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, γ and the decay times, τ_f of fluorescence are measured for deaerated and non-deaerated cyclohexane solutions. The oscillator strengths, f_e of the $S_0 \rightarrow S_p$ ($^1A \rightarrow {}^1L_a$) and $S_0 \rightarrow S_\alpha$ ($^1A \rightarrow {}^1L_b$) transitions, fluorescence, k_f and intersystem crossing, k_{ST}, rate constants, and natural lifetimes, τ_0^T are calculated. The lowest ^1L_b, ^1L_a and ^3L_b (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(*p*-terphenyl)benzene will acquire fluorescence of $^1L_a \rightarrow {}^1A$ 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(*p*-quaterphenyl)benzene will also acquire $^1L_a \rightarrow {}^1A$ 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 for passive mode locking but some may also be used as laser dyes and scintillators. 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-

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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_3 symmetry and hence can be classified into two series, the C_2-series and the D_3-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_1 state of an aromatic molecule can possess either S_p (^1L_a) or S_α (^1L_b) orbital nature depending on the structure and number of π-electrons. Fluorescence will thus be produced by either $^1L_a \rightarrow {}^1A$ ($S_p \rightarrow S_0$) or $^1L_b \rightarrow {}^1A$ ($S_\alpha \rightarrow S_0$) 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 $^1L_b \rightarrow {}^1A$ transition, but also by the fact that the majority of molecules that have an S_1 state with ^1L_b nature have lower k_{ST} values than family related molecules with ^1L_a S_1 states [4,9]. Organic molecules do not show laser action if the S_1 state is of ^1L_b nature [2,4]. Moreover, the threshold of laser oscillation is significantly affected by the ^1L_b–^1L_a energy gap [10,11]. It has been shown that the oscillator strength of the p-band, f_e ($S_0 \rightarrow S_p$) of *m*-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_1 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.

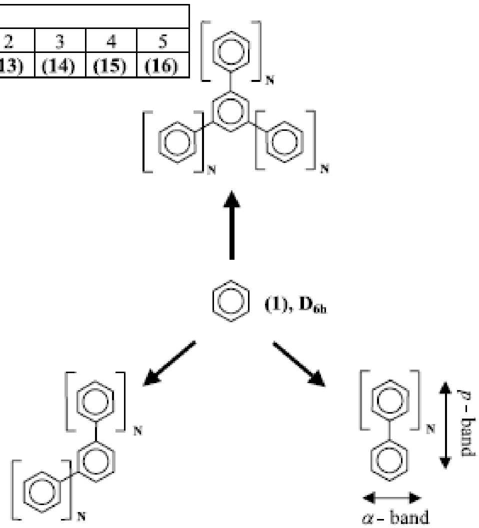
The objectives of the current work are 2-fold. Firstly, to observe and compare the fluorescence and laser properties of *p*- and *m*-oligophenylenes of the D_2-, C_2- and D_3-series. Secondly, to estimate/predict (by extrapolation from experimental data, on the basis of trends observed in the D_2-series and properties of early compounds in the C_2- and D_3-series) the properties of those members of the C_2- and D_3-series unavailable for experimental measurement. The compounds of the D_2-series are: (**2**) biphenyl, (**3**) *p*-terphenyl, (**4**) *p*-quaterphenyl, (**5**) *p*-quinqiphenyl 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(*p*-quinquiphenyl)benzene. Compounds of the D_3-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*-quaterphenyl)benzene, (**16**) 1,3,5-tri(*p*-quinquiphenyl)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-diphenylanthracene was measured using the method described in [13] and found to be 0.90. The decay times of fluorescence, τ_f, were measured using either an 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 [15]:

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

where $\theta = 9n/(n^2+2)^2$ is the Lorentz–Lorenz fac-



D_3 Series					
N=	1	2	3	4	5
No.	**(12)**	**(13)**	**(14)**	**(15)**	**(16)**

C_2 Series					
N=	1	2	3	4	5
No.	**(7)**	**(8)**	**(9)**	**(10)**	**(11)**

D_2 Series					
N=	1	2	3	4	5
No.	**(2)**	**(3)**	**(4)**	**(5)**	**(6)**

Fig. 1. Schematic representation of the molecular structure of oligophenylenes of the D_2-, C_2- and D_3-series. N is the number of phenyl rings in the branch attached to the central benzene hub.

