_{98} \) 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, \( 9,10 \text{-diphenylanthracene} \) is much more stable than anthracene. Biphenyl is more stable than phenanthrene, \( p \)-terphenyl (PPP) is most 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. Dimerization is also much less possible between non-planar and non-rigid molecules. The observation of the dependence of photochemical 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 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.

References