

# Comprehensive investigation of the solution photophysics and theoretical aspects of oligothiophenes of 1–7 rings

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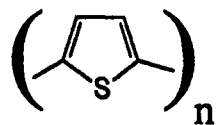
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**Abstract** Photophysical ( $\phi_F$ ,  $\tau_F$ ,  $\phi_T$ ,  $\tau_T$ ), absorption ( $S_0 \rightarrow S_x$  and  $T_1 \rightarrow T_x$ ) and emission (fluorescence and phosphorescence) have been evaluated for thiophene ( $n=1$ ) and oligothiophenes ( $n=2-5, 7$ ). In addition  $k_F$ ,  $k_{IC}$  and  $k_{ISC}$  have been evaluated for  $n=2-5, 7$ . In general  $\phi_F$  increases from  $n=2$  to 5 and becomes constant ( $n=5-7$ ) whereas  $\phi_T$  decreases overall from  $n=2,3$  (nearly same) to constancy at  $n=5, 7$ . The  $k_{ISC}$  progressively decreases and  $k_F$  remains approximately constant as  $n$  increases from  $n=3$  to 7. The  $\tau_F$  progressively gets longer while  $\tau_T$  gets shorter as  $n$  increases and both become constant at  $n=5, 7$ . Based on  $k_F$  (or  $\tau_F$ ) and other data, it is clear that the <sup>1</sup>B-type state is always below the <sup>1</sup>A-type state from  $n=2$  to and including  $n=7$ , in contrast to other existing predictions (for  $n=6$  and greater). Although fluorescence exists for all compounds, except thiophene, no phosphorescence has been observed ( $\phi_p \leq 5 \times 10^{-4}$ ), except thiophene. Mechanisms rationalizing the photophysical behavior are given.

## INTRODUCTION

The  $\alpha$ -oligothiophenes (designated  $n=2, 3 \dots$  or  $\alpha 2, \alpha 3 \dots$ ), particularly those with higher  $n$  value, are very important for their use in molecular electronics, charge storage and non-linear optical applications (1-3). The lower oligomers ( $n=2,3$ ) act as biophotosensitizers (for example 4,5) and  $n=3$  acts as a singlet oxygen sensitizer (for example 6). Some absorption and fluorescence studies of solid films have been done (for example 7-9) and more quantitative data on fluorescence quantum yields ( $\phi_F$ ) (6,9,10) for some compounds has been done in solution. There is very little fluorescence lifetime ( $\tau_F$ ) data in solution (10) and for the solids (11). Triplet data in solution is available on only two compounds where the triplet yield ( $\phi_T$ ) value for  $n=3$  has ranged from 0.2 (6) to 0.75 (12) to  $\geq 0.9$  (13,14). It is quite probable that the early estimate (6) is not correct. Data is also available for  $n=4$  (6). The singlet oxygen yield ( $\phi_\Delta$ ) is known for several compounds now (9, 12, 13, 15) and for  $n=3$ , the value is  $\approx 0.8$  (9,12) around 0.8 (15) and  $\approx 0.7$  (13). There is some substantial disagreement in an impossible direction between  $\phi_T$  and  $\phi_\Delta$  for  $n=4$  [ $\phi_T = 0.2$  (6) and  $\phi_\Delta = 0.7$  (9)]. Triplet lifetimes ( $\tau_T$ ) have been obtained (6, 9, 12, 16, 18) for  $n=3, 4$  and 5 in solution and there is some disagreement. For the couple of cases where there is  $\tau_T$  data for the solid film, the lifetimes are considerably shorter (15-30+ fold) for the film than in solution. This likely originates because of the oxygen quenching for the film but even then, there is some considerable disparity in the lifetime for the same compound (18,19).



One of the big questions concerns the state order, particularly regarding the lower two ( $\pi, \pi^*$ ) states. In polyene type molecules, the state order between the 1-photon (allowed) and the 2-photon (considered forbidden in conventional spectroscopy) states is dependent upon the length of the polyene where the electron-electron interaction is important and varies significantly with the chain length (see for examples 20, 21). In this series when there are 4 or more double bonds, the forbidden <sup>2</sup>Ag-like state is below the <sup>1</sup>Bu-like state. In the case of  $\alpha$ -oligothiophenes it appears based on solution data, that even up to eight-ten double bonds ( $n=4,5$ ) the <sup>1</sup>Bu-like state is lowest (22). Two photon spectroscopy has located an <sup>1</sup>Ag state above the <sup>1</sup>Bu state in  $n=2$  (solution) and  $n=6$  (film) and these have been assigned as the <sup>2</sup>Ag (7,22). It has been claimed (23) that for  $n=6$  in a solution environment, the <sup>2</sup>Ag state is below the