tor [16], n is the refractive index of the solvent, $\tilde{\nu}$ is the frequency in cm^{-1} and $\varepsilon(\tilde{\nu})$ is the molar extinction coefficient. Deaeration was carried out using the method described in [17]. Assuming that the quantum yield of highly dilute, dearated solutions of photostable compounds is determined only by monomolecular quenching processes, the quantum yield, γ^* is related to k_f, k_{ST} and k_S (rate constants for fluorescence, intersystem crossing and internal conversion, respectively) as follows [16]:

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

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. It has been shown that for molecules with an S_1–S_0 energy gap greater than 24 000 cm^{-1}, $k_S \ll k_{ST}$ [18,19]. Hence:

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

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

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

where

$$\tilde{\nu}_a^{c.g} = \frac{\int \tilde{\nu}_a \varepsilon(\tilde{\nu}_a) d\tilde{\nu}_a}{\int \varepsilon(\tilde{\nu}_a) d\tilde{\nu}_a}$$

and

$$\tilde{\nu}_f^{c.g} = \frac{\int \tilde{\nu}_f I(\tilde{\nu}_f) d\tilde{\nu}_f}{\int I(\tilde{\nu}_f) d\tilde{\nu}_f}.$$

$\tilde{\nu}_a^{c.g}$ and $\tilde{\nu}_f^{c.g}$ are the 'centers of gravity' or 'first moments' of the long-wave absorption band and fluorescence spectrum, respectively. $\tilde{\nu}_a$ and $\tilde{\nu}_f$ are the frequencies in the range of the absorption and fluorescence spectra and $I(\tilde{\nu}_f)$ is the photon intensity of fluorescence. The experimental natural fluorescence lifetime of the solution, τ_0^{Ex} and that of the deaerated solution, τ_0^{Ex*} were calculated using the following formulae:

$$\tau_0^{Ex} = \frac{\tau_f}{\gamma}$$

and

$$\tau_0^{Ex*} = \frac{\tau_f^*}{\gamma^*}.$$

If τ_f, γ, τ_f^* and γ^* are measured accurately, with little uncertainty then τ_0^{Ex} and τ_0^{Ex*} will be almost equal.

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

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

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

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

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

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

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_p-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_α-levels of *p*-oligophenylenes 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_b–^1L_a energy gaps with appropriate accuracy. The same method was used to simulate the direction of polarization for the $S_0 \rightarrow S_p$ and $S_0 \rightarrow S_\alpha$ transitions.

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 shift, ±200 cm^{-1}, k_{ST} and k_f values, ±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*-oligophenylenes and a KrF (248 nm) laser for pumping the *m*-oligophenylenes.

3. Results and discussion

According to the classification scheme of [22], compounds of the D_2-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_2- and D_3-series belong to class II. They are non-planar in the S_1 state as well as in the S_0 state, although the geometry of compounds (7) and (8), from the C_2-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 $S_p(^1L_a)$, $S_\alpha(^1L_b)$ and $T_p(^3L_a)$ states, energy intervals between them and f_e of the $S_0 \rightarrow S_\alpha$ and $S_0 \rightarrow S_p$ 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_2- and D_3-series that were unavailable for experimental investigation are given in Table 3. The absorption and fluorescence spectra of *p*-oligophenylenes (D_2-series) are presented in Fig. 2. Analysis of the experimental data

Table 1
Experimental and calculated values for the main fluorescence parameters of dilute cyclohexane (1–4, 7, 12) and 9:1 cyclohexane:benzene (5, 6, 8, 12) solutions of the investigated compounds

