Fluorescence and laser properties of D$_2$-, C$_2$- and D$_3$ symmetry series oligophenylenes

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Abstract

The fluorescence and laser properties of ten aromatic compounds, specially chosen from the $p$-oligophenylenes (D$_2$ symmetry) or $m$-oligophenylenes (C$_2$ or D$_3$ symmetry) are studied experimentally (at 293 K) and quantum chemically. The quantum yields, $\gamma$, and the decay times, $\tau$, of fluorescence are measured for deuterated and non-deuterated cyclohexane solutions. The oscillator strengths, $f_\text{osc}$, of the $S_0\rightarrow S_1$ ($^1\text{A} \rightarrow ^1\text{I}_\text{u}$) and $S_0\rightarrow S_2$ ($^1\text{A} \rightarrow ^1\text{I}_\text{g}$) transitions, fluorescence, $\lambda_f$ and intrasystem crossing, $\tau_{\text{IC}}$, rate constants, and natural lifetimes, $\tau_0^0$ are calculated. The lowest $^1\text{I}_\text{u}$, $^1\text{I}_\text{g}$ and $^1\text{A}$ (77 K) levels are determined. It is found that all $p$-oligophenylenes from $p$-terphenyl onwards are excellent, photochemically stable laser dyes although the solubility in this series decreases dramatically. On the basis of trends observed in $p$-oligophenylenes (D$_2$-series) and on the properties of the experimentally studied $m$-oligophenylenes of the C$_2$- and D$_3$-series, the fluorescence and laser properties of other compounds from these series are estimated/predicted. It is shown, for the first time, that $m$-oligophenylenes of the C$_2$-series, from 1,3-di(4-p-terphenyl)benzene will acquire fluorescence of $^1\text{I}_\text{g} \rightarrow ^1\text{A}$ nature and could be extremely effective laser dyes. It is also shown that $m$-oligophenylenes of the D$_3$-series, from 1,3,5-tri(4-p-terphenyl)benzene will also acquire $^1\text{I}_\text{g} \rightarrow ^1\text{A}$ nature fluorescence and laser ability, although this would not be as good as that of compounds in the C$_2$-series. It is concluded that $m$-oligophenylenes can be used not only as passive mode locking but some may also be used as laser dyes and semiconductors. The results obtained are important for various practical purposes and theoretical considerations.

Keywords: $p$-Oligophenylenes, $m$-Oligophenylenes, Fluorescence properties, Laser properties

1. Introduction

The possibility of using $p$-oligophenylenes and their derivatives as active media in dye lasers, producing coherent emission in the near ultraviolet, has been shown in [1,2] and more recently in [3–5]. It has also been pointed out that some $m$-oligophenylenes, while unable to show laser ac-
tion, can be used for passive mode locking [4,5]. Repeated addition of a phenyl ring onto the terminal 'para' position of \( p \)-oligophenylenes forms a single series of compounds of \( D_2 \) symmetry. However, \( m \)-oligophenylenes can possess either \( C_2 \) or \( D_4 \) symmetry and hence can be classified into two series, the \( C_2 \)-series and the \( D_4 \)-series. Until now, the fluorescence and laser properties of these different oligophenylene series have not been subjected to systematic investigation, nor have they been investigated in comparison with each other.

The lowest \( S_0 \) state of an aromatic molecule can possess either \( S_0 \) \((1L_a)\) or \( S_0 \) \((1L'_a)\) orbital nature depending on the structure and number of \( \pi \)-electrons. Fluorescence will thus be produced by either \( 1L_a \rightarrow 1A \) \((S_p \rightarrow S_0)\) or \( 1L'_a \rightarrow 1A \) \((S_a \rightarrow S_0)\) transitions, respectively. The former transition is essentially an allowed one-electron transition while the latter are biconfigurational, asymmetric and forbidden [6]. Many researchers have reported that the properties of the fluorescence produced by the two different types of transitions are completely different in nature [7,8]. The differences in fluorescence properties are explained not only by the forbidden nature of the \( 1L'_a \rightarrow 1A \) transition, but also by the fact that the majority of molecules that have an \( S_0 \) state with \( 1L_a \) nature have lower \( k_{\text{ad}} \) values than family related molecules with \( 1L'_a \) \( S_0 \) states [4,9]. Organic molecules do not show laser action if the \( S_0 \) state is of \( 1L_a \) nature [2,4]. Moreover, the threshold of laser oscillation is significantly affected by the \( 1L_a \rightarrow 1L_a \) energy gap [10,11]. It has been shown that the oscillator strength of the \( p \)-band, \( f \) \((S_0 \rightarrow S_p)\) of \( n \)-oligophenylenes is usually two or even three times higher than that of the corresponding \( p \)-oligophenylenes [4]. Hence, if an \( m \)-oligophenylene compound were to have an \( S_0 \) state of \( 1L_a \) nature it would be an extremely effective laser dye. However, to date no \( m \)-oligophenylene compound has been reported with \( 1L_a \rightarrow 1A \) nature fluorescence.