<sup>1</sup>Bu state (23) – we will show that this is not the case. As implied it has been accepted that the allowed <sup>1</sup>Bu state is always below the “forbidden” 2<sup>1</sup>Ag state, from n=2 to 5. Recent SCF, multi CI calculations on thiophene itself (2 double bonds) (24) present an interesting potential dilemma since in this case, the 2<sup>1</sup>A<sub>1</sub> state (42900 cm<sup>-1</sup>, 232 nm) is predicted to be below the 1<sup>1</sup>B<sub>2</sub> state (46140 cm<sup>-1</sup>, 216 nm, and in contrast to n=2-5). Also of notable importance, the oscillator strengths for each is nearly the same. Others (25) have reported, via MCD, at least two bands in the region calculated above (at 42430 cm<sup>-1</sup>, 235 nm and 45490 cm<sup>-1</sup>, 219nm with the overall maximum at 43315 cm<sup>-1</sup>, 230nm). A 3<sup>1</sup>A<sub>1</sub> state is calculated to be at 53960 cm<sup>-1</sup>, 185nm. Although we will discuss more on state order later, the specter arises that if the state order is correct for thiophene (2<sup>1</sup>A<sub>1</sub> below 1<sup>1</sup>B), and the 1<sup>1</sup>B state is below the 2<sup>1</sup>A state for n=2-5 as accepted, and if the state order predicted for n=6,7 etc. were to be true (2<sup>1</sup>A<sub>1</sub> below 1<sup>1</sup>B<sub>2</sub>), then the 2<sup>1</sup>A state would cross to first above (n=2) then below (n=6) the 1<sup>1</sup>B state – a wholly unknown phenomenon! Others (26) have predicted the 1<sup>1</sup>A state below the 1<sup>1</sup>B state (n=2 to 4) with crossing occurring between n=4 and 5; however, by reduction in the amount of configurational interaction (CI) (which seems not to have any rational justification), the 1<sup>1</sup>B state was predicted to be lowest for all α-oligothiophenes through n=6,7 [which for the latter, others have predicted the 1<sup>1</sup>A state lower (23)]. The latter authors (23) have also done restriction of CI plus some empiricism to treat dithienyl polyenes (27) and extended it to the polythiophene members, *vide infra*.

## RESULTS AND DISCUSSION

Recall in the Introduction we noted the problem of state order as a function of the number of rings in the oligomer. Before we consider this important aspect in more detail, we present in Table 1 considerable photophysical data with the absorption and fluorescence data primarily in dioxane and the

**Table 1. Photophysical Data in Dioxane and Acetonitrile at 298 K**

Cpd. (n)	Abs. <sup>(1)</sup> max	F <sup>(2)</sup> max	φ <sub>F</sub> <sup>(3)</sup>	τ <sub>F</sub> <sup>(4)</sup> (ns)	k <sub>F</sub> <sup>(5)(6)</sup> (ns <sup>-1</sup> )	k <sub>IC</sub> <sup>(7)</sup>	k <sub>ISC</sub> <sup>(7)</sup>	T-T <sup>(7)</sup> max	φ <sub>T</sub> <sup>(7)</sup>	τ <sub>T</sub> <sup>(7)</sup> (μs)
1	232	–	≤ 5x10 <sup>-4</sup>	–	–	–	–	–	–	–
2	303	362	0.018	0.046	0.37					
					0.38	1.1	18.6	370	0.93	124
3	354	407,426	0.066	0.21	0.31					
					0.33	0.26	5.3	460	0.90	62
4	391	437,478	0.18	0.49	0.37					
					0.34	0.28	1.5	560	0.71	32
5	416	482,514	0.36	0.82	0.44					
					0.39	0.047	0.74	630	0.63	20
6	434(P)	510(P)	0.40,0.32	0.73	0.43	–	–	685(P)	–	–
7	441	522,560	0.34	0.85	0.40					
					0.35	0.049	0.73	740	0.60	21
8	446(P)	538(P)								
9	454(P)	548(P)								
10	460(P)	554(P)								
11	464(P)	563(P)								
12	469(P)	569(P)								
13	474(P)	573(P)								

- (P) indicates predicted values based on a 1/n vs. E(max) plot.
- (P) indicates first fluorescence band maximum based on a plot of 1/n vs. E(max). For n=3, 4, the second band is the maximum whereas for n=5, 7, it is the first band.
- At 77K a weak phosphorescence is seen for n=1 (thiophene) with a maximum at ≈ 431 nm (0–0 at ≈ 355 nm). The values for n=6 are from references 10 and 9 respectively.
- The 46 ps value is in benzene, all the remainder are in dioxane. The value for n=6 is from reference 10.
- For k<sub>F</sub> of n=2, τ<sub>F</sub> considered to be 46 ps.
- Values above the line are in dioxane while those below are in acetonitrile.
- Values in acetonitrile except n=7 in benzene; for k<sub>IC</sub> and k<sub>ISC</sub> of n=2, the τ<sub>F</sub> is considered to be 46 ps.

triplet data in benzene and acetonitrile. Of first concern to us relative to the state order assignment is the  $k_F$  information ( $k_F=1/\tau_F^\circ$  where  $\tau_F^\circ=\tau_F/\phi_F$ ).