No	S	ν_{00} (cm^{-1})	$\Delta\nu_{ST}$ (cm^{-1})	γ	τ_f (ns)	τ_0^{Ex} (ns)	γ^{*a}	τ_f^{*} (ns)[a]	τ_0^{Ex*} (ns)[a]	τ_0^{T} (ns)	k_f (10^7 s^{-1})	k_{ST} (10^7 s^{-1})	f_e	Nature of S_1
1	D_{6h}	37 080	4780	0.07	31.00	442.90	0.13	62.00	447.00	481.00	0.21	1.40	0.004	$S_\alpha(^1L_b)$
2	D_2	34 600	9620	0.17	16.00	94.10	0.25	22.20	89.00	–	1.12	3.38	0.025[b]	$S_\alpha(^1L_b)$
3	D_2	31 960	7860	0.84	1.00	1.19	0.88	1.05	1.19	1.50	83.80	11.40	2.060	$S_p(^1L_a)$
4	D_2	30 100	7640	0.81	0.85	1.05	0.82	0.87	1.06	1.45	94.25	20.68	2.360	$S_p(^1L_a)$
5	D_2	29 060	7460	0.89	0.82	0.92	0.89	0.82	0.92	1.15	108.70	13.41	2.600	$S_p(^1L_a)$
6	D_2	28 460	7320	0.93	0.78	0.84	0.93	0.78	0.84	1.03	119.30	8.97	2.800	$S_p(^1L_a)$
7	C_2	32 700	11 320	0.26	28.50	109.60	0.44	44.50	101.10	–	0.99	1.26	0.024[b]	$S_\alpha(^1L_b)$
8	C_2	30 840	7600	0.20	13.50	67.50	0.30	20.00	67.70	–	1.50	3.50	0.054[b]	$S_\alpha(^1L_b)$
12	D_3	31 700	11 760	0.26	42.50	163.50	0.50	81.00	162.00	–	0.62	0.62	0.015[b]	$S_\alpha(^1L_b)$
13	D_3	30 300	8200	0.18	20.00	111.10	0.32	32.00	100.00	–	1.00	2.13	0.038[b]	$S_\alpha(^1L_b)$

Headings from left to right: No, compound number; S, symmetry group; ν_{00}, symmetry line wavenumber; $\Delta\nu_{ST}$, 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 and with Platt's notation in parenthesis.

[a] Parameters for deaerated solutions.

[b] Values calculated using Eq. (4).

Table 2
The lowest singlet and triplet levels, energy intervals between and oscillator strengths, f_e of the $S_0 \rightarrow S_\alpha$ and $S_0 \rightarrow S_p$ transitions of the experimentally investigated compounds

No	Experimental energy levels and energy gaps (cm^{-1})					Absorption			Fluorescence		Laser action
	$S_\alpha(^1L_b)$	$S_p(^1L_a)$	$T_\beta(^3L_a)$	$^1L_a \leftrightarrow {}^3L_a$	$S_\alpha \leftrightarrow S_p$	$f_e(S_0 \rightarrow S_\alpha)$	$f_e(S_0 \rightarrow S_p)$	FWRE (cm^{-1})[a]	FWRE (cm^{-1})[a]	Nature	
1	38 240	47000	29470	17 530	−8760	0.004	0.280	3540	3500	$S_\alpha \rightarrow S_0$	NO
2	34 600	36400	22800	13 600	−1800	0.025[b]	0.950	6700	3780	$S_\alpha \rightarrow S_0$	NO
3	33 500	31960	20500	11 460	1540	–	2.060	6750	4240	$S_p \rightarrow S_0$	YES
4	32 650	30100	19300	10 800	2550	–	2.360	6500	4220	$S_p \rightarrow S_0$	YES
5	32 100	29060	18700	10 360	3040	–	2.600	6300	4200	$S_p \rightarrow S_0$	YES
6	31 800	28460	18260	10 200	3340	–	2.800	6140	4060	$S_p \rightarrow S_0$	YES
7	32 700	35520	22400	13 120	−2820	0.024[b]	2.800	6800	3960	$S_\alpha \rightarrow S_0$	NO
8	30 840	31240	20200	11 040	−400	0.054[b]	3.700	6740	4370	$S_\alpha \rightarrow S_0$	NO
12	31 700	35100	22200	12 900	−3400	0.015[b]	3.400	6500	3860	$S_\alpha \rightarrow S_0$	NO
13	30 300	31050	20100	10 950	−750	0.038[b]	5.600	6100	3890	$S_\alpha \rightarrow S_0$	NO

