

Comprehensive Evaluation of the Absorption, Photophysical, Energy Transfer, Structural, and Theoretical Properties of α -Oligothiophenes with One to Seven Rings

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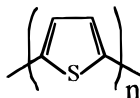
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A large basis set of α -oligothiophenes with two to seven rings ($\alpha 2$ – $\alpha 7$), also including thiophene, $\alpha 1$, have been investigated in five solvents regarding absorption, fluorescence and phosphorescence, quantum yields of fluorescence (ϕ_F) and triplet formation (ϕ_T), lifetimes of fluorescence and the triplet state, quantum yields of singlet oxygen production (ϕ_Δ), all rate constants k_F , k_{IC} , k_{ISC} , and several of the foregoing as a function of temperature. Ten different theoretical calculations across several levels including three levels of *ab initio* have been carried out regarding which conformer is lowest in energy and the ΔH 's among all conformers of $\alpha 2$, $\alpha 3$ and $\alpha 5$, as well as calculations of transitions energies of the α -oligothiophenes. We have shown that the (1) ¹Bu state is the lowest singlet state for all $\alpha 2$ – $\alpha 7$ in any solvent, in contradiction to previous predictions for the higher members. Based on absorption and fluorescence data and calculations of atomic charges in S_0 and S_1 , the ground state is twisted while the excited state is planar (quinoidal-like). Significant charge transfer occurs between S_0 and S_1 but not S_0 and T_1 . For all $\alpha 2$ – $\alpha 7$, ϕ_{IC} is small, k_F^0 is approximately constant while k_{ISC} decreases significantly from $\alpha 2$ to $\alpha 7$. The decrease in k_{ISC} is believed to arise from a decrease in matrix elements of the type $\langle {}^1\Psi_{CT} | H' | {}^3\Psi_1 \rangle$. The essential lack of phosphorescence is assigned as originating from inter-ring twisting mode coupling between T_1 and S_0 . Triplet energy transfer to ³O₂ to produce ¹O₂ is highly efficient for $\alpha 2$ – $\alpha 5$. Based on all data, the first αn representative of α -polythiophene is $\alpha 5$.

Introduction

The α -oligothiophenes (designated $\alpha 1$, $\alpha 2$, $\alpha 3$, ... where $n = 1, 2, 3, \dots$, respectively)



are currently of keen interest because (1) they are interesting analogues of polyenes, (2) they are good singlet oxygen sensitizers and biophotosensitizers, and (3) particularly those with higher n are important for their use in nonlinear optics applications, charge storage, and molecular electronics.

There has been only limited information available on the fluorescence, fluorescence quantum yields (ϕ_F) and lifetimes (τ_F), triplet yields (ϕ_T) and lifetimes (τ_T), singlet oxygen yields (ϕ_Δ), and the rate constants connecting the excited states and those connecting excited states to the ground state. Recently,¹ all the above aspects except ϕ_Δ were evaluated in one solvent. Also, $\alpha 2$ – $\alpha 6$ have been studied^{2,3} relative to ϕ_F and ϕ_T for $\alpha 2$ – $\alpha 6$ and ϕ_Δ for $\alpha 3$ – $\alpha 6$.⁴ Other scattered data exist for some αn 's regarding some of the photophysical parameters. Some information exists for films, but again it is limited, even more than for solutions, in terms of the number of oligothiophenes and the photophysical parameters evaluated. One area receiving considerable attention is theoretical, especially regarding torsional (inter-ring) barriers, ΔH of trans and cis conformers, and

energy of states, but again, these have been limited essentially to $\alpha 2$ – $\alpha 3$, particularly $\alpha 2$. We shall again consider all of the foregoing at the appropriate time.

One of the dominant questions of importance is the state order, particularly relating to the two lowest singlet π, π^* states. The symmetry of the trans oligothiophenes varies depending upon the odd–even number of rings, C_{2v} for odd, C_{2h} for even. The states of interest are the ¹Bu and ¹Ag ones within C_{2h} symmetry, and this notation, or ¹B and ¹A, is commonly carried through for C_{2v} symmetry. This order is considered important in terms of the relationship/identity of α -oligothiophenes and polyenes with the same number of double bonds. For $\alpha 2$, in solution the (1)¹Bu-like state is the lowest where the (2)¹Ag-like state has been located above it by two-photon spectroscopy,⁵ and this (2)¹Ag-like state also has been located above the (1)¹Bu-like state in a *crystalline film* of $\alpha 6$ ⁶ (all state symbols should read “like”, since the exact molecular symmetry and degree of state mixing is not known; however, we shall drop this addition for simplicity). Based on some spectroscopic data on α, ω -dithienylpolyenes, restricted CI (configuration interaction) calculations, extrapolated curves of ¹Ag and ¹Bu states energies of some polythiophene oligomers, and the difference in state energies expected for $\alpha 6$ in the crystalline state vs alkane solution, the (2)¹Ag state was assigned *below* the (1)¹Bu state for $\alpha 6$ and all other polythiophene oligomers with more than six rings ($\alpha 6, \alpha 7, \dots$).⁷ We will show that this is not the case.

Other calculations⁸ predict the (2)¹Ag state already below the (1)¹Bu state at $\alpha 2$ – $\alpha 4$, with crossing occurring between $\alpha 4$ and $\alpha 5$. However, by restriction of the CI (which seems to have no real rational justification as was also done before),⁷ the (1)¹Bu state was now predicted to be lowest for all αn 's through $\alpha 6, \alpha 7$. Still other calculations^{9–11} on $\alpha 2$ and some higher αn 's in

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some cases give varying results regarding the relative ordering of the states for $\alpha 2$ and place the $(2)^1\text{Ag}$ state lowest for $\alpha 3$ and $\alpha 4$.⁹

We will show that despite any theoretical and/or comparative experimental data to the contrary, *the $(1)^1\text{Bu}$ state is the lowest excited singlet state in all α -oligothiophenes from $\alpha 2$ to and including $\alpha 7$* . We will also determine the following in five solvents for $\alpha 2$ – $\alpha 7$: (1) fluorescence (ϕ_F) and triplet (ϕ_T) quantum yields, (2) fluorescence (τ_F) and triplet (τ_T) lifetimes, (3) all determinable rate constants k_F^0 , k_{ISC} (intersystem crossing), k_{IC} (internal conversion), and k_{NR} (nonradiative), (4) absorption (and ϵ values) and fluorescence spectra (and phosphorescence for $\alpha 1$) at 298 and 77 K, (5) singlet oxygen quantum (ϕ_Δ) yields of $\alpha 2$ – $\alpha 5$ and $\alpha 7$, (6) τ_F and ϕ_F as a function of temperature for $\alpha 3$ and $\alpha 7$, (7) 10 different theoretical calculations of various levels for a broad variety of αn 's, including three levels of *ab initio* that evaluate which conformer is the lowest in energy for all conformers of $\alpha 2$, $\alpha 3$, $\alpha 5$, (8) calculations of atomic charges and their changes between S_0 and S_1 as well as T_1 , (9) calculation of transition energies and oscillator strengths for $\alpha 1$ – $\alpha 5$, and (10) correlation of absorption, emission, and photophysical parameters as a function of n or $1/n$ where n is the number of rings. All these will be integrated to elucidate the behavior of the absorption and photophysical properties of $\alpha 1$ – $\alpha 7$.

Experimental Section

Thiophene was purchased from Riedel de Haen and was used as received. Bithiophene and terthiophene were purchased from Aldrich and were respectively purified by sublimation and recrystallization. Tetrathiophene and dibutylheptathiophene were a kind gift from J. Kagan and H. Winberg, respectively. These were purified by column chromatography. Hexathiophene was provided by H. Naarmann (BASF).

Pentathiophene was synthesized by bromination of terthiophene in the α positions followed by reaction with 2-bromothiophene *via* Grignard coupling in the presence of a nickel catalyst ($\text{Ni}[\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]\text{Cl}_2$) synthesized as elsewhere reported (and dried with SOCl_2).¹² The final product, $\alpha 5$, was recrystallized from dichloromethane.

All the solvents were of spectroscopic or equivalent grade, except for methylcyclohexane (which was purified over a mixture of $\text{H}_2\text{SO}_4/\text{HNO}_3$, then distilled, and finally chromatographed on an $\text{Al}_2\text{O}_3/\text{SiO}_4$ column) and ethanol (dried and purified by distillation over CaO). All the other solvents were used without further purification. The solutions used (1×10^{-5} to 10^{-6} M) were deoxygenated by either N_2 or Ar bubbling. Anthracene, naphthalene (J. K. Baker Chemical Co.), and benzophenone (Aldrich Chemical Co.) were used without further purification.

Absorption and fluorescence spectra were run with a Beckman DU-70 and a SPEX Fluorolog spectrometer, respectively. All the fluorescence spectra were corrected for the wavelength response of the system.

The fluorescence quantum yields at 293 K were measured using several standards, namely, methyl 1-pyrenoate ($\phi_F = 0.83$ in cyclohexane) and 3-chloro-7-methoxy-4-methylcoumarin ($\phi_F = 0.12$ in cyclohexane¹³). Terthiophene in ethanol ($\phi_F = 0.054$) was also used for internal verification of the obtained values. The fluorescence quantum yields at 77 K were obtained by running under the same experimental conditions the solution done at 293 K, avoiding by this way external interferences. The ϕ_F value was than obtained by assuming a 20% "shrinkage" of the ethanol solvent on going from 293 to 77 K.

The molar extinction coefficients (ϵ) were obtained with *seven* solutions of different concentrations. The slope of the plot of the absorption values (at the maximum wavelength of absorption) vs the concentration values gave us the ϵ values with correlation values ≥ 0.999 .