Note that all  $k_F$  values correspond to  $\tau_F^\circ$  values of  $\approx 2.5$ –3 ns, typical of emission lifetimes from allowed states. Furthermore, we calculated the expected  $k_F$  values based on the Strickler-Berg equation over the first absorption band for  $n=2$ –5, and 7. The agreement between the measured  $k_F$ , Table 1, and the calculated values was excellent, ranging from 0% to 14% deviations (one case only for 14%, all of the rest were less than 7%). These results provide very convincing evidence that the first observed transition and lowest excited state is a (1-photon) allowed transition/state and of (1)  $^1B$ -type, and not of (2)  $^1A$ -type (generally 1-photon forbidden, at least by comparison to  $^1B$ -type). This is true for  $n=2$ –5 and 7.

Based on some spectroscopic data for  $\alpha$ ,  $\omega$ -dithienyl polyenes, restrictive CI calculations, extrapolated curves of  $^1A$  and  $^1B$  state energies of some polythiophene oligomers and the difference in state energies expected for  $n=6$  in a crystal state as in an alkane host, it was stated that the  $2^1A$  state would be below the  $1^1B$  state for  $n=6$  and all polythiophene oligomers containing more than 6 rings (23). It is clear for  $n=7$  that the  $1^1B$  state is below the  $2^1A$  state and therefore we are convinced that this same order must be true for the  $n=6$  oligomer. Consequently, the predicted state (23) orders for  $n=6$ , 7 at least, are not correct and the projected  $2^1A$ ,  $1^1B$  energy curves as a function of  $n$  (23) are also not correct.

Based on the location of the  $2^1A$  state in bithiophene ( $n=2$ ) in solution (7) and for sexithiophene ( $n=6$ ) in the crystal (22) which we have corrected for a crystal to solution spectral shift, and a plot of this data (as well as that for the  $1^1B$  state) vs.  $1/n$ , we believe the crossing point of the  $2^1A$  state and the  $1^1B$  states could occur near/at  $n=9$ . Polythiophenes where  $n=9$  and 11 exist (albeit they have several alkyl groups), so these would be worth examining regarding  $\tau_F$ ,  $\phi_F$ ,  $k_F$  and  $\tau_F^\circ$  to determine if the latter two are compatible with an  $^1A$  or  $^1B$  state. In addition,  $\phi_T$  and  $\tau_T$  data would permit comparison of all the measurable and determinable data ( $k_{IC}$ ,  $k_{ISC}$ ) with  $n=5$  and 7.

The  $\phi_F$  is very low for  $n=2$  and increases to  $n=5$  and then, becomes constant through  $n=7$ , Table 1. The general behavior is parallel for  $\tau_F$  which is very short for  $n=2$  and increases and becomes constant from  $n=5$  to 7. Note the relatively small variation for  $k_F$  as a function of the number of rings, Table 1. As we will show elsewhere, this is also true across a number of solvents for  $n=3$ –7, where more commonly,  $k_F$  is very constant for  $n=4$  and greater (we have restricted data for  $n=2$  because of the very short life-

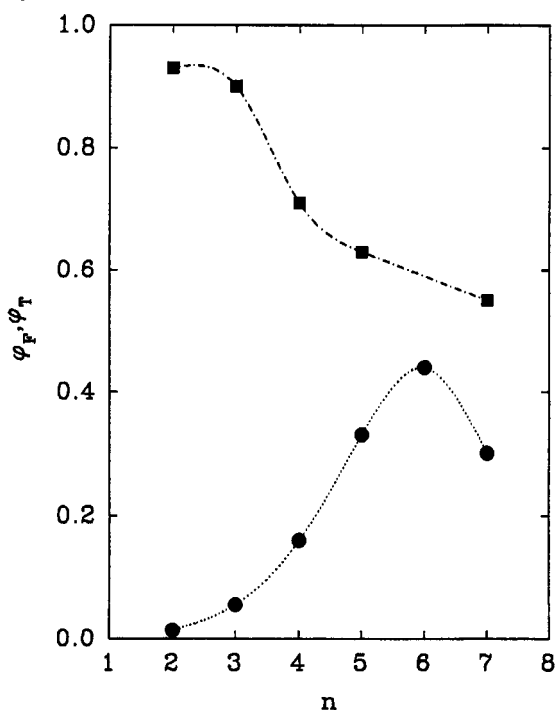


Fig. 1  $\phi_F$  and  $\phi_T$  as a function of  $n$  where ■ ( $\phi_T$ ) and ● ( $\phi_F$ ).