The objectives of the current work are 2-fold. Firstly, to observe and compare the fluorescence and laser properties of \( p \)- and \( m \)-oligophenylenes of the \( D_2 \)-, \( C_2 \)- and \( D_4 \)-series. Secondly, to estimate/predict (by extrapolation from experimental data, on the basis of trends observed in the \( D_2 \)-series and properties of early compounds in the \( C_2 \)- and \( D_4 \)-series) the properties of these members of the \( C_2 \)- and \( D_4 \)-series unavailable for experimental measurement. The compounds of the \( D_2 \)-series are: (2) biphenyl, (3) \( p \)-terphenyl, (4) \( p \)-quaterphenyl, (5) \( p \)-quinquinphenyl and (6) \( p \)-sexiphenyl. Compounds of the \( C_2 \)-series are: (7) \( m \)-terphenyl, (8) 1,3-di(biphenyl)benzene, (9) 1,3-di(\( p \)-terphenyl)benzene, (10) 1,3-di(\( p \)-quaterphenyl)benzene, (11) 1,3-di(quinquinphenyl)benzene. Compounds of the \( D_4 \)-series are: (12) 1,3,5-triphenylbenzene, (13) 1,3,5-tri(biphenyl)benzene, (14) 1,3,5-tri(\( p \)-terphenyl)benzene, (15) 1,3,5-tri(\( p \)-quinquinphenyl)benzene, (16) 1,3,5-tri(quinquinphenyl)benzene. The general structures of these compounds are illustrated in Fig. 1. In addition, benzene (1) is included as the elementary building block of the oligophenylenes.

2. Experimental

The compounds studied were recrystallized, sublimed or distilled and purity controlled using chromatography. Solutions of compounds (1–4, 7, 12) were prepared with spectro-grade cyclohexane as the solvent. Compounds (5, 8, 13) and particularly (6) are of low solubility and so were dissolved using a 9:1 cyclohexane:benzene mixture in an ultrasonic bath. The quantum yields of fluorescence were measured using the method described in [12] and a dilute solution of 9,10-diphenylanthracene in cyclohexane served as a standard. The fluorescence quantum yield of 9,10-diphenylanthracone was measured using the method described in [13] and found to be 0.90. The decay times of fluorescence, \( \tau_f \), were measured using either an SLM-480S phase fluorimeter or installations based on the stroboscopic principle combined with single photon counting measurements [14], depending on the value of \( \tau_f \). The natural lifetimes were calculated using the formula presented in [15]:

\[
\frac{1}{\tau_f} = 2.88 \times 10^{-9} \eta^2 \langle \nu_i \rangle^{-1} \theta \int d\nu \frac{d\Phi}{\nu}
\]

(1)

where \( \theta = \eta \mu/(n^2 + 2) \) is the Lorentz–Lorenz fac-
Fig. 1. Schematic representation of the molecular structure of oligophenylene of the D₂, C₂- and D₂-series. N is the number of phenyl rings in the branch attached to the central benzenoid hub.

tor [16], n is the refractive index of the solvent, v is the frequency in cm⁻¹ and ε(0) is the molar extinction coefficient. Deaeration was carried out using the method described in [17]. Assuming that the quantum yield of highly dilute, deaerated solutions of photostable compounds is determined only by monomolecular quenching processes, the quantum yield, γ*, is related to kᵣ, kₛ and kₛ (rate constants for fluorescence, intersystem crossing and internal conversion, respectively) as follows [16]:

\[ γ* = \frac{kᵢ}{(kᵣ + kₛ + kₛ)} \]  

From Eq. (2) one obtains:

\[ kₛ + kₛ = (1 - γ*) \]

where τᵣ is the fluorescence decay time for the deaerated solution. It has been shown that for molecules with an S₁ – S₀ energy gap greater than 24 000 cm⁻¹, kₛ ≪ kₛ [18,19]. Hence:

\[ kₛ = \frac{(1 - γ*)}{τᵣ} \]

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

\[ Δεₛ = \overline{εₛ} - \overline{εᵣ} \]

where

\[ \overline{εₛ} = \frac{\int νₛ(νₛ)dνₛ}{\int ε(νₛ)dνₛ} \]

and

\[ \overline{εᵣ} = \frac{\int νᵣ(νᵣ)dνᵣ}{\int I(νᵣ)dνᵣ} \]