The radiative rate constant k_R was calculated with the Strickler–Berg¹⁴ equation

$$k_R^{\text{SB}} = (2.88 \times 10^{-9}) n^2 \langle \bar{\nu}_F^{-3} \rangle_{\text{AV}^{-1}} \int \frac{\epsilon(\bar{\nu})}{\bar{\nu}} d\bar{\nu}$$

with

$$\langle \bar{\nu}_F^{-3} \rangle_{\text{AV}^{-1}} = \frac{\int I(\bar{\nu}) d\bar{\nu}_F}{\int \bar{\nu}_F^{-3} I(\bar{\nu}_F) d\bar{\nu}_F}$$

using the integrated first absorption band and the fluorescence band. For thiophene, since there is no fluorescence, the use of the equation of Forster¹⁵ was needed:

$$k_R^{\text{F}} = (2.88 \times 10^{-9}) n^2 \int \frac{\epsilon(\bar{\nu})(2\bar{\nu}_0 - \bar{\nu})^3}{\bar{\nu}} d\bar{\nu}$$

Fluorescence decays were obtained using a time-correlated single-photon-timing technique with a home-built apparatus as previously described¹⁶ except for the wavelength shift, which is now 300 fs/nm. The obtained fluorescence decays were deconvoluted in a Microvax 3100 employing the method of modulating functions.¹⁷

The experimental setup used for triplet spectra and triplet yields of $\alpha 2$ – $\alpha 5$ was that described elsewhere.^{18,19} Absorption spectra were recorded every 10 nm averaging at least 5 shots per wavelength recorded. The triplet–triplet molar extinction coefficients (ϵ_T) were evaluated using the energy transfer method from naphthalene (in benzene, dioxane, and ethanol) and from benzophenone (in benzene and acetonitrile) to αn 's. A solution of the sensitizer, S, had an absorbance of 1.5–1.6 and the αn had an absorbance of 0.15–0.25 at the excitation wavelengths of 308 and 347 nm for naphthalene and benzophenone, respectively.

The equation²⁰

$$\epsilon_T(\text{A}) = \epsilon_T(\text{S}) \frac{\Delta A_{\text{A}} - \Delta A_{\text{dir}}}{\Delta A_{\text{S}} f_{\text{S}}} \left\{ \frac{k_2 - k_1}{k_2} \exp \left[- \frac{\ln(k_2/k_3)}{(k_2/k_3) - 1} \right] \right\}^{-1}$$

was used where the acceptor $\text{A} = \alpha n$ and S is the sensitizer. This equation takes into account the following: ΔA_{S} , the absorbance change of sensitizer alone; ΔA_{A} , the absorbance change of the maximum; k_2 , the decay rate constant of the sensitizer in the presence of the acceptor; k_3 , the decay rate constant of the sensitized triplet of the acceptor; ΔA_{dir} , the direct excitation of the acceptor; f_{S} , the fraction of light absorbed by the sensitizer in the solution of S + A with respect to the sensitizer alone. Triplet properties of the sensitizers in some solvents were taken from the literature^{21,22} (ϵ_T in $\text{M}^{-1} \text{cm}^{-1}$): for naphthalene (benzene), $\epsilon_T = 13\,200$ (420 nm), $\phi_T = 0.75$; for naphthalene (ethanol), $\epsilon_T = 40\,000$ (420 nm); for benzophenone (benzene), $\epsilon_T = 7200$ (530 nm), $\phi_T = 1.0$; for benzophenone (acetonitrile), $\epsilon_T = 6500$ (530 nm), $\phi_T = 1.0$. The ϵ_T values of anthracene and naphthalene in dioxane were determined in this work. The ϕ_T of anthracene was determined by the heavy atom effect of 4-bromo-*N,N'*-dimethylaniline on the fluorescence quantum yield and triplet population.^{19,23} Energy transfer between naphthalene (donor) and anthracene (acceptor) were used to obtain ϵ_T of naphthalene in dioxane: for

TABLE 1: Photophysical and ϕ_{Δ} Data for α -Oligothiophenes in Benzene^{a,b}

cpd	ϕ_F	τ_F (ns)	k_F^0	k_{NR}	ϕ_T	ϕ_{Δ}	k_{IC}	k_{ISC}	τ_T (μ s)
α_2	0.026	0.046	0.55	21 ^e	0.99	0.96	0.11 ^c	22	104
α_3	0.07	0.16	0.44	5.8 ^e	0.95	0.81 ^d	0.03 ^e	5.9	88
α_4	0.18	0.44	0.41	1.9	0.73	0.72	0.20	1.7	38
α_5	0.34	0.82	0.41	0.81	0.59	0.56	0.098	0.72	24
α_6	0.44	0.97	0.45	0.58		$\sim 0.36^f$			$\geq 17^g$
α_7	0.36	0.82	0.43	0.79	≤ 0.6	<i>h</i>	0.049	0.73	21

^a Solutions degassed with nitrogen or argon by bubbling. k 's are 10^9 s⁻¹, and α_7 is the di-*n*-butyl-substituted α_7 . ^b Also see Table 2, acetonitrile. ^c Assumes $(1 - \phi_T - \phi_F) = 0.005$. ^d The value of ϕ_{Δ} ranged from 0.65 to 0.85 depending on the technique used (see Experimental Section for techniques). This value was that from measuring emission of ¹O₂. In acetonitrile a value of 0.74 was obtained by measuring ¹O₂ emission. ^e k_{NR} obviously cannot be less than $k_{ISC} + k_{IC}$, but recall that errors in ϕ_T for large ϕ_T particularly effect the accuracy of k_{IC} ; see text. ^f Reference 4. We were unable to obtain sufficient concentration in benzene or dioxane to obtain a value using our techniques (see Experimental Section for techniques). ^g Wintengs, V.; Valat, P.; Garnier, F. *J. Phys. Chem.* **1994**, *98*, 228 indicate 24 μ s in dichloromethane and also $\alpha_4 = 35$ μ s. ^h We have determined a tentative value of 0.25 in dioxane.

naphthalene (dioxane), $\epsilon_T = 15\ 000$ (420 nm); for anthracene (dioxane), $\epsilon_T = 50\ 000$ (430 nm), $\phi_T = 0.62$.

The product $\epsilon_T\phi_T$ for each αn was obtained by the laser energy effect on the change of absorbance of an αn measured at the λ_{max} of optically matched solutions ($A \approx 0.08$) compared with benzophenone in acetonitrile and naphthalene in benzene as references/standards. Plots of ΔA vs laser dose were linear and passed through zero, indicating that only one-photon processes were occurring. Moreover, there was only a <5% difference between $\epsilon_T\phi_T$ calculated with the two different references/standards. The triplet yield of αn 's was then calculated from the $\epsilon_T\phi_T/\epsilon_T$ ratio.

For α_7 , the spectra and triplet parameters were obtained using the third harmonic of a Q-switched Nd:YAG laser where spectra and ΔA changes were obtained. The ϵ_T was obtained by the partial depletion technique²¹ using benzophenone in benzene as a reference (actinometer) to measure ϕ_T ($\epsilon = 7200$ at 530 nm, $\phi_T = 1^{22,24}$). When the triplet yield was measured, special care was taken to have optically matched dilute solutions ($A \approx 0.2$ in a 10 mm cell) and a low laser energy (≤ 1.8 mJ) to avoid multiphoton and T–T annihilation effects. The region monitored for α_7 was at the depletion minimum of 450 nm (± 10 nm), which appeared to be outside the T–T absorption. Nonetheless, the ϕ_T obtained should be an upper limit, since, if the triplet absorbs here, the ϵ_T obtained will be too small. In our case a value of $87\ 000$ M⁻¹ cm⁻¹ ($\pm 15\%$) was obtained. The ϕ_T was $0.60 \pm 15\%$.

The singlet oxygen yields (ϕ_{Δ}) of αn 's were determined by measuring the emission of ¹O₂ in air-equilibrated benzene and acetonitrile solutions with a germanium diode detector. The luminescence emerging from the cuvette was passed through a filter combination (Glenn-Creston, cutoff 1050 nm, and Kodak Wratten 87c gelatin filter, cutoff 870 nm) and collected by a germanium diode (Judson J16 85p, 5 mm diameter). The detection system was at right angles to the excitation beam. After amplification with a homemade amplifier (100 MHz, 14 dB), the output was fed into a Tektronix DSA 602 digital sampling analyzer. The amplified signal extrapolated to zero time (in mV) was plotted as a function of laser dose and compared with that of a reference, phenalenone, where ϕ_{Δ} is 0.98.²⁵ The ϕ_{Δ} of the αn 's was obtained from a ratio of the slopes and the known ϕ_{Δ} of phenalenone.

Results

Table 1 presents comprehensive photophysical data of α_1 – α_7 (di-*n*-butyl), including singlet oxygen quantum yields (ϕ_{Δ}) in benzene. Table 2 contains much of the same photophysical data, except for some ϕ_{Δ} and ϕ_T values, with four additional solvents. In most cases α_6 could not be included because of its limited solubility. Table 3 presents data regarding absorption

spectra and extinction coefficients, fluorescence and T–T maxima, as well as the experimental k_F^0 and k_{NR}^0 from the Strickler–Berg equation (SB).¹⁴ Other tables will be considered in the Results and Discussion sections.

Absorption and Emission. Dependence on Solvent and Temperature. The solution absorption spectra at room temperature in any solvent for α_2 – α_7 are generally devoid of structure (Figure 1). Table 3 gives representative absorption spectral data in dioxane. There is a relatively small effect of solvent on these maxima. However, the low-temperature absorption, as represented by the fluorescence excitation spectra, can have significant structure (Figure 2 and ref 1), particularly for α_2 and α_3 . Moreover, there is a considerable red shift, ~ 1600 cm⁻¹, in the maxima. There is an excellent linear correlation between $1/n$ and the maximum of the first transition, as well as the 0–0 energy particularly for α_4 – α_7 (Figure 3). If α_2 and α_3 are included, these points scatter somewhat compared to the others and change the slope slightly. Nonetheless, the linearity is good. This observation regarding the deviation of α_2 in particular occurs for other kinds of relationships involving $1/n$ (or $1/N$ where N is the length of the molecule in Å) such as that for the maximum of the T–T absorption, among others (Figure 3). These types of data plus photophysical results indicate that α_2 , and even α_3 , are not yet legitimate representatives of a polythiophene and that such a representation seemingly begins with α_4 . Actually, additional consideration of all the photophysical data indicates that *the first true representative of a polythiophene is α_5* .