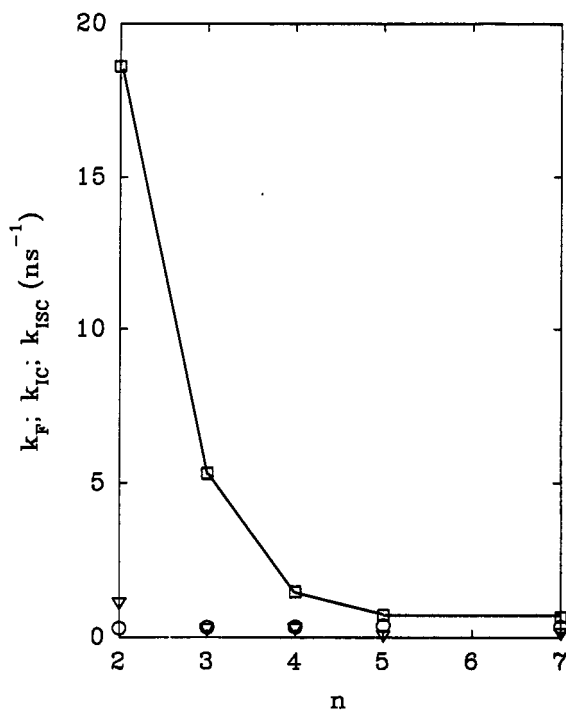


Fig. 2 Rate constants  $k_F$ ,  $k_{IC}$  and  $k_{ISC}$  as a function of  $n$  where □ is  $k_{ISC}$ , ○ is  $k_{IC}$  and ▽ is  $k_F$ .

time). Moreover, the values of  $k_F$  are in general quite similar for a given  $n$  (for  $n=3/4$  and greater) among the various solvents. In Table 1,  $\phi_T$ ,  $\phi_F$ ,  $\tau_F$  and  $\tau_T$  data are presented. From this data we can determine the fluorescence rate constant  $k_F = \phi_F/\tau_F$ , the internal conversion rate constant (from  $S_1$ )  $k_{IC} = (1 - \phi_F - \phi_T)/\tau_F$  and the intersystem crossing rate constant  $k_{ISC} = \phi_T/\tau_F$ . All of the foregoing are presented in Table 1. There is no linear relationship between  $\phi_F$  and  $n$  or  $1/n$  — note that from our data,  $\phi_F$  becomes essentially constant from  $n=5$  (for 5 and 7) and, the inclusion of data for  $n=6$  of others (see Table 1) strongly supports this contention. In the case of  $\phi_T$  there also does not appear to be any linear relationship with  $n$  or  $1/n$  — note that  $\phi_T$  of  $n=2$  and 3 are both very high and similar and then  $\phi_T$  does undergo a progressive decrease as  $n$

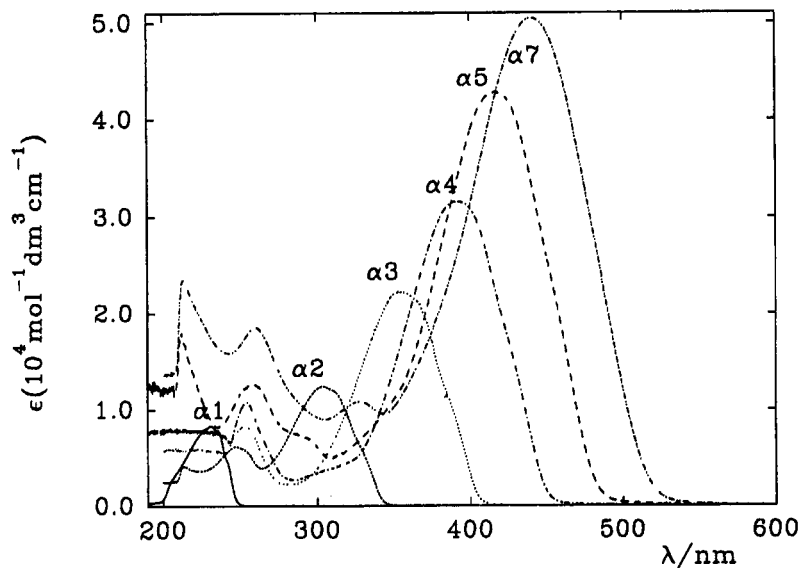


Fig. 3 Absorption spectra of oligothiophenes  $n=5, 7$ .

increases and becomes constant. Recall that the  $\tau_F$  becomes progressively longer as  $n$  increases whereas  $\tau_T$  becomes progressively shorter. However, note in both cases a leveling off clearly occurs from  $n=5$  to greater  $n$ . This is parallel to the behavior of  $\phi_F$  and  $\phi_T$ , Figure 1 and Table 1.