\( \overline{εₛ} \) and \( \overline{εᵣ} \) are the 'centers of gravity' or 'first moments' of the long-wave absorption band and
fluorescence spectrum, respectively. \( \tilde{r}_q \) and \( \tilde{r}_v \) are the frequencies in the range of the absorption and fluorescence spectra and \( I(\tilde{r}_v) \) is the photon intensity of fluorescence. The experimental natural fluorescence lifetime of the solution, \( \tau^\text{ex} \), and that of the deaerated solution, \( \tau^\text{ex*} \), were calculated using the following formulas:

\[
\tau^\text{ex} = \frac{\tilde{r}_v}{\gamma}
\]

and

\[
\tau^\text{ex*} = \frac{\tilde{r}_v}{\gamma^*}
\]

If \( \tilde{r}_v, \gamma, \gamma^* \) and \( \gamma^* \) are measured accurately, with little uncertainty then \( \tau^\text{ex} \) and \( \tau^\text{ex*} \) will be almost equal.

The oscillator strengths of well resolved long-wave absorption bands were determined using formula Eq. (3) [16]:

\[
f_e = 1.3 \times 10^{-3} \int_{\tilde{r}_v}^\infty \sigma d\tilde{r}
\]

where the oscillator strengths of low intensity or submerged bands were determined using the formula:

\[
f_e = \frac{4.514 \tilde{r}_v^{4,7}}{n^2(\tilde{r}_v)^3 \gamma}
\]

which is obtained by dividing Eq. (3) by a simplified version of Eq. (1), when:

\[
(\tilde{r}_v)^{4,7} \propto (\tilde{r}_v)^3.
\]

The fluorescence spectra were studied at 293 K and the energy of \( S_1 \) (the fluorescent state) was assumed to correspond to the energy at the point of intersection of the absorption and fluorescence spectra. The energy of the lowest triplet level, \( T_1 \), was determined from the phosphorescence spectrum at 77 K. At this temperature, if freezing is rapid, the cyclohexane solutions of the compounds change to a snow-like mass [20] and so, the emission spectra were recorded with reflected light.

The energy of the \( S_2 \)-level, in cases where it was not the lowest, but was well defined, was estimated using the long-wave slope of the p-band. The energies of completely submerged \( S_2 \)-levels of \( p \)-oligophenylene were found with the help of the absorption spectra of thin films at 77 K and were also estimated using the PPP-CI method. Though this method predicts the energy of the Frank-Condon transition, it allows the simulation of the \( ^1L_\text{b} ^1L_\text{u} \) energy gaps with appropriate accuracy.

The same method was used to simulate the direction of polarization for the \( S_0 \rightarrow S_p \) and \( S_p \rightarrow S_u \) transitions.

The error limits determined for the various fluorescence parameters are as follows: quantum yield, \( \pm 10\% \), decay time, \( \pm 5\% \), symmetry line frequencies, \( \pm 60 \text{ cm}^{-1} \), Stokes shift, \( \pm 200 \text{ cm}^{-1} \), \( k_\text{ex} \) and \( k_\text{f} \) values, \( \pm 15\% \). A routine transverse and longitudinal pumping procedure [21] was used to investigate possible laser action of the compounds studied experimentally. A XeCl (308 nm) laser was employed for pumping the \( p \)-oligophenylene and a KrF (248 nm) laser for pumping the \( m \)-oligophenylene.