[a] Full width at reciprocal 'e' (FWRE) of the absorption or fluorescence spectra.
[b] Values calculated using Eq. (4).

clearly shows that inversion of the S_p and S_α levels occurs between biphenyl and *p*-terphenyl. Biphenyl fluorescence is of $^1L_b \rightarrow {}^1A$ nature, while that of *p*-terphenyl is of $^1L_a \rightarrow {}^1A$ nature. For this reason, γ and τ_f of compounds (**2**) (0.17 and 16.0 ns) and (**3**) (0.84 and 1.0 ns) are very different. k_f increases from 1.12×10^7 to 83.80×10^7 s^{-1} and k_{ST} also increases but to a lesser extent (3.38×10^7–11.40×10^7 s^{-1}). This increase in k_{ST} (which occurs even though the symmetry group remains the same) is explained by the fact that the S_p state is allowed while the S_α state is forbidden. Hence, the S_p state is able to mix with T_i states more readily than the S_α state [9,23]. The S_α–S_p gap is -1800 cm^{-1} in biphenyl while in *p*-terphenyl it is 1540 cm^{-1}. This gap increases through compounds (3) → (4) → (5) → (6) (1540 → 2550 → 3040 → 3340 cm^{-1}) because the S_p level energy decreases more than the S_α level. k_f also increases, but k_{ST} seems to behave inconsistently. Initially k_{ST} increases, but then it decreases ($11.40 \times 10^7 \rightarrow 20.68 \times 10^7 \rightarrow 13.41 \times 10^7 \rightarrow 8.97 \times 10^7$ s^{-1}). This, apparently strange, behavior is explained by the inversion of the $S_p(^1L_a)$ and $T_\beta(^3B_b)$ levels. According to the luminescence–laser classification scheme for aromatic compounds suggested in [11] compound (4) belongs to class IV (T_β lower than S_p) and compound (5) belongs to class V (T_β is higher than S_p). In compound (5) the T_β–S_p interval is not large (< 1000 cm^{-1}) but this interval is increased in compound (6). This makes the $S_p \rightsquigarrow T_\beta \rightsquigarrow T_p$ channel less effective for the depopulation of S_p and explains the behavior of k_{ST}. A detailed discussion of the absorption and fluorescence of compounds (2–6), including the localization of the electronic excitation of the $(S_0 \rightarrow S_1)(^1A \rightarrow {}^1L_a)$ transition and bond orders in the S_0 and S_1 states was presented in [4].

Investigation of the laser properties of the *p*-oligophenylenes showed that, beginning at compound (3), they are all excellent at producing laser oscillation in the near UV-region. The tuning ranges of compounds (3–6) are 322–365, 344–388, 357–402 and 365–411 nm, respectively. The laser properties of (3–6) are almost the same, the thresholds are practically the same and approximately twice as high as that of POPOP [2,21]. Each of these compounds is also very photochemically

Table 3
Lowest singlet and triplet levels and nature of fluorescence of compounds (9–11) and (14–16) estimated by extrapolation from experimental data and observed trends in the D_2-series

No	ν_{00} (cm^{-1})	$S_\alpha(^1L_b)$	$S_p(^1L_a)$	$T_p(^3L_a)$	$^1L_a \leftrightarrow {}^3L_a$	$S_\alpha \leftrightarrow S_p$	Nature of fluorescence	Laser action
9	29 650	30 150	29 650	19 150	10 500	500	$S_p \rightarrow S_0$	YES
10	28 750	29 500	28 750	18 650	10 100	750	$S_p \rightarrow S_0$	YES
11	28 250	29 150	28 250	18 250	10 000	900	$S_p \rightarrow S_0$	YES
14	29 400	29 400	29 500	19 050	10 450	−100	$S_\alpha \rightarrow S_0$	NO
15	28 600	28 800	28 600	18 550	10 050	200	$S_p \rightarrow S_0$	NO
16	28 100	28 400	28 100	18 150	9950	300	$S_p \rightarrow S_0$	YES

stable but the solubility of the compounds decreases dramatically through the series. The absorption and fluorescence spectra and S_p and S_α 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_e 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_e 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