All of the above translates into some interesting results for  $k_F$ ,  $k_{IC}$  and  $k_{ISC}$  as a function of the number of rings, Table 1 and Figure 2. Note that in both dioxane and acetonitrile,  $k_F$  does not undergo significant variation, as the number of rings increases ( $\phi_F$  and  $\tau_F$  are increasing in a quite parallel manner and becoming relatively constant by  $n=5$ ). On the other hand,  $k_{ISC}$  shows a progressive and notable decrease to  $n=5$ . In the case of  $k_{IC}$  there is a significant overall decrease from  $n=2$  to 5 (with  $n=3$  and 4 being close in value). The total non-radiative rate constant  $k_{NR} = k_{ISC} + k_{IC}$  is dominated by  $k_{ISC}$  which of course means  $k_{ISC}$  is significantly greater than  $k_{IC}$  (up to 20x). With  $k_F$  remaining constant while  $k_{IC}$  and  $k_{ISC}$  are decreasing,  $\phi_F$  increases as  $n$  increases; moreover, although  $\phi_T$  decreases, it is not anywhere near as significant as the  $\phi_F$  increase, Figure 1. Of course the latter result occurs because  $k_{IC}$  is decreasing and  $k_{ISC}$  is approaching  $k_F$ . In fact, the total quantum yield of  $\phi_T + \phi_F$  stays above 0.90 in all cases, and is as high as 0.99.

Despite the very high values of  $\phi_T$  for  $n=2$  and 3 (near 1) and high values for  $n=4, 5$ , we have not observed

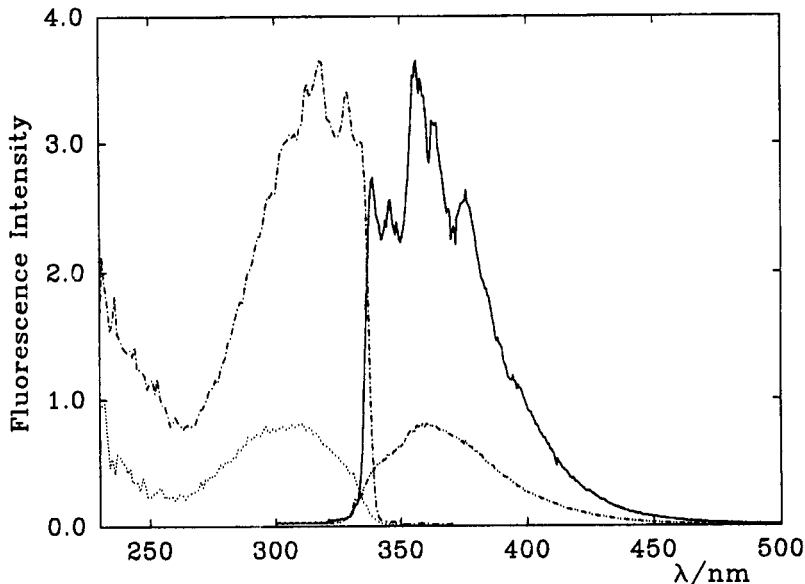


Fig. 4 Room temperature absorption (···) and fluorescence (---) and 77K absorption (-·-) and fluorescence (—) of  $n=2$ .

any phosphorescence for  $n=2$  and 3 at 77 K in an ethanol glass or a mixed aliphatic hydrocarbon glass, or even in the presence of 10% ethyl iodide. These emissions would be easy to observe for  $n=2$  and 3 even with a quantum yield of  $10^{-3}$  (or even lower) since they are expected to emit in spectral regions easily accessible by sensitive photomultiplier tubes (550–650 nm and 700–800 nm). This clearly infers that the radiationless rate constant out of the lowest triplet to the ground state is very large compared to the radiative one which is not true out of the lowest singlet. Note however we do believe we see phosphorescence for  $n=1$ , thiophene, with a maximum near 435 nm (0–0 near 355 nm).