On the basis of the plot of $1/n$ vs absorption maxima of α_4 – α_7 (corrected for the presence of two *n*-butyl groups), we can predict the expected maxima for α_8 – α_{13} and α_{∞} : α_8 , 456 nm; α_9 , 466 nm; α_{10} , 473 nm; α_{11} , 480 nm; α_{12} , 485 nm; α_{13} , 489 nm; α_{∞} , 555 nm. The latter value for the absorption maximum of α_{∞} is quite insensitive to a change in the number of rings down to 50 ($\lambda_{max} = 538$ nm), 40 ($\lambda_{max} = 535$ nm), or even 30 ($\lambda_{max} = 526$ nm), any one of which numbers may be a realistic value for the number of thiophene units in a real polythiophene

Figure 4 shows plots of ϵ vs n and $1/n$ for α_1 – α_7 . If you plot ϵ values for α_3 – α_5 vs $1/n$ and n , both plots are very linear. If you then use these to predict the extinction coefficients of α_6 and α_7 by extrapolation, the results are excellent from the $1/n$ plot (ϵ of α_6 predicted to be 47 400 compared to the experimental 47 910; ϵ of α_7 predicted to be 50 800 compared to the experimental 50 470). On the other hand, extrapolation of the n (vs ϵ) plot gives 63 400 for α_7 vs 50 470 found. This is a warning that even though there may be a linear relationship over a restricted basis set, it may in fact not permit any accurate predictive capability for other members of higher or lower αn . We will see later that this is true for other kinds of considerations

TABLE 2: Photophysical Properties of α -Oligothiophenes for $n = 1-7$ in Various Solvents^a 1

Methylcyclohexane									
cpd	ϕ_F	τ_F (ns)	k_F^0	k_{NR}					
$\alpha 2$	0.014	≤ 0.1	≥ 0.14	≥ 9.9					
$\alpha 3$	0.057	0.19	0.30	5.0					
$\alpha 4$	0.18	0.49	0.37	1.7					
$\alpha 5$	0.33	0.83	0.39	0.81					
$\alpha 7$	0.32	0.76	0.42	0.90					
Ethanol									
cpd	ϕ_F	ϕ_F (77 K)	τ_F (ns)	k_F^0	k_{NR}	ϕ_T	k_{IC}	k_{ISC}	τ_T (μ s)
$\alpha 2$	0.014	0.04	0.046 ^b	0.35	~ 21	1.0	0.10	~ 21	100
$\alpha 3$	0.054	0.12	0.19	0.28	5.0	0.96	0.03 ^c	5.1	91
$\alpha 4$	0.18	0.18	0.52	0.34	1.6	0.70	0.23	1.3	43
$\alpha 5$	0.32	0.34	0.88	0.36	0.77				20
$\alpha 7$	0.29	0.28	0.82	0.35	0.87	$\leq 0.6^b$	0.13	0.73	
Acetonitrile									
cpd	ϕ_F	τ_F (ns)	k_F^0	k_{NR}	ϕ_T	ϕ_Δ	k_{IC}	k_{ISC}	τ_T (μ s)
$\alpha 2$	0.013	≤ 0.1	≥ 0.133	≥ 10.1	0.93	0.98	≥ 0.6	≥ 9.5	124
$\alpha 3$	0.056	0.18	0.311	5.1	0.90	0.74	0.24	5.0	62
$\alpha 4$	0.16	0.48	0.33	1.8	0.71	0.72	0.27	1.5	40
$\alpha 5$	0.33	0.90	0.37	0.74	0.63	0.50	0.011	0.70	20
$\alpha 7$	0.30	0.90	0.33	0.78	$\leq 0.6^b$		0.011	0.67	
Dioxane									
cpd	ϕ_F	τ_F (ns)	k_F^0	k_{NR}	ϕ_T	k_{IC}	k_{ISC}	τ_T (μ s)	
$\alpha 2$	0.017	0.046 ^b	0.37	21	0.94	0.93	20	146	
$\alpha 3$	0.066	0.21	0.31	4.5	0.93	0.019	4.4	108	
$\alpha 4$	0.18	0.49	0.36	1.7	0.67	0.31	1.4	48	
$\alpha 5$	0.36	0.82	0.44	0.78	0.6 ^d	0.05	0.73	29	
$\alpha 6^e$	0.41	1.0	0.41	0.55					
$\alpha 7$	0.34	0.85	0.40	0.78	$\leq 0.6^b$	0.07	0.71	≥ 15	

^a Solutions degassed with nitrogen or argon by bubbling. k 's are 10^9 s⁻¹ and $\alpha 7$ is the di-*n*-butyl-substituted $\alpha 7$. The lifetime of thiophene ($\alpha 1$) is ~ 1 μ s (by sensitization from xanthone). ^b Assumes value in benzene. ^c Assumes $(1 - \phi_T - \phi_F) = 0.005$. ^d Assumes average of values in acetonitrile and benzene. ^e $\alpha 6$ is "not soluble" in methylcyclohexane, acetonitrile, and ethanol.

TABLE 3: Absorption, Fluorescence, Fluorescence Rate Constants and Triplet-Triplet Data in Dioxane^a at Room Temperature

cpd	abs max λ_{max}/nm	$\epsilon/mol^{-1} dm^3 cm^{-1}$	$k_F^0(SB)/10^9 s^{-1}$	$k_F^0/10^9 s^{-1}$	fluoresc max ^b	T-T max ^a
$\alpha 1$	231	8340 ^c	0.33 ^d	0.023 ^d		305
$\alpha 2$	303	12440			0.22 ^e 0.38 ^e	385
$\alpha 3$	354	22080 ^f	0.30		0.31	460
$\alpha 4$	392	31560 ^g	0.34		0.36	437, 478
$\alpha 5$	417	42670	0.38		0.44	482, 514
$\alpha 6$	436	47910			0.41	502, 537
$\alpha 7^h$	441	50500	0.39	0.40		522, 560

^a T-T maxima in other solvents vary by only 10 nm at the maximum. The $\alpha 1$ datum is with acetonitrile. ^b The italicized wavelength is the band maximum. The other one is another distinct band (see Figure 4). The $\alpha 1$ does not fluoresce but shows phosphorescence (see text). ^c Assumes same value as for ethanol. ^d First value using Försters equation instead of Strickler-Berg (SB) with integration from 38 000 cm⁻¹ (263 nm) to 48 000 cm⁻¹ (208 nm). Second (lower) value from integration over entire first absorption band (same wavelength/wavenumber) limits but different ν_0 (absorption maximum value). ^e First (upper) value using a τ_F from cyclohexane (0.081 ns) and second one using τ_F value in benzene of 0.046 ns with a different instrument. First value has more potential error because normal τ lower limit is ≥ 100 ps with the instrument used. ^f $\epsilon(\text{benzene}) = 22\ 540$ M⁻¹ cm⁻¹, $\epsilon(\text{acetonitrile}) = 24\ 215$ M⁻¹ cm⁻¹ and $\epsilon(\text{ethanol}) = 23\ 590$ M⁻¹ cm⁻¹ at their maxima of 354, 352, and 355 nm, respectively. ^g $\epsilon(\text{acetonitrile})$ is 34 700 at its maximum. ^h For the di-*n*-butyl-substituted $\alpha 7$.

as well—for example, ϕ_F and ϕ_T of $\alpha 3$ – $\alpha 5$ vs n if used to predict $\alpha 2$, $\alpha 6$, and $\alpha 7$.

The room temperature solution fluorescence of $\alpha 2$ – $\alpha 7$ is shown in Figure 5. Note that there is definitely more resolution than for absorption. Table 3 gives representative fluorescence spectra maxima in dioxane. As in the case of absorption, there is little solvent effect on fluorescence. Note in Figure 5 at 77 K (as well as in ref 1) that there is some considerable increase in vibrational resolution compared to that at room temperature, particularly noticeable for $\alpha 2$, less for $\alpha 3$, and continuing to be less as the number of rings increases to $\alpha 4$ and on to $\alpha 7$. Of notable importance is the fact that there is almost no red shift

(100–200 cm⁻¹) in the fluorescence maxima between room temperature and 77 K. This is in marked contrast to that of absorption (see above). Note also that there can be a switch between the first two bands regarding which one is the maximum at room temperature as the number of rings increases (from the second band to first band from $\alpha 4$ on) and between room- and low-temperature (77 K) bands for a given αn —for example, see $\alpha 4$ in particular. We have also found an excellent correlation between the energy of the first (and second) band of fluorescence vs $1/n$ (or $1/N$).

We were unable to see phosphorescence in three different laboratories for $n = 2$ or $n = 3$ at 77 K in various glasses

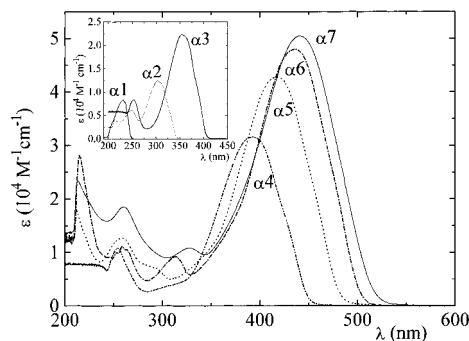


Figure 1. Room temperature absorption spectra of $\alpha 1$ – $\alpha 7$ in dioxane.