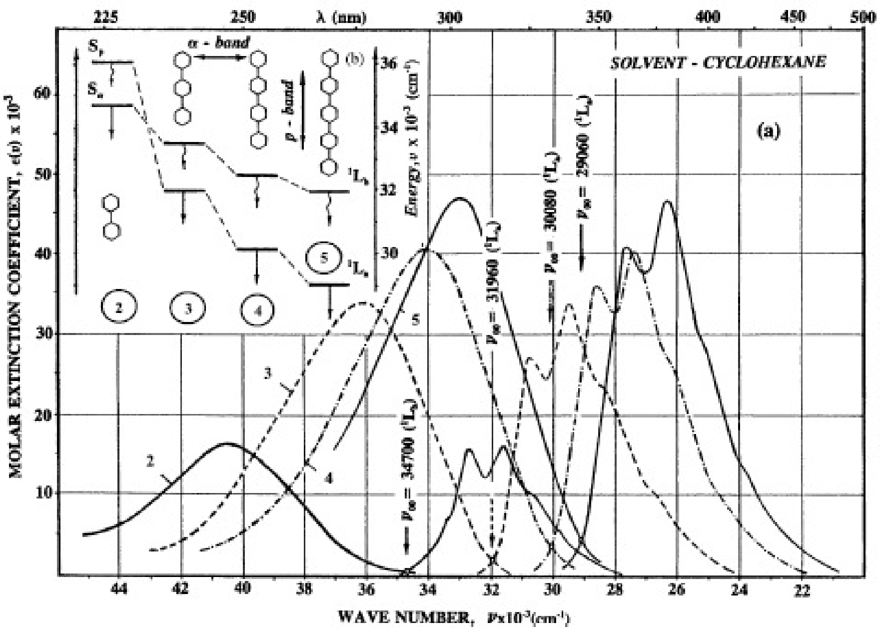


Fig. 2. Absorption and fluorescence spectra (a) and energies (b) of the S_p and S_α states of p-oligophenylenes.

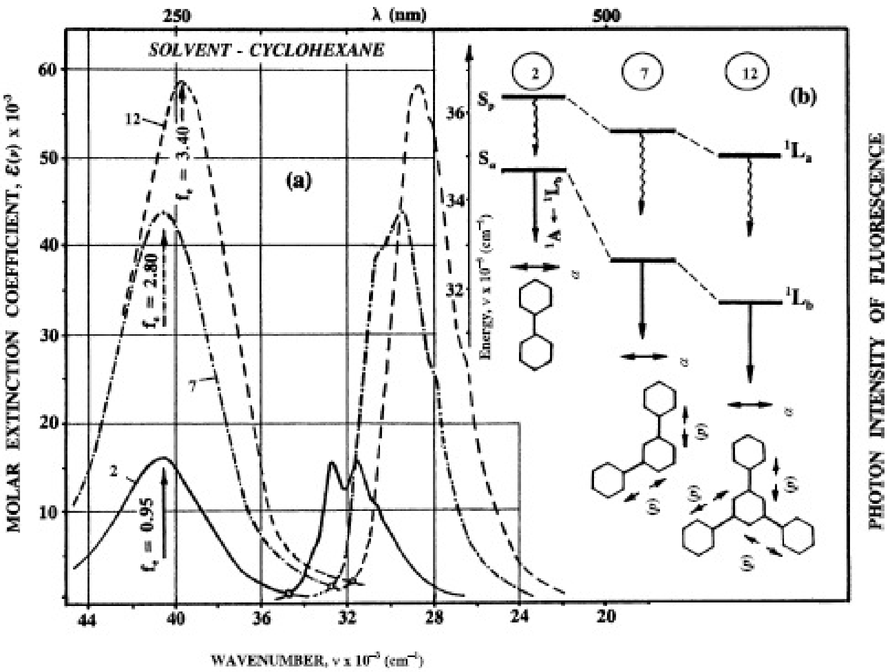


Fig. 3. Absorption and fluorescence spectra (a) and energies (b) of the S_p and S_α states of biphenyl (2), *m*-terphenyl (7) and 1,3,5-triphenylbenzene (12). The symbol '↔' indicates the direction of the polarization of the fluorescence and '← →' indicates possible polarizations of the p-band.