3. Results and discussion

According to the classification scheme of [22], compounds of the D_{2h}-series belong to class III: non-planar in the \( S_0 \) state and planar in the \( S_1 \) state. Their absorption spectra are eroded and non-structural, while their fluorescence spectra are structural. Compounds of the C_{2v} and D_{2h}-series belong to class II. They are non-planar in the \( S_0 \) state as well as in the \( S_1 \) state, although the geometry of compounds (7) and (8), from the C_{2v}-series are nearer planarity in the \( S_1 \) state. The main fluorescence parameters of non-deaerated and deaerated cyclohexane solutions of the experimentally studied compounds are given in Table 1. The energy of the lowest \( S_0 \left( ^1L_\text{b} \right), S_0 \left( ^1L_\text{u} \right) \) and \( T_1 \left( ^1L_\text{u} \right) \) states, energy intervals between them and \( f_e \) of the \( S_0 \rightarrow S_p \) and \( S_p \rightarrow S_u \) transitions are given in Table 2. The estimated energies of the singlet and triplet levels and the nature of fluorescence of the compounds in the C_{2v} and D_{2h}-series that were unavailable for experimental investigation are given in Table 3. The absorption and fluorescence spectra of \( p \)-oligophenylene (D_{2h}-series) are presented in Fig. 2. Analysis of the experimental data
<table>
<thead>
<tr>
<th>No</th>
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<th>( \Delta \lambda_{ST} ) (nm)</th>
<th>( \beta )</th>
<th>( \eta ) (nm)</th>
<th>( \epsilon_\ell ) (mol)</th>
<th>( \epsilon_\ell^0 ) (mol)</th>
<th>( \epsilon_\ell^0 ) (mol)</th>
<th>( k_e ) (10^7 s(^{-1}))</th>
<th>( k_{ST} ) (10^7 s(^{-1}))</th>
<th>( f_0 )</th>
<th>Nature of S</th>
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<td>100.00</td>
<td>-</td>
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<td>2.13</td>
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Headsings from left to right: No, compound number; S, symmetry group; \( \lambda_0 \), symmetry line wavenumber; \( \Delta \lambda_{ST} \), Stokes shift; \( \eta \), fluorescence quantum yield; \( \epsilon_\ell \), fluorescence decay time; \( \epsilon_\ell^0 \), experimental natural fluorescence lifetime; \( \epsilon_\ell \), natural lifetime; \( k_e \), fluorescence rate constant; \( k_{ST} \), intersystem crossing rate constant; \( f_0 \), (S\(_2\) \(

* Parameters for deuterated solutions.
* Values calculated using Eq. (4).
Table 2

The lowest singlet and triplet levels, energy intervals between and oscillator strengths, $f$, of the $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_0$ transitions of the experimentally investigated compounds.

<table>
<thead>
<tr>
<th>No</th>
<th>Experimental energy levels and energy gaps (cm⁻¹)</th>
<th>Absorption</th>
<th>Fluorescence</th>
<th>Laser action</th>
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<td></td>
<td>$S_0(1\bar{A})$</td>
<td>$S_1(1\bar{A})$</td>
<td>$1\bar{A} - 1\bar{A}$</td>
<td>$\xi(S_0 \rightarrow S_1)$</td>
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<td>47,000</td>
<td>29,740</td>
<td>17,530</td>
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<td>34,600</td>
<td>36,400</td>
<td>21,200</td>
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</tr>
<tr>
<td>3</td>
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* Full width at reciprocal $e^2$ (FWRE) of the absorption or fluorescence spectra.

* Values calculated using Eq. (4).
stable but the solubility of the compounds decreases dramatically through the series. The absorption and fluorescence spectra and $S_p$ and $S_a$ levels of compounds (2, 7, 12), which are the first members of the $D_2$, $C_2$– and $D_3$-series, respectively, are given in Fig. 3. The absorption spectra of the second members of each of these series (3, 8, 13) are given in Fig. 4. Comparison of these two figures allows the conclusion that $f_p$ of the $S_0 \rightarrow S_p$ transition of a compound in the $C_2$-series is two or more times greater than for the corresponding compound (same $N$) in the $D_2$-series. $N$ is the number of phenyl units attached to the central benzene hub in each branch of the oligophenylene molecule in a given series. For the $D_3$-series $f_p$ of the $S_0 \rightarrow S_p$ transition is three times larger than the corresponding $D_2$-series compound. This increase in oscillator strength arises from the fact that in molecules of the $C_2$-series there are two different regions of the molecule that cause give rise to the

<table>
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<th>$S_p$ (L$_p$)</th>
<th>$T_{de}$ (L$_{de}$)</th>
<th>$L_{d0} \rightarrow L_{p0}$</th>
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Fig. 2. Absorption and fluorescence spectra (a) and energies (b) of the $S_p$ and $S_a$ states of $p$-oligophenylenes.
Fig. 3. Absorption and fluorescence spectra (a) and energies (b) of the $S_0$ and $S_1$ states of biphenyl (2), m-terphenyl (7) and 1,3,5-tri-terphenyl (12). The symbol '---' indicates the direction of the polarization of the fluorescence and '---' indicates possible polarizations of the p-band.