We are unaware of any data for  $n=2$  to compare with our important photophysical parameters. Some data exists for  $\phi_T$  for  $n=3$ . For  $\phi_T$ , values of 0.2 (6),  $\geq 0.9$  (13), 0.95 (14) exist vs. our value of 0.93. It is very likely that the 0.2 value is incorrect. In the case of the 0.95 value (14), a value of  $\phi_T$  for the naphthalene sensitizer of 24,500 was used (from cyclohexane data), yet the experiments were done in ethanol where a value of 40,000 exists (28) — in such a case  $\phi_T$  would then be  $\approx 0.6$ . The  $\geq 0.9$  value was determined from  $\phi_T \cdot E_T$  data and a value of  $E_T$  (from singlet-triplet absorption)(13). Also  $\phi_F$  data exists, varying from 0.05–0.08.

For  $n=4$ ,  $\phi_T$  was determined to be 0.2 (6) vs. our value of 0.71 (and  $\phi_F$ : 0.11 cyclohexane and 0.20 ethanol vs. our value of 0.18).  $\phi_F$  has also been found to be 0.12 (95% ethanol) (29). For  $n=5$  and  $n=7$  we are unaware of any solution photophysical data.

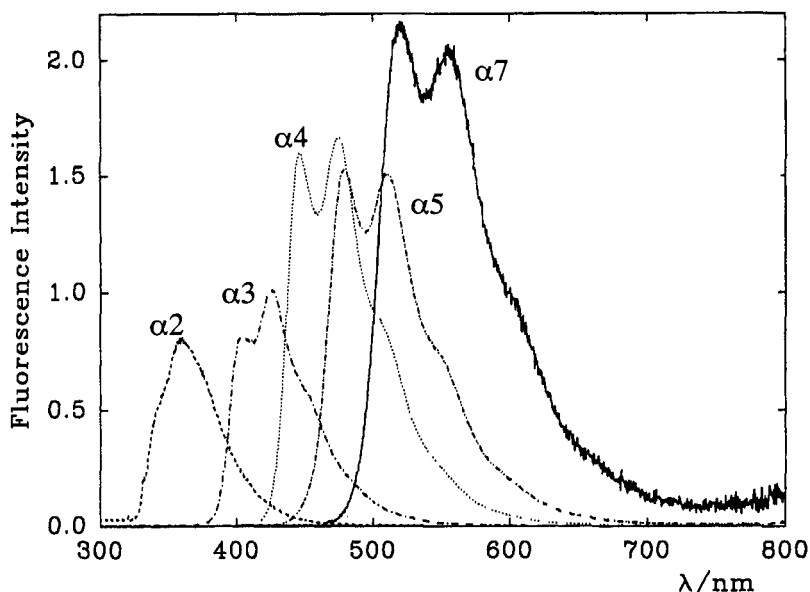


Fig. 5 Fluorescence spectra of oligothiophenes  $n=2-5, 7$ .

The solution absorption spectra of the compounds at room temperature are generally devoid of structure, Figure 3. However, the low temperatures (77K spectra) as represented by the fluorescence excitation spectra can be quite structured as for example in Figure 4. This resolution increase is particularly noticeable for  $n=2$  and 3, and although present for  $n=4-7$ , it is less pronounced. We have found an excellent linear correlation between  $1/n$  and the energy of the maximum (and 0–0) of the first transition. From the correlation with  $E(\text{max})$ , we have predicted (P) the location of the maxima for  $n=6, 8-13$ , Table 1 (in the case of  $n=6, 9$  and 11, some experimental data was available for comparisons). The predictions are in general in excellent agreement with experiment. Extrapolation to polythiophene itself gives an absorption at  $\approx 535$  nm.

The solution fluorescence spectra of  $n=3-7$  show some degree of resolution while for  $n=2$ , only one clear band exists, Figure 5. At room temperature the second band is the maximum for  $n=3, 4$  but the first is the maximum for  $n=5$  and greater (almost equal in  $n=5$ ). Table 1 summarizes the data for  $n=2-7$ . At 77K, there is again a marked increase in the resolution, particularly for  $n=2$  (and 3), Figure 4. At 77K, the band that was the maximum (first or second) may ( $n=4, 7$ ) or may not ( $n=3, 5$ ) invert regarding which is the maximum. We have found an excellent linear correlation between  $1/n$  (or  $1/N$  where  $N$  is the length of the molecule in Å) and the energy of the first and second fluorescence bands. From this correlation we have predicted the location of the first band for  $n=6, 8-13$  in Table 1. Extrapolation to polythiophene gives values of  $\approx 619$  and  $\approx 705$  nm for the first and second bands respectively.