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_3-series there are three possible directions of polarization of this band. Hence, one molecule of the D_3-series performs as three molecules of the D_2-series. Thus, f_e of the $S_0 \rightarrow S_p$ transition increases throughout the sequence D_2-, C_2-, D_3-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 ((**2**, 7, **12**) and (3, **8**, **13**)) the energy of the S_α level decreases faster than that of the S_p level. This results in such a change in the gap between the S_α and S_p 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 $^1L_a \rightarrow {}^1A$ in nature while for (**8**) it is $^1L_b \rightarrow {}^1A$ 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_3-series show no laser action under any experimental conditions, even at low temperature. This is explained by the forbidden nature of the $^1A \rightarrow {}^1L_b$ 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_p–S_α energy gap decreases (compare compounds (7, **8**) and (**12**, **13**)). This gives evidence that inversion of the S_α and S_p levels is inevitable in the C_2- and D_3-series. $^1L_b \rightarrow {}^1A$ nature fluorescence will be replaced by $^1L_a \rightarrow {}^1A$ fluorescence. Hence, with increasing N, *m*-oligophenylenes of the C_2- and D_3-series will acquire

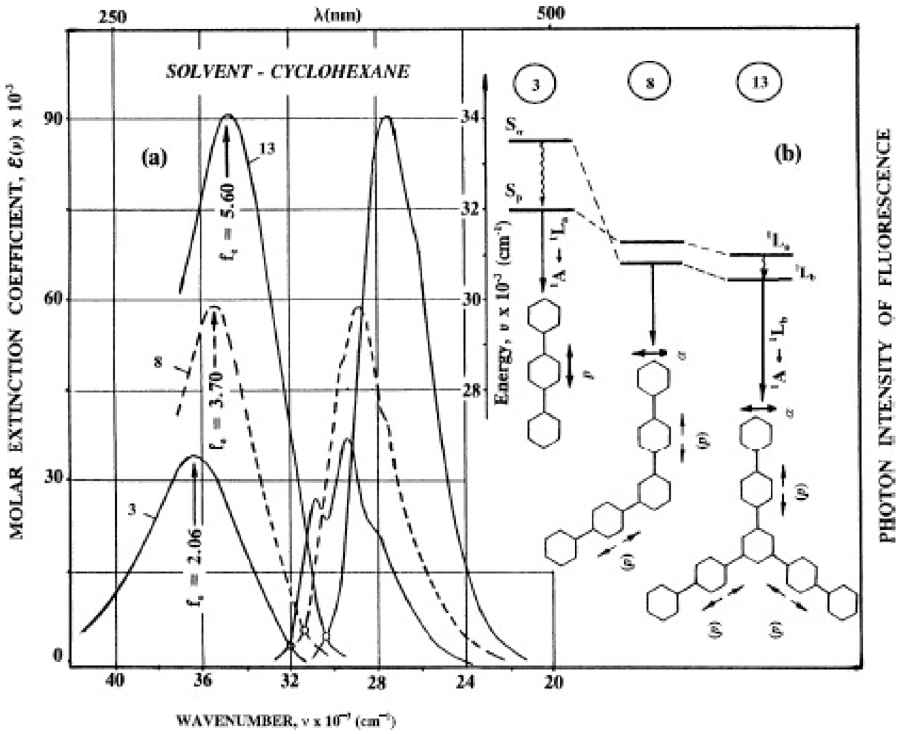


Fig. 4. Absorption and fluorescence spectra (a) and energies (b) of the S_p and S_α states of *p*-terphenyl (3), 1,3-di(biphenyl)benzene (8) and 1,3,5-tri(biphenyl)benzene (13). The symbol '↔' indicates the direction of the polarization of the fluorescence and '← →' indicates possible polarizations of the p-band.

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_α 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_α 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_α and S_p 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_α 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_α 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_α states [11,23]. As in the D_2-series, the solubility of the compounds in the C_2- and D_3-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_α levels when N tends to infinity. For example $\lim_{N\to\infty} S_p = 28000$ cm^{-1} for the D_2 series, $\lim_{N\to\infty} S_p = 27900$ cm^{-1} for the C_2-series and $\lim_{N\to\infty} S_p = 27800$ cm^{-1} for the D_3-series.