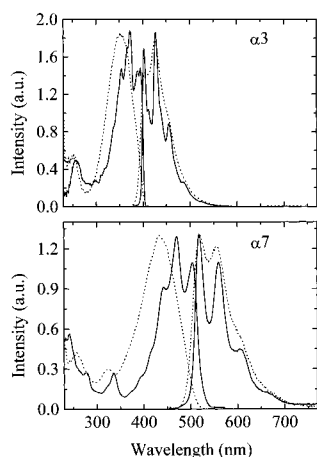


Figure 2. Absorption and fluorescence at room temperature (···) and fluorescence and fluorescence excitation spectra (—) at 77 K for $\alpha 3$ and $\alpha 7$ in ethanol.

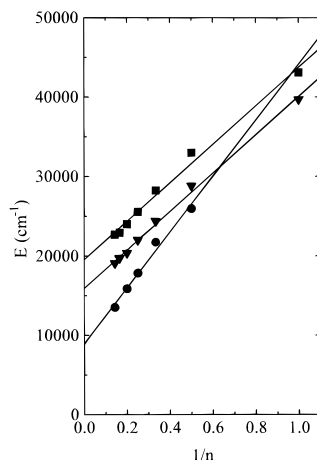


Figure 3. $E_{T_1-T_n}(\text{max})$ ●, $E_{S_0-S_1}(\text{max})$ ■, and $E_{S_0-S_1}(0-0)$ ▼ vs $1/n$.

including an aliphatic hydrocarbon, ethanol, and one containing 10% ethyl iodide, and others could not see phosphorescence for $\alpha 3$ and $\alpha 4$.^{1,26–28} Particularly, $n = 2$ (as well as $n = 3$) emission(s) should be quite easy to observe even with a quantum yield of 10^{-3} (or even lower), since they are expected to emit in a spectral region (500–700 nm) easily detectable by sensitive photomultiplier tubes. Also, no phosphorescence was observed for dodecyl-substituted $\alpha 6$, $\alpha 7$, and longer ones.²⁷ However, it has been reported²⁹ that $\alpha 3$ (in undefined environmental and temperature conditions) showed a sharp, single band phosphorescence at 826 nm, which was stated to be identical with that in shape and energy of poly(3-hexylthiophene) in a thin film at 18 K. This phosphorescence emission from $\alpha 3$ seems very strange particularly from the point of view that it is at the same wavelength as a multithiophene component polymer—surely the

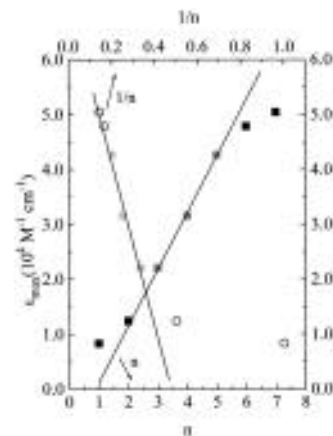


Figure 4. Extinction coefficients (ϵ) in dioxane vs $1/n$ (○) and n (■).

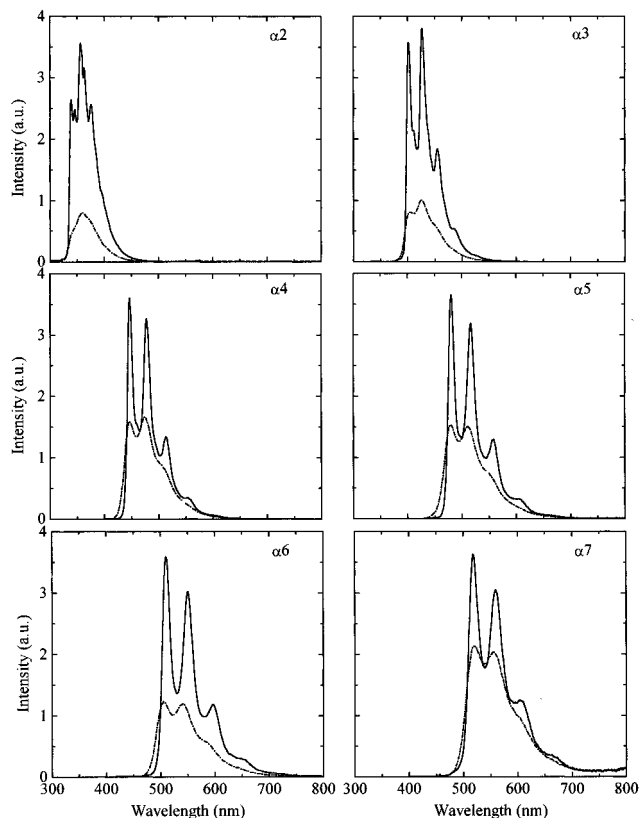


Figure 5. Room- (···) and low-temperature (77 K) (—) fluorescence spectra of $\alpha 2$ – $\alpha 7$ in ethanol, except for $\alpha 6$ where the solvent is 2-methyltetrahydrofuran.

triplet energies could not be the same. Furthermore, there is some published evidence that the lowest triplet of $\alpha 3$ is near 720 nm (0–0)³⁰ and we have evidence that it may be at still lower in energy at ~ 788 nm (0–0) based on photoacoustical experiments. Presumably, $\alpha 3$ could possibly have a maximum at such a wavelength (826 nm), but then surely the polymer must be at considerably longer wavelength.

Very interestingly, we did see a weak phosphorescence of thiophene, $\alpha 1$, with a maximum at ~ 430 nm and a 0–0 band near 362 nm (27600 cm^{-1}). Others^{31,32} found the lowest $S_0 \rightarrow T_1$ absorption by electron impact to have an onset near 370–375 nm. Thus, there is excellent agreement for the energy origin (0–0) of the lowest triplet state being very close to $27\,300 \text{ cm}^{-1}$. This would give a singlet–triplet (S_1-T_1) separation of close to $12\,300 \text{ cm}^{-1}$. For $\alpha 3$ using 720 nm³⁰ ($\sim 13\,900 \text{ cm}^{-1}$) as the origin of T_1 , there is a S_1-T_1 separation of $10\,800 \text{ cm}^{-1}$,

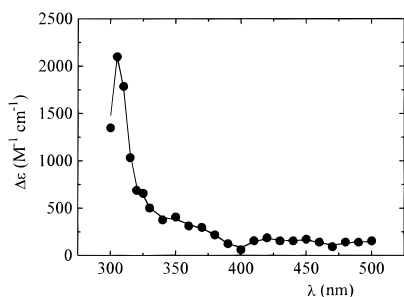


Figure 6. Triplet-triplet absorption spectrum of $\alpha 1$ at room temperature in benzene.

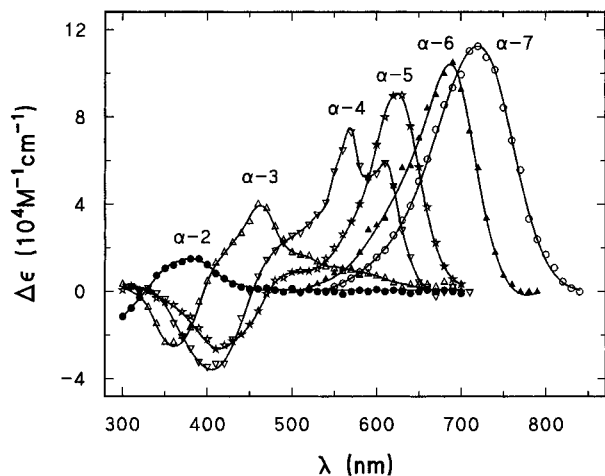


Figure 7. Triplet-triplet absorption spectra of $\alpha 2$ – $\alpha 7$ at room temperature in benzene.

whereas using 788 nm ($\sim 12\,700\text{ cm}^{-1}$), the separation is $12\,000\text{ cm}^{-1}$, close to that of thiophene.

Triplet-Triplet Absorption. Our triplet-triplet absorption data are shown in Figure 6 for $\alpha 1$ and in Figure 7 for $\alpha 2$ – $\alpha 7$. Table 3 gives representative spectral data in dioxane. As before, there is little effect of solvent on these values. Note again the shift of the absorption maximum to progressively longer wavelengths as the number of rings increase. We also consider this point in Figure 3 where the energy of the T–T maxima are plotted as a function of $1/n$. Thiophene has a weak shoulder at a wavelength longer than that of the maximum, near 360 nm, and $\alpha 3$ and $\alpha 4$ clearly have band shoulders (bands for $\alpha 4$) at wavelengths both shorter and longer than that of the main maximum. Also, the onset of the 460 nm band maximum of $\alpha 3$ is at an unusually long wavelength, essentially equal to that of $\alpha 5$ (where the maximum is at 630 nm). It appears that for $\alpha 3$ there must be more than one $T \rightarrow T_n$ transition in the broad absorption region of ~ 700 –460 nm, and probably for $\alpha 4$ also. The extinction coefficient of the principal maximum progressively increases as n increases. Some other data exist for some of the individual oligomers.^{1,4,26–28,30} For different alkyl-substituted $\alpha 9$ and $\alpha 11$, T_1 – T_n maxima occur at 774 and 805 nm, respectively.²⁷ The longer (dodecyl) alkyl chain substitutions cause a blue shift in the maxima compared to shorter ones (butyl).

Quantum Yields, Lifetimes, and Rate Constants. The ϕ_F and ϕ_T values are remarkably solvent independent (Tables 1 and 2), but ϕ_F clearly increases and ϕ_T clearly decreases as the number of rings increase and both become essentially constant from $\alpha 5$ to $\alpha 7$ (also see Figure 8). The τ_F values are also quite solvent independent, but clearly, the τ_F increases as the number of rings increase, becoming essentially constant from $\alpha 5$ to $\alpha 7$. The $k_F^0 = 1/\tau_F^0$ values, where $\tau_F^0 = \tau_F/\phi_F$, derived from ϕ_F and τ_F data in Tables 1 and 2 are quite constant as a function of the

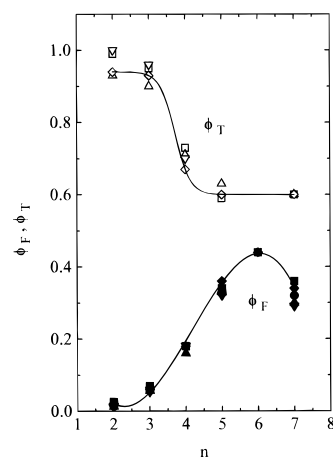


Figure 8. ϕ_F (dark symbols) and ϕ_T (open symbols) vs n for $\alpha 2$ – $\alpha 7$ in four solvents.