When cooling to 77K (a rigid matrix) not only does the resolution of the absorption spectra increase, but there is a noticeable red shift of the absorption maximum from  $1300 \text{ cm}^{-1}$  ( $n=2, 4, 5$ ) to  $1600 \text{ cm}^{-1}$  ( $n=3$ ) to  $1900 \text{ cm}^{-1}$  ( $n=7$ ). However, there is essentially no shift ( $\leq 125 \text{ cm}^{-1}$ ) for the first or the

second fluorescence band. Given the Franck-Condon forbidden shape of the first transition, there is obviously a change in the geometry in the excited state. This could be consistent with a quinoid-like structure in the excited state, also see later discussion. Remembering that there is a significant red shift of the absorption maximum on cooling, we believe that the shift results from reduction of "single" bond-between-the-rings twisting in the ground state making the molecules more planar and conjugated. In the case of fluorescence, there is essentially no shifting on cooling. At room temperature, solvent shell relaxation around the now quinoidal excited state can occur. However, it cannot occur at the low temperature in the rigid solvent matrix and emission is to a "planar" ground state (vs. a twisted one at room temperature). This combination of circumstances results in essentially no shifting of the fluorescence bands.

Although we shall publish more elsewhere, different theoretical calculations gave different results regarding the nature of the most stable conformer. For example, for  $n=3$ , MM2 (Force Field Optimization) and MNDO93/PM3 showed the all-*s*-trans conformer to be the most stable while MOPAC and MNDO93/AMI showed that it was the all-*s*-cis conformer. However, except for MM2, the relative energy difference between any of the three possible conformers (planar) was only 0.9 K cal/mole. Even higher level calculations for  $n=3$  of the D Gauss and *ab initio* types showed only a 2.4 K cal/mole difference among any of the conformers (as did MM2), with the all-*s*-trans conformer lowest. Thus it would be highly questionable if it would be possible to predict the most stable isomer using MOPAC, MNDO93/PM3 or MNDO93/AMI and at least questionable for the others. Literature data (30) is clear that in the solid, the all-*s*-trans form is the stable conformer. For  $n=5$ , using MM2, D Gauss and *ab initio* methods, the difference between the all-*s*-trans and all-*s*-cis conformers became much more demarked (5–8 K cal/mole) with the all-*s*-trans the lowest. Other methods give results parallel to those for  $n=3$  with some increase in the energy difference (up to 1.5 K cal) albeit they may predict the wrong conformer as the most stable (MOPAC and MNDO93/PM3).

We have calculated transition energies using ZINDO (with MOPAC geometries). In the case of  $n=5$ , the energy of the lowest transition predicted for the all-*s*-trans conformer was within  $\approx 400\text{cm}^{-1}$  of the experimental value (422nm vs.  $\approx 415\text{nm}$  experiment) while for the all-*s*-cis conformer, the predicted value was  $3000\text{cm}^{-1}$  too low an energy (473nm). We can thus feel confident that the conformer present in solution for  $n=5$  is the all-*s*-trans albeit it may have some S–C( $\alpha$ )–C( $\alpha$ )–S twisting. In the case of  $n=2$  and  $n=3$ , the predicted differences in the absorption maxima for the all-*s*-trans and all-*s*-cis are too small to use the same technique of comparison with experiment to distinguish the dominant conformer.

Now that we have the critical information on (1) state order, (2) how  $\phi_F$ ,  $\phi_T$ ,  $k_F$ ,  $k_{ISC}$  and  $k_{IC}$  vary with  $n$ , (3) how the absorption and fluorescence vary with temperature and why, (4) the lack of emission from the triplet, and (5) some information on geometry, we shall try to explain the behavior of  $k_F$ ,  $k_{IC}$  and  $k_{ISC}$  as a function of  $n$  and the lack of phosphorescence. First recall  $k_F$  is quite constant as a function of  $n$ , a 20% variation, while  $k_{ISC}$  undergoes up to a 20 fold decrease as  $n$  increases and, becomes essentially constant at  $n=5$  and greater. There is expected to be only a small error in each of  $k_F$  and  $k_{ISC}$  relative to that possible in  $k_{IC}$ . The error in  $\tau_F$  is expected to be 5–8%, and  $\approx 5$ –10% in  $\phi_F$ . Although the error in  $\phi_T$  is very probably no better than 15%, the  $k_{ISC}$  change would be no worse than about this same error. However,  $k_{IC}$  depends on a difference term:  $k_{IC} = (1 - \phi_F - \phi_T) / \tau_F$  that approaches zero, particularly for the cases of  $n=2$  and 3. For example for  $n=3$  in benzene, the determined values of  $\phi_F$  and  $\phi_T$  are 0.07 and 0.95 respectively. Obviously  $\phi_F + \phi_T$  is greater than 1 which cannot be true. However, assuming the  $\phi_F$  value and  $\phi_T$  values of 0.92, 0.91 and 0.90, we obtain values of 0.06, 0.13 and  $0.19 \times 10^9\text{sec}^{-1}$  for  $k_{IC}$  respectively — thus a 2% change in  $\phi_T$  results in a 300% change in  $k_{IC}$ . Also,  $k_{ISC}$  would only change  $\approx 3.5\%$  over this same  $\phi_T$  range ( $\tau_F$  constant). It does appear that for the case with acetonitrile as the solvent, there is an overall decrease although not systematic, in  $k_{IC}$  from  $n=2$  to  $n=7$ , Table 1. In other solvents, there appears to be more scatter. Much of the problem very likely originates in errors primarily of  $\phi_T$ .