p-band (the two branches). Thus there are two different, but energetically identical possible p-type transitions and hence two directions of polarization of the p-band. In molecules of the $D_2$-series there are three possible directions of polarization of this band. Hence, one molecule of the $D_2$-series performs as three molecules of the $D_2$-series. Thus, $f_s$ of the $S_0 \rightarrow S_1$ transition increases throughout the sequence $D_2$, $C_2$, $D_2$-series for the same value of $N$, while at the same time there is very little bathochromic shift of the p-band. In these sequences (12, 7, 12) and (3, 8, 13) the energy of the $S_0$ level decreases faster than that of the $S_0$ level. This results in such a change in the gap between the $S_0$ and $S_1$ levels that inversion of these levels occurs between compounds (3) and (8) for the second of these sequences. Thus the fluorescence of compound (3) is $1L_0 \rightarrow 1A$ in nature while for (8) it is $1L_0 \rightarrow 1A$ and all fluorescence parameters change dramatically. For this reason, unlike compound (3), compounds (8) and (13) do not show laser action. In fact, compounds (7, 8) of the $C_2$-series or (12, 13) of the $D_2$-series show no laser action under any experimental conditions, even at low temperature. This is explained by the forbidden nature of the $1A \rightarrow 1L_0$ transition. However, some of these compounds can be used for passive mode locking [4,5].

Figs. 3 and 4 show that within a particular symmetry series the $S_0$--$S_1$ energy gap decreases (compare compounds (7, 8) and (12, 13)). This gives evidence that inversion of the $S_0$ and $S_1$ levels is inevitable in the $C_2$- and $D_2$-series. $1L_0 \rightarrow 1A$ nature fluorescence will be replaced by $1L_0 \rightarrow 1A$ fluorescence. Hence, with increasing $N$, m-oligophenylene of the $C_2$- and $D_2$-series will acquire
laser action. Furthermore, since the p-band of these compounds should be extremely intense they should be extremely effective in laser oscillation.

Careful analysis of the observed trends in the behavior of the $S_p$ and $S_s$ levels of the compounds of the $D_2$-series, (7, 8) of the $C_2$-series and (12, 13) of the $D_3$-series allows one to estimate the $S_p$, $S_s$ and $T_p$ level energies of (9–11) and (14–16). The results of such estimation are presented in Fig. 5. As this figure shows, the inversion of the $S_p$ and $S_s$ levels (and hence change in fluorescence nature) occurring between compounds (2) and (3) in the $D_2$-series is predicted to be between compounds (8) and (9) of the $C_2$-series and (14) and (15) of the $D_3$-series. Put in terms of the number of rings in the branches of the oligophenylenes, between $N = 1$ and 2 in the $D_2$-series, $N = 2$ and 3 in the $C_2$-series and $N = 3$ and 4 in the $D_3$-series. Hence, in the $C_2$-series all compounds with $N = 3$ or greater will be able to give laser action. Compound (11), for example, where $N = 5$ could be expected to be an excellent laser dye since the $S_p$–$S_s$ separation is as great as 900 cm$^{-1}$. Compounds of the $D_3$-series, starting at (15) ($N = 4$) have the possibility of laser action. However, in compound (15) the $S_p$–$S_s$ gap is rather small (see Table 3) and any laser ability will be strongly diminished by the intensity of the coupling of the $S_p$ and $S_s$ states [11,23]. As in the $D_2$-series, the solubility of the compounds in the $C_2$- and $D_1$-series is expected to decrease as $N$ increases. Extrapolation of the observed trends will also allow estimation of the energies of the $S_p$ and $S_s$ levels when $N$ tends to infinity. For example $\lim_{N \rightarrow \infty} S_p = 28000$ cm$^{-1}$ for the $D_2$ series, $\lim_{N \rightarrow \infty} S_p = 27900$ cm$^{-1}$ for the $C_2$-series and $\lim_{N \rightarrow \infty} S_p = 27800$ cm$^{-1}$ for the $D_3$-series.
Finally the authors would like to mention that the synthesis of the higher members of the C-4 and D-5 series is planned in the near future.

4. Conclusion

From the experimental data presented and analyzed in this paper the following conclusions may be drawn:

1) All $p$-oligophenylene (of the D-5-series) from $p$-terphenyl are excellent, photochemically stable laser dyes and scintillators (although the solubility in this series dramatically decreases).

2) All $m$-oligophenylene of the C-4-series from 1,3-di($p$-terphenyl)benzene will acquire fluorescence of $1Lz \rightarrow 1A$ nature and could be extremely effective scintillators and laser dyes due to the inversion of the $S_n$ and $S_p$ levels.

3) All $m$-oligophenylene of the D-5-series from 1,3,5-tri($p$-quaterphenyl)benzene will also acquire $1Lz \rightarrow 1A$ nature fluorescence and laser ability, although this would not be as good as that of the C-4-series $m$-oligophenylene since the gap between the $S_n$ and $S_p$ levels will not be large. They may also be used as scintillators.
4) Some \(m\)-oligophenylene derivatives of the C2- and D3-series can be used for passive mode locking.

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References