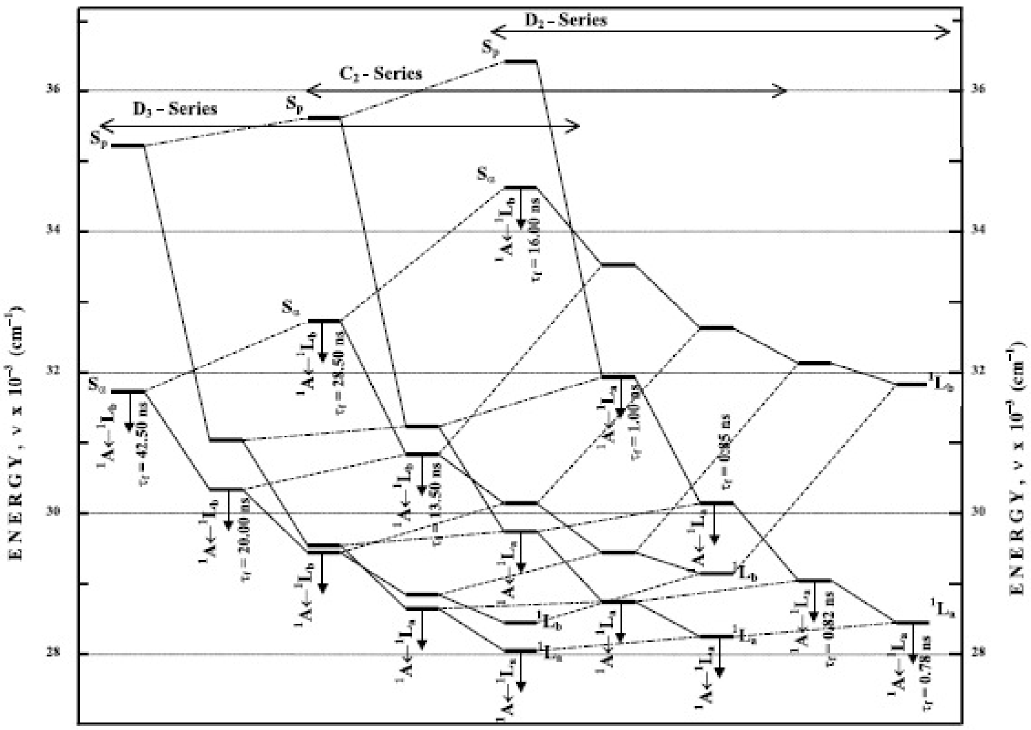


Fig. 5. Experimentally studied and estimated energies of the $S_p(^1L_a)$ and $S_\alpha(^1L_b)$ states of D_2-, C_2- and D_3-series oligophenylenes, the nature of fluorescence and decay times (τ_f). (—) joins states of the same orbital nature of compounds within the same series, (– –) joins S_p states with the same N from different series and (- - - -) joins S_α states of compounds with the same N from different series.

Finally the authors would like to mention that synthesis of the higher members of the C_2- and D_3-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*-oligophenylenes (of the D_2-series) from *p*-terphenyl are excellent, photochemically stable laser dyes and scintillators (although the solubility in this series dramatically decreases).
2) All *m*-oligophenylenes of the C_2-series from 1,3-di(*p*-terphenyl)benzene will acquire fluorescence of $^1L_a \rightarrow {}^1A$ nature and could be extremely effective scintillators and laser dyes due to the inversion of the S_α and S_p levels.
3) All *m*-oligophenylenes of the D_3-series from 1,3,5-tri(*p*-quaterphenyl)benzene will also acquire $^1L_a \rightarrow {}^1A$ nature fluorescence and laser ability although this would not be as good as that of the C_2-series *m*-oligophenylenes since the gap between the S_α and S_p levels will not be large. They may also be used as scintaillators.

4) Some *m*-oligophenylenes of the C_2- and D_3-series can be used for passive mode locking.

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