Despite the lack of clarity in the trend of  $k_{IC}$ , it is quite clear that  $k_{ISC}$  dominates both  $k_F$  and  $k_{IC}$  and that in general,  $k_F$  is greater than  $k_{IC}$ . However, recall no emission is seen from the triplet so that the radiationless process from this state are very highly dominant which is not true for the singlet state at all. Given the fact that  $^1B$  state is the lowest singlet state, none of the considerations given above are explicable in terms of state order change in the singlet manifold. We believe all of this can be understood by a combination of factors. There is evidence from our absorption and emission work (and we could sepa-

rately theorize) of the possible existence of a lowest excited singlet state having some quinoid character. Furthermore this quinoid character would involve some charge transfer compared to the ground state. This circumstance could account for small internal conversion since inter-ring torsional twisting mode coupling to the ground state would be minimal. Also the charge transfer character could enhance singlet-triplet coupling and thus intersystem crossing. We also surmise that in the triplet state the charge densities are much more similar to the ground state, compared to  $S_1$ , and that the geometry is also similar to that of the ground state, compared to  $S_1$ . In such a circumstance, single bond inter-ring twisting torsional coupling to the ground state could occur resulting in a significant radiationless mechanism/process (apparently  $\approx 100\%$ ). The decrease in  $k_{isc}$  as  $n$  increases could originate from a progressively more delocalized charge transfer character with accompanying decreased singlet-triplet coupling.

In order to obtain some verification of the foregoing qualitative mechanism, we have carried out charge density calculations in the ground and excited states. For thiophene there is large change in charge on sulfur (formal charge + 0.02 to - 0.22) and  $\alpha$ -carbons (- 0.14 to + 0.03). For bithiophene, similar large changes occur for each of the sulfur atoms (+ 0.004 to - 0.15) and for the inter-ring  $\alpha$ -carbons (- 0.035 to + 0.05). The charge change on the other  $\alpha$ -carbons is also large (- 0.14 to - 0.01). The  $\beta$ -carbons also undergo changes, one of which is about double those of thiophene (0.02). It is clear that there is in fact very significant charge transfer occurring between the ground state and first excited singlet state. It is unequivocal that a change in electronic structure has occurred and although it is less certain, the data seems compatible with contribution from a quinoidal form. Also with the large increase of formal negative charge on sulfur in the excited state (from + 0.004 to - 0.15), there is the possibility of increased H-bonding with the H on the nearest  $\beta$ -carbon.

Regarding the foregoing, we must keep in mind that we do not know the  $\phi_T$ ,  $k_{IC}$  or phosphorescence yield for thiophene. We do not observe any fluorescence at room temperature and this also seems to be the case at 77K. This is not true for the oligothiophenes. The phosphorescence seems to be quite weak for thiophene but we do not know whether this originates from a large  $k_{IC}$  or a large radiationless rate constant out of  $T_1$ . The point is that there may be some radiationless modes intrinsically present in the thiophene ring which we have not adequately considered in the discussion of the  $n=2-5, 7$  compounds. Also of course, there could be significant singlet-triplet coupling occurring via the intramolecular heavy atom route in thiophene, which in theory would be present in the oligothiophenes. Even if this is true, it is clear that this factor alone is insufficient to account for the large change (decrease) in singlet-triplet coupling (as reflected by  $\phi_T$  or  $k_{isc}$ ) that occurs as  $n$  increases.

## EXPERIMENTAL

Fluorescence quantum yields were measured using methyl-1-pyrenoate ( $\phi_F = 0.83$  in cyclohexane) and 3-chloro-7-methoxy-4-methyl-coumarin ( $\phi_F = 0.12$  in cyclohexane) as standards. All fluorescence spectra were corrected for the wavelength response of the instrumental system. Fluorescence decays were obtained using a time correlated single-photon-timing technique with a wavelength shift of 300fs/nm. The decays were deconvoluted using a Microvax 3100 employing the method of modulating functions (31).

The triplet yields were obtained using energy transfer from benzophenone to the oligothiophenes ( $\epsilon_T$ ) and obtaining the product  $\phi_T \cdot \epsilon_T$  (32-33).

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