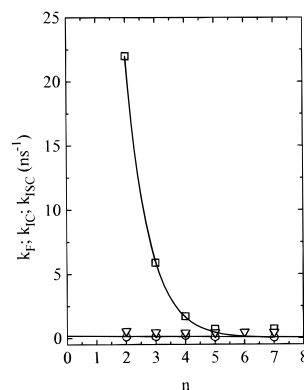


Figure 9. k_F (∇), k_{ISC} (\square), and k_{IC} (\circ) vs $1/n$ for $\alpha 2$ – $\alpha 7$ in benzene.

number of rings except perhaps for $\alpha 2$. Also, for $\alpha 3$, k_F^0 (in Table 2) seems somewhat different (lower) than for $\alpha 4$ – $\alpha 7$, except for perhaps benzene and acetonitrile. The k_F^0 values in benzene generally appear larger than in the other solvents (Tables 1 and 2). Despite this, it is generally valid that k_F^0 is quite constant as a function of both solvent and the number of rings. The k_{NR} values show a clear decreasing trend with increasing number of rings (Tables 1 and 2), but apparently, k_{NR} attains a nearly constant value from $\alpha 5$ to $\alpha 7$. Since we have all the photophysical data required, we can further determine both $k_{ISC} = \phi_T/\tau_F$ and $k_{IC} = (1 - \phi_F - \phi_T)/\tau_F$, which are shown in Tables 1 and 2. It is clear that k_{ISC} decreases with increasing number of rings, reaching a constant value from $\alpha 5$ to $\alpha 7$. The trend in k_{IC} is much more difficult to discern, but from $\alpha 2$ to $\alpha 5$ – $\alpha 7$, there is a decrease in k_{IC} with the data for acetonitrile, while the other solvents produce a scatter on the way from $\alpha 2$ to $\alpha 5$ – $\alpha 7$. All the above rate constants are illustrated in Figure 9. The reason for the scatter of k_{IC} is that k_{IC} depends on the difference $1 - \phi_T - \phi_F$ and $\phi_T + \phi_F$ is close to 1 for $\alpha 2$ and $\alpha 3$. Moreover, the error in ϕ_T is $\pm 15\%$ so that the k_{IC} value can be very sensitive to this (where $\phi_T = 0.90$ –0.99 and a 2% change in ϕ_T results in a minimum of a 300% change in k_{IC}). This is not true for k_{ISC} where the change expected in the k_{ISC} is essentially no more than about the same as the error in ϕ_T ($\phi_T = \pm 15\%$, only $\sim 7\%$ error in τ_F).

Our lifetimes of fluorescence data are given in Tables 1 and 2, and other fluorescence lifetime data also exist for some of the oligomers. Data on $\alpha 3$ – $\alpha 6$ ^{2–4} are within a few percent to 10% of ours.² Other data³³ for $\alpha 3$ and $\alpha 6$ are $\sim 30\%$ shorter than ours (theirs in dichloromethane), and for others³⁴ the $\alpha 3$ is some 30% longer than ours while $\alpha 4$ is close to ours. The

$\alpha 5$ in rigid poly(methyl methacrylate) has $\tau_F = 0.9$ ns,⁴ similar to ours in five solvents.

Recently, others have measured some photophysical parameters but there is no complete set even on any one compound; commonly, data on $\alpha 2$ are missing, and there is no data on $\alpha 7$. Our ϕ_F and τ_F data are given in Tables 1 and 2. The ϕ_F values of $\alpha 3$ – $\alpha 6$ have been determined by Chosrovian et al.² and Colditz et al.³ ($\alpha 2$ – $\alpha 6$), and generally they are within 10% of our values. The former authors believed that k_{NR} was largely due to $S_1 \rightarrow S_0$ internal conversion. However, this was based on ϕ_T values of approximately 0.2 for $\alpha 3$ and $\alpha 4$, which are certainly not correct (see later discussion). Others^{3,4} have measured ϕ_F of $\alpha 2$ – $\alpha 6$, and except for $\alpha 2$, these were also within 10% of our values. Moreover, ϕ_F data³³ are available on $\alpha 2$ – $\alpha 4$ and $\alpha 6$ and all agree with ours except for $\alpha 6$ (which is lower than ours and that of others given above). In addition, some data are available on the scattering of compounds: ϕ_F of $\alpha 3$ is similar to ours and others^{26,30,34} but $\alpha 4$ is noticeably lower³⁴ than ours and that of others^{2–4,26} (and τ_F 's are reasonably similar to ours).

Triplet yields for $\alpha 3$ of 0.2,²⁶ ≥ 0.9 ,³⁰ and 0.95³⁵ exist vs our values of 0.90–0.96 (Tables 1 and 2). Based on all available data, a ϕ_T for $\alpha 3$ of 0.2 cannot be correct. For $\alpha 4$, a value of ~ 0.2 ²⁶ exists for ϕ_T vs our values of 0.63–0.73 (Tables 1 and 2). On the basis of our ϕ_T data and ϕ_A for $\alpha 4$ (0.69),⁴ we believe the value of ~ 0.2 for ϕ_T of $\alpha 4$ is not correct.

In Tables 1 and 2 our triplet state lifetimes are shown. Some other data also exist: for $\alpha 3$, a value of 30 μ s in methanol at zero laser dose and concentration has been given.²⁸ Nonetheless, this is much shorter than our values ranging from ~ 62 (acetonitrile) to 108 μ s (dioxane) (Table 2). For $\alpha 3$ and $\alpha 4$, others²⁶ report a value of 57 ($\alpha 3$) and 45 μ s ($\alpha 4$) in ethanol vs our values of 91 ($\alpha 3$) and 43 μ s ($\alpha 4$) in the same solvent. The lifetime of $\alpha 5$ in dioxane in nitrogen has been given⁴ to be 7.7 μ s (0.24 μ s in air), which is considerably shorter than our value in dioxane and all other solvents (Tables 1 and 2). Based on induced dichroism decay, the decay of the triplet of $\alpha 3$ in a viscous medium has been given to be a few nanoseconds.³⁶ Presumably, oxygen was present, but nonetheless, this is an unusually short lifetime for a highly viscous medium even in the presence of oxygen. Lifetimes of 1- to 3-dodecyl-substituted $\alpha 6$, $\alpha 7$, $\alpha 9$, and $\alpha 11$ were determined in frozen 2-methyltetrahydrofuran at 80 K by monitoring the photoinduced absorption assigned as T_1 – T_2 absorption.²⁷ Lifetimes were 380–470 μ s for $\alpha 6$, 350–380 μ s for $\alpha 7$, 300 μ s for $\alpha 9$, and 250 μ s for $\alpha 11$. The trend to shorter lifetimes with increasing number of rings is the same as what we find for $\alpha 2$ – $\alpha 7$ (Tables 1 and 2). An interesting case is that of $\alpha 2$ in a seeded free-jet expansion where the triplet lifetime has been given as 550 ns.³⁷ This is extremely short compared to our values of 100–146 μ s (~ 225 -fold) at room temperature in fluid solution. This also seems to be very short for a triplet of an isolated, cold molecule (of $\alpha 2$) (see later discussion).

Calculations, Geometry, Stability of Conformers, and Transition Energies. We have done an extensive number (10) of different types of calculations and at a number of levels including three at the *ab initio* level regarding the relative stability of the all-cis and all-trans conformers of $\alpha 2$ (Table 4), as well as $\alpha 3$ – $\alpha 5$ (Table 5). In Table 4, for $\alpha 2$ we compared a number of calculations of the literature with those of ours and proposed ΔH values between cis and trans. We did significantly more and higher level calculations on $\alpha 3$ and $\alpha 5$, since their was very little or no significant data on these latter α -oligothiophenes. It can be seen in Table 4 that for $\alpha 2$, the two experimental ΔH values are quite different from one

TABLE 4: Relative Stabilities of Cis and Trans Conformers of $\alpha 2$ by Various Theoretical Approximations^a

method	result (kcal/mol)	ref/footnote
exptl	t < c, 1.16 \pm 0.13 ^b ; 0.2	41, 32, 39, 40
MM2	t < c, 1.04	this work
MOPAC	c < t, 0.46	this work
AMPAC/AM1	t < c, 0.16	this work
AMPAC/AM1	t < c, 0.25	54
<i>ab initio</i> STO 3G	t < c, 1.3	c
<i>ab initio</i> STO 3G	t < c, 1.20	d
<i>ab initio</i> 3-21G*	t < c, 0.64	e
<i>ab initio</i> RHF/DPZ	t < c, 0.8	f
plus electron correlation	t < c, 0.4	f
<i>ab initio</i> 3-21G	t < c, 1.9	f
<i>ab initio</i> 3-21G, 631	t < c, 0.6–0.7	40
Columbus ACPF gradient	t < c, 0.5	g

^a See Table 5 for more details on our calculations regarding other α -oligothiophenes and their conformers. ^b See text for a possible caveat regarding whether this truly represents the ΔH of cis and trans conformers (ref 41). ^c Bredas, J. L.; Street, G. B.; Thiemans, B.; Andre, J. M. *J. Chem. Phys.* **1985**, 83, 1323. ^d Jones, D.; Guerra, M.; Favaretto, L.; Modelli, A.; Fabrizio, M.; Distefano, G. *J. Phys. Chem.* **1990**, 94, 5761. ^e Distefano, G.; Colle, D.; Jones, D.; Zambianchi, M.; Favaretto, L.; Modelli, A. *J. Phys. Chem.* **1993**, 97, 3504. ^f Quattrocchi, C.; Lazzaroni, R.; Bredas, J. L. *Chem. Phys. Lett.* **1993**, 208, 120. ^g Kofranck, M.; Kovar, T.; Lischka, H.; Karpfen, A. *J. Mol. Struct.* **1992**, 259, 181.

TABLE 5: Relative Stability of the Conformers All-Cis and All-Trans α -Oligothiophenes (this Work)

cpd	method ^{a,b}	rel stability	ΔH cis–trans (kcal)
$\alpha 2$	MOPAC	c < t	0.46
	MM2	t < c	1.04
	AMPAC/AM1	t < c	0.16
	exptl	t < c	1.16 \pm 0.13; ^c 0.2
$\alpha 3$	MOPAC	cc < tt	0.89
	AMPAC/AM1	tt < cc	0.35
	MM2	tt < cc	2.12
	MNDO 93, AM1	tt < cc	0.42
	MNDO 93, PM3	cc < tt	0.83
	DGauss-LDF	tt < cc	1.39
	DGauss-NLSD	tt < cc	1.18
	<i>ab initio</i> STO 3G	tt < cc	2.41
<i>ab initio</i> 6–311 G	tt < cc	2.22	
<i>ab initio</i> 6–31 G(d)	tt < cc	1.47	
$\alpha 4$	AMPAC/AM1	ttt < ccc	2.73
$\alpha 5$	MOPAC	cccc < tttt	1.54
	AMPAC/AM1	tttt < cccc	1.41
	MM2	tttt < cccc	8.4
	MNDO 93, AM1	tttt < cccc	1.72
	MNDO 93, PM3	cccc < tttt	1.52
	DGauss-LDF	tttt < cccc	6.46
	DGauss-NLSD	tttt < cccc	5.79
<i>ab initio</i> STO 3G	tttt < cccc	4.81	

^a Gaussian 92 code was used for all *ab initio* calculations. For one of them, 6-31G(d), a polarization function (d-orbital) was added for C and S atoms. For DGauss, double- ζ potential basis sets were used for orbital functions and a nonlocal spin density (NLSD) correction was used in one of the calculations with DGauss. ^b For MNDO 93 (AM1 or PM3) and *ab initio* STO 3G calculations, initial input geometries were from MM2. For DGauss, input geometries were planar. For *ab initio* 6-311 G and 6-31G(d), input geometries were from STO3G optimized geometries (planar). A second set of calculations using MNDO 93, AM1 geometry as input gave ~ 0.2 kcal difference from planar input but did not change the relative stability. ^c See text for possible caveat regarding whether this truly represents the ΔH of cis and trans conformers.

another. This potentially complicates the comparison with theory. Nonetheless, it appears that the trans conformer of $\alpha 2$, albeit twisted around the inter-ring bond, is lower in energy.^{32,38–40} Note that MOPAC and MNDO93,PM3 incorrectly predict the

cis conformer as the more stable one. Also, the presumably less sophisticated MM2 approach predicts ΔH in the same vicinity as several of the other methods including the *ab initio* level calculations.

Some literature data propose that for $\alpha 2$ in the ground state, both cis and trans conformers coexist in an $\alpha 2$ -seeded free-jet expansion and that the inter-ring twisting is about the same in both conformers.⁴¹ The ΔH between cis and trans was given to be 1.16 ± 0.13 kcal/mol (406 ± 46 cm⁻¹) with the trans conformer being the more stable. On the other hand, different but parallel supersonic jet experiments⁴² involving $\alpha 2$ and using the same emission techniques, plus hole burning, point to the existence of a torsionally twisted equivalent pair (a double minimum) around the trans conformer in the ground state *in place of* identifying the coexistence of cis and trans conformers as done earlier.⁴¹ The equilibrium structure (trans) existed with a twist of $\sim 21^\circ$ from planarity and with a barrier of ~ 25 cm⁻¹ between the two minima (at 21°). In the first excited state by contrast, $\alpha 2$ was found to be trans and planar with a deep, steep single minimum torsional potential well around the equilibrium structure. As we will see later, our spectroscopic data strongly indicate a similar situation in the first excited state. The difference in the supersonic jet experiments^{41,42} makes it difficult to be certain that the proposed⁴¹ ΔH (1.16 kcal) between ground state cis and trans is actually appropriate.

For $\alpha 3$, the higher level calculations (DGauss and several levels of *ab initio*) predict the tt conformer as the more stable as does the MM2 approach and with a fairly comparable ΔH (Table 5). If all three conformers are calculated (tt, ct, cc), then tt is still the most stable except by MOPAC and MNDO93,-PM3. The ΔH between tt and cc in general seems to be in the 2.0 kcal/mol range (± 0.4) for *ab initio* methods and ~ 1.2 kcal/mol for the DGauss approach (lower for AMPAC and MNDO, AM1) (Table 5). Again, MOPAC and MNDO93,PM3 very likely predict stability in the wrong order, cc < tt.

For $\alpha 4$ and $\alpha 5$, all methods except MOPAC and MNDO93,-AM1 predict the all-t conformer as the most stable. The ΔH between the all-trans and all-cis conformer varies according to the calculation method (Table 5). If we consider all possible conformers of $\alpha 5$ (10 of them), the all-trans conformer is still the most stable where generally the greater the number of adjacent cis pairs, the higher the relative energy.

We have determined the dihedral angle of all the conformers of $\alpha 3$ and for the all-cis and all-trans conformers for $\alpha 5$. All *ab initio* STO3G, DGauss (with planar input), and MM2 predict either planar (*ab initio* STO3G) or near planar geometry (essentially no twisting) for the cc and tt conformers of $\alpha 3$. This is also true for MOPAC, but remember, it predicts the cc conformer as the more stable vs tt for the other calculations considered here (and all the rest except MNDO93,PM3). X-ray data of trithiophene ($\alpha 3$)⁴³ give a clear indication that the tt is the more stable, that is, this *is* the conformeric form in the crystal with inter-ring angles of about 6° – 9° . Also, a dibutyl-substituted trithiophene has a tt configuration⁴⁴ with a higher angle of inter-ring twist than for $\alpha 3$ itself (not unexpected). However, the barrier to rotation was given to be 19.7 kcal/mol in the ground state and 4.2 kcal/mol in the lowest excited singlet state using ¹H NMR. This seemed quite incompatible with a "single" inter-ring bond in the ground state and a more double inter-ring bond in the lowest excited singlet state. Very recently, reinvestigation⁴⁴ of the same molecule at higher resolution now suggests a ground state barrier of 0.5–1 kcal/mol with the excited state barrier similar to that reported earlier.⁴⁴ These new data are now compatible with our findings (see later discussion). In the case of $\alpha 5$, only STO3G gives planar

TABLE 6: Calculated and Experimental First Transition Energies of Some α -Oligothiophenes^a

cpd	geometry opt method	conformer	transition energy, ^b nm	
			theory (f)	exptl ^c
di-	MM2 (S, sp ²)	t	348 (0.70)	302 (303)
		c	345 (0.72)	
	MOPAC	t	336 (0.65)	302 (303)
		c	335 (0.66)	
tri-	AMPAC/AM1	t	345	302 (303)
		c	325	
	MOPAC	all-t	398 (1.07)	350 (354)
		all-c	397 (1.09)	
tetra-	AMPAC/AM1	all-t	373	350 (354)
		all-c	354	
	AMPAC/AM1	all-t	398	386 (392)
		all-c	333	
quinque- ^d	MM2 (S, sp ²)	all-t	431 (1.65)	410 (417)
		all-c	480 (1.68)	
	MOPAC	all-t	422 (1.59)	410 (417)
		all-c	473 (1.60)	
	AMPAC/AM1	all-t	405	410 (417)
		all-c	355	
	STO 3G	all-t	405 (1.56)	410 (417)

^a See Table 7 for calculations on more αn 's and by different methods. Here, ZINDO is used for theory. All are this work. ^b See Table 7 for other transitions for these and other α -oligothiophenes. ^c Values in methylcyclohexane. Values in dioxane are in parentheses. ^d In all cases except STO3G there were finite values of twist for the S–C–C–S dihedral angle while for STO 3G there was no twist (totally planar).

geometry (no twisting) for the all-trans conformer, as well as for the all-cis one (interestingly enough, essentially *all* the calculation methods give near planar geometry for the all-cis conformer). Some X-ray data on $\alpha 4$ and $\alpha 6$ ⁴⁵ give evidence for an all-trans, nearly planar (0 – 10° twist) geometry. There would be no reason to believe $\alpha 5$ should be different.

In Table 6 we present the lowest transition energy predicted for the all-trans and all-cis conformers of $\alpha 2$, $\alpha 3$, and $\alpha 5$ and a comparison with experimental data. It can be clearly seen that for $\alpha 5$, all three methods of geometry optimization show that the all-trans conformer spectral data are very much closer to experimental results than the all-cis. The best agreement is from STO3G, and recall that this was *the* one that gave no twisting of the inter-ring bond. We believe this is perhaps the strongest evidence that $\alpha 5$ is all-trans with very little inter-ring twisting, and a similar situation should be true for $\alpha 3$.

Table 7 gives experimental data for the discernible transitions in $\alpha 1$ – $\alpha 7$, extinction coefficients, and theoretical predictions for a number of α -oligothiophenes.

Discussion

State Order. One of the most important questions for the α -oligothiophenes (hereafter denoted αn) concerns the state order: does the state order change with increasing n , and if so, when?

Based on earlier spectroscopic data of α, ω -dithienylpolyenes, calculations, and some extrapolated data, the (2)¹Ag state was assigned below the (1)¹Bu for oligothiophenes of $n = 6$ and greater.⁷ For $\alpha 2$, two-photon spectroscopy⁵ has located the ¹Ag above the ¹Bu. Theoretically, it has been predicted⁸ that the ¹Ag state would be below the ¹Bu state for $\alpha 2$ – $\alpha 4$ with crossing between $\alpha 4$ and $\alpha 5$. However, reduction in the degree of CI (with no rational justification) now resulted in the ¹Bu state being lowest from $\alpha 2$ to $\alpha 7$ (others predicted ¹Ag to be lowest for $\alpha 6$ and longer chain). Also, more recent calculations⁹ for $\alpha 1$ – $\alpha 4$ predicted that the ¹Ag state (0 level) would be below the ¹Bu state (0 level). They believed the ¹Ag state observed was the (3)¹Ag state. Multi-CI *ab initio* calculations on

TABLE 7: Experimental (with ϵ) and Theoretical^a Energies (with f) for All-Trans Conformers of Some α -Oligothiophenes

cpd	exptl ^b		theoretical			
	λ (nm)	ϵ (M ⁻¹ cm ⁻³)	λ (nm)	f		
thiophene	232	8340	227	0.26 (PPP) ^d		
			211	0.27		
			170, 169	1.5		
di-	303 (302) ^c 247	12440 6200	311	0.83 (PPP) ^d		
			257	0.39		
			204	0.19		
tri-	354 (350) ^c	22100	342	1.40 (PPP) ^d		
			276	0.02		
			250, 245	0.24		
			234	0.15		
			222	0.22		
quater-	391 (386) ^c 308 (sh)	31560 4300	252	10700		
			205			
			417 (410) ^c ~340 (sh)	42650	405	1.56 (ZINDO)
			290	7300	286	0.12
quinque-	256 207–214	12700	256, 260	0.06		
			236	0.10		
			196	1.71		
			436	47910		
			314			
sexi-	259	50460	441 (433) ^c			
			361 (sh)			
			325	10900		
			282, 298 (sh)			
			256	18200		
septa-	205					

^a PPP model with geometries from an MMX (force field) approximation (Serena Software, Bloomington IN) for thiophene, bithiophene, and trithiophene. For quinquethiophene data are from ZINDO using geometry obtained via STO 3G. ^b In ethanol for thiophene, all others in dioxane. See Experimental Section for methodology for determining ϵ . ^c Values in parentheses are for the compound in methylcyclohexane. ^d Parameters for PPP calculation were $I_P(C) = 11.20$, $\gamma(C) = 11.10$, $I_P(S) = 17.20$, $\gamma(S) = 10.00$, $\beta_{CS} = -1.8$, $\beta_{CC} = -2.4$.

thiophene ($\alpha 1$) place the (2)¹A₁ state below the ¹B₂.⁴⁶ More recently, *ab initio* calculations¹¹ (multi-CI) for $\alpha 2$ give a ¹Bu state below the ¹Ag state and, in fact, predicts two ¹Bu states below the lowest ¹Ag. Very recent calculations³ used CNDO/S both with single and single plus double CI to calculate transition energies and state orders. Good results compared with experimental results were obtained with single CI but not with single plus double CI. This problem with double CI and of rationalizing the results when ignoring double CI has been a major problem (see refs 3, 7, and 8).

From our *experimental* data the k_F^0 values in benzene (Table 1) for six oligothiophenes, $\alpha 2$ – $\alpha 7$, show that the k_F^0 is remarkable constant. Furthermore, k_F^0 is essentially constant in all *four additional solvents* in Table 2, especially for $\alpha 4$ – $\alpha 7$. Moreover, the k_F^0 values for all the α -oligothiophenes in *all* the solvents only vary from $(0.28$ – $0.45) \times 10^9$ s⁻¹, most values being in a narrower range still (others³ found a range of $(0.25$ – $0.33) \times 10^9$ s⁻¹ in dioxane). These correspond to τ_F^0 values of 2.3–3.5 ns, which are clearly typical of emission lifetimes from allowed π, π^* states. Also, as given earlier¹, k_F^0 values calculated based on the Strickler–Berg (SB) equation over the first absorption band for $\alpha 2$ – $\alpha 5$ and $\alpha 7$ agreed within 0–14% (only one case was as large as 14%; others were less than 7%) of those from experiment. The result of all of these considerations provides *experimental convincing evidence that the lowest*

excited state for $\alpha 2$ – $\alpha 7$ is of allowed character and is (1)¹Bu and not (2)¹Ag. This was noted earlier¹ for $\alpha 2$ – $\alpha 5$ and $\alpha 7$ in benzene, but we can now *include $\alpha 6$* as well and, moreover, safely conclude that this *order is independent of the solvent for $\alpha 2$ – $\alpha 7$.*

Relative to the question of whether the (1)¹Bu and (2)¹Ag state cross and, if so, when, it is difficult to answer when, but surely they will cross, since the two states are getting closer as n increases (for αn). Earlier, on the basis of only two data points for extrapolation of the (2)¹Ag energy, we believed crossing might occur between $n = 9$ and $n = 11$. However, the (2)¹Ag data were from different phases of different αn 's, so we no longer believe the crossing will occur at these low n values. Others³ also note that the states will cross, but based on some CNDO/S and FEMO models, they predicted crossing would be beyond $n = 50$.

Temperature Effect on Absorption and Ground-State Geometry. Recall earlier in the Results section that we noted the very significant red shift (~ 1600 cm⁻¹) of the absorption maxima of $\alpha 2$ – $\alpha 7$ upon going from 298 to 77 K (see Figure 3 and ref 1). If, however, we look at the 0–0 band (as determined by the overlap of absorption and fluorescence spectra at 298 and 77K), the shift is greatly reduced to only ~ 200 cm⁻¹ for $\alpha 2$ and $\alpha 3$, ~ 300 cm⁻¹ for $\alpha 4$, and ~ 400 cm⁻¹ for $\alpha 5$ and $\alpha 7$. We interpret the absorption results to mean that as the temperature is lowered, there is a greater average planarity among existing conformers; said in another way, the virtual molecule at 77 K is more planar than one at 298 K. That is, the potential energy minimum in the ground state becomes more vertically aligned to that of the excited state such that the vertical transition now is to a lower vibronic level of the excited state, *yet the actual state energy difference (0–0's) has changed relatively little.* Usually, the red shift seen in the absorption upon going to low temperature is ascribed to increased planarity of the ground state with subsequent greater conjugation, lengthening of the π -electron path, and decreased energy gap between S₀ and S₁. However, based on our spectroscopic data as described above, this is not what principally occurs. It does appear that there is some small effect on relative state energies for $\alpha 5$ – $\alpha 7$ and perhaps for $\alpha 4$.

There are clear indications that $\alpha 2$ is twisted in both the cis and trans forms, that they coexist, and that the trans is more stable than the cis. Furthermore, the absorption (and fluorescence) of $\alpha 2$ undergo the most dramatic increase in vibrational resolution as a function of temperature compared with all other αn 's (see Figure 5 and ref 1). However, the red shift of the absorption maxima at low temperature is essentially the same as for $\alpha 3$ – $\alpha 5$ (~ 1600 cm⁻¹) and for the others, while the fluorescence maximum shows essentially no shift (≤ 200 cm⁻¹). We interpret all the absorption results to mean that for $\alpha 2$ the ground state becomes more planar, as it is for all αn 's, and a greater population of a more singular conformer exists for $\alpha 2$ compared to other αn 's at low temperature.

Temperature Effect on Fluorescence and Excited-State Geometry. A negligible shift of the maximum of fluorescence (100 – 200 cm⁻¹) as well as the 0–0 band occurs upon lowering the temperature. We believe that based on the Franck–Condon forbidden shape of the first absorption band, an obvious change in geometry has occurred. This could be consistent with a quinoidal-like contribution to the structure of the excited state—we will support this belief more fully shortly. At room temperature, solvent shell relaxation around the now quinoidal-like excited state *can* occur, so emission occurs from the equilibrium excited state to a twisted ground state. However, at 77 K in a rigid matrix environment solvent shell relaxation

TABLE 8: Atomic Charges and Dipole Moments in the Ground and Excited States^a

cpd	atom	GS charge	μ (D)	ES (S_1) charge	μ (D)	ES (T_1) charge
$\alpha 1$	S5	+0.02	1.84	-0.22	2.52	
	C1, C2 (α -C)	-0.14		+0.03		
	C3, C4 (β -C)	-0.03		-0.01		
$\alpha 2$	S5, S13	+0.004 (+0.58)	0.007	-0.15 (+0.38)	0.009	(+0.53)
	C4, C11 (α -C)	-0.14 (-0.45)		-0.01 (-0.35)		(-0.47)
	C1, C10 (β -C)	-0.03 (-0.15)		+0.015 (-0.09)		(-0.10)
	C2, C9 (β -C)	-0.04 (-0.16)		-0.025 (-0.11)		(-0.20)
	C3, C12 (α -C, bonded)	-0.035 (-0.30)		+0.05 (-0.29)		(-0.24)
	H7, H14	+0.075		+0.04		
$\alpha 3$	S5, S20	+0.004	1.84	-0.14	1.77	
	C4, C18 (α -C)	-0.14		-0.02		
	C1, C17 (β -C)	-0.03		+0.01		
	C2, C8 (β -C)	-0.04		-0.014		
	C3, C19 (α -C, bonded)	-0.035		+0.04		
	S14	+0.001		-0.16		
	C12, C13 (α -C, bonded)	-0.04		+0.04		
	C10, C11 (β -C)	-0.04		-0.005		
	H7	+0.074		+0.04		
	H15	+0.077		+0.04		
	H16	+0.076		+0.04		
	H21	+0.074		+0.04		
	$\alpha 5$	S26, S34		+0.02		2.11
C25, C19, C18, C11, C12, C4, C3, C32 ^c		-0.05 ^c	+0.03 ^c			
C16, C31 (β -C)		-0.04	+0.00			
C23, C30 (β -C)		-0.03	+0.01			
C24, C33 (α -C)		-0.15	-0.04			
H27, H22, H21, H15, H14, H7, H6, H36		+0.075 ^b	+0.04			
S10, S13, S5		+0.02	-0.14			
C17, C1 (β -C)		-0.035	+0.005			
C10, C9, C8, C2 (β -C)		-0.04	-0.003			

^a See Figure 10 for structures and numbering of atoms. Charges are formal charges calculated by the ZINDO approximation, and for $\alpha 2$, the numbers in parentheses are those calculated using the AMPAC approximation using the AM1 Hamiltonian (full SCF and configuration interaction). ^b This represents an average of values between 0.074 and 0.077. ^c α -C, bonded.

cannot occur and emission is from the Franck–Condon excited state to a “planar” ground state. It is this combination of the different circumstances that results in essentially no shifting of fluorescence bands between 298 and 77 K. The above interpretations regarding absorption (previous section) and fluorescence behavior are supported in two major ways. One source of support regards the spectroscopic studies of bithiophene ($\alpha 2$) in a supersonic jet⁴² where there is a clear indication that in S_1 the $\alpha 2$ is trans planar with a single minimum and that a deep, steep potential well exists. However, in S_0 , a much broader potential well exists (and in fact there is a double minimum, and equivalent twisted forms exist). There is no reason to believe a parallel situation is not true in general for all of the αn 's *albeit* the ground state may not have multim minima *but* that the excited state has a higher bond order for the inter-ring bonds and is planar quinoidal-like compared to the ground state. A second source of support involves a consideration of changes in atomic charges between the S_0 and S_1 state (as well as the T_1 state, which we will need to consider shortly). Table 8 gives the atomic charge and dipole moments in the ground state and S_1 state for all atoms in $\alpha 1$ – $\alpha 3$ and $\alpha 5$ and atomic charges in T_1 for $\alpha 2$, where Figure 10 gives the appropriate structures and numbering for these four molecules. Note that in all cases, there is large change in charge on sulfur and the α -carbon (non inter-ring bonded) between S_0 and S_1 (Table 8). In the case of sulfur, the change involves a large *addition* of negative charge [~ 0.14 – $0.24e$] while for α -carbons that are

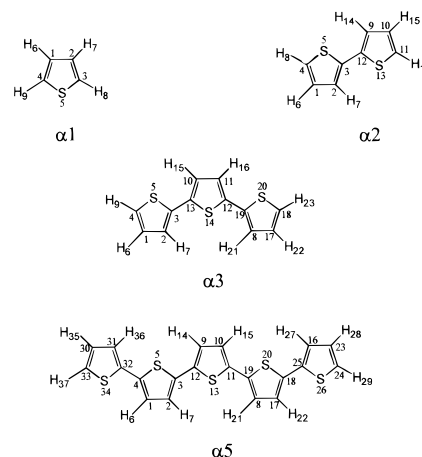
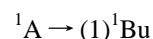


Figure 10. Numbering of atoms of various oligothiophenes for reference to atomic charges given in Table 8.

non-inter-ring bonded, there is a quite large *subtraction* of negative charge (~ 0.12 – $0.19e$). The bonded α -carbons (to another α -carbon) still show *subtraction* of negative charge but smaller in magnitude ($\sim 0.07e$). One obvious important implication of this is that the lowest energy transition (longest wavelength one) now clearly established to be



has some charge transfer character. Secondly, with such large changes in atomic charges there must be an accompanying change in the geometry of the excited singlet state (as previously noted, based simply on the Franck–Condon forbidden shape of the first transition). A quinoidal-like structure is compatible with these charge changes *and* totally in harmony with the change in the ground and excited singlet state potential energy curves along the inter-ring $\alpha\text{C}-\alpha\text{C}$ torsional coordinate found in supersonic jet experiments⁴² where for $\alpha 2$, the inter-ring $\alpha\text{C}-\alpha\text{C}$ bond was clearly much more double bonded in S_1 compared to S_0 .

In addition to studying the effect of temperature on absorption and fluorescence spectral maxima and 0–0 origins, we examined the dependence of ϕ_F on temperature. In Table 2 for ethanol as the solvent, it is interesting to note that ϕ_F for $\alpha 2$ and $\alpha 3$ clearly increase from 298 to 77 K by 2.8-fold and 2-fold, respectively. However, there is essentially *no change in ϕ_F for the other αn 's ($\alpha 4-\alpha 7$)*. Others³⁵ also found a very similar change for $\alpha 3$ and, furthermore, by assuming that the only temperature dependent process was nonradiative, calculated an activation energy of ~ 1.2 kcal/mol. We also examined the effect of temperature on ϕ_T of $\alpha 3$ and found little or no change over the range 290–140 K. Others³⁵ believed that the activation energy was for $S_1 \rightarrow T_n$ and that about 55% of the ϕ_T arose from this path.

Variation of Rate Constants. Geometry and Charge Transfer Mixing. First of all, recall that based on the k_F^0 and τ_F^0 values in the *five* solvents (Tables 1 and 2) and the correlation with those determined by the Strickler–Berg equation, the evidence is totally convincing that the ^1Bu state is the lowest for all αn 's from $\alpha 2$ to $\alpha 7$, and moreover, this order is solvent independent.

In general, the k_F^0 is quite constant ($\sim 20\%$) as a function of the number of rings ($\alpha 2-\alpha 7$) and solvent (except perhaps benzene where it is sometimes greater) while k_{ISC} undergoes at least a 20-fold (vs 20% for k_F^0) decrease between $\alpha 2$ and $\alpha 5$ and a leveling of k_{ISC} occurs from $\alpha 5$ to $\alpha 7$. The trend of k_{IC} is not so definitive because as noted earlier $\phi_T + \phi_F \approx 1$ and because of the potentially significant error in ϕ_T ($\pm 15\%$); the difference term ($1 - \phi_T - \phi_F$) required to calculate k_{IC} can generate notable error in the k_{IC} . However, it is clear that it is significantly smaller than k_{ISC} (Tables 1 and 2). Furthermore, there is a clear, progressive decrease in k_{NR} (Tables 1 and 2) from $\alpha 2$ to $\alpha 5$ and then a leveling from $\alpha 5$ to $\alpha 7$ (as for k_{ISC}). A similar trend is apparent for k_{IC} in dioxane (Table 2). On the basis of the relationship of k_{ISC} , k_F , and k_{IC} as well as the fact that $\phi_F + \phi_T$ generally is > 0.92 , k_{IC} is very small, and therefore, internal conversion from S_1 is small or negligible ($\phi_{\text{IC}} \approx 0.1-0.0$).

We believe that the preceding facts can be understood by a combination of circumstances. There is evidence from two sources that the first excited singlet state has a quinoidal-like character that would account for the very small internal conversion observed, since there would be very little torsional mode coupling (around the inter-ring bond) to the ground state. There is obviously significant spin–orbit coupling that has to be due in part to the heavy atom effect⁴⁷ of the sulfur. Nonetheless, ϕ_T and k_{ISC} show a progressive *decrease* from $\alpha 2$ to $\alpha 5$ and then a leveling off (while ϕ_F shows a progressive *increase* from $\alpha 2$ to $\alpha 5$ and then a leveling off from $\alpha 2$ to $\alpha 7$). We believe that most of the spin–orbit coupling is not due to the classical heavy atom effect⁴⁷ but that this coupling is mediated by charge transfer (CT) mixing involving matrix elements of the type

$$\langle ^1\psi_{\text{CT}} | H' | ^3\psi_i \rangle$$

where H' is the spin–orbit (coupling) operator and contains the atomic spin–orbit coupling factor ζ for sulfur, which is large, 363 cm^{-1} . Remember that the decrease in ϕ_T (and increase in ϕ_F) is not due to some significant increase in k_F^0 , which is *essentially constant*, or k_{IC} (k_{NR} as the number of rings increases) *but* is due to a real *decrease* in k_{ISC} (Tables 1 and 2). It is clear that as the number of rings is increased, a like number of heavy atom sulfur centers is also increased. Yet, k_{ISC} (and f_T) *still decreases*. We believe this occurs because of a decrease in the magnitude of the matrix elements described above, resulting from a decreased charge transfer mixing of $^1\psi_{\text{CT}}$ and $^3\psi_i$ as the number of rings increases. This may result from the smaller overlap of the electron donor–electron acceptor molecular orbitals because of the more spread-out nature of the molecular orbitals proceeding from $\alpha 2$ to $\alpha 5$, which becomes essentially constant from $\alpha 5$ to $\alpha 7$.

Absence of Phosphorescence and Triplet State Lifetimes. Significant inter-ring bond torsional (twisting) coupling to the ground state could occur, resulting in a large radiationless rate constant for $T_1 \rightarrow S_0$ with a quenching of phosphorescence emission. Recall that the lifetime of the triplet state undergoes a substantial decrease from $\alpha 2$ to $\alpha 7$ in all solvents (see Tables 1 and 2) by 5- to 10-fold. If the lifetimes are considered to be essentially the radiationless lifetimes, then the radiationless intersystem crossing $T_1 \rightsquigarrow S_0$ would strongly dominate and phosphorescence would be “absent”. In such a case, the lifetimes would be expected to decrease because of the decrease in the T_1-S_0 energy gap ($\alpha 2-\alpha 7$) resulting in a significant increase in the Franck–Condon overlap integrals between T_1 and S_0 upon which the radiationless rate constants depend.⁴⁷

We make one additional observation regarding $\alpha 2$. Some two-photon photoionization experiments³⁷ assign the final state as a triplet state (related to the dominant photoionization channel). Earlier in the Results section, we compared some triplet lifetimes and in the particular case of $\alpha 2$, we determined τ_T to be 100–146 μs (solvent dependent) at room temperature in a fluid solution (Tables 1 and 2). The τ_T given for the triplet state of $\alpha 2$ in the supersonic jet experiment above³⁷ was 550 ns. This triplet lifetime seems to be extraordinarily short for a molecule in a nearly isolated condition presumably without (or nearly without) external intermolecular interaction (at the usually expected chamber background pressures) and where, although it is not strictly possible to define the temperature, a temperature on the order of 10 K seems reasonable. The lifetime is ~ 225 -fold shorter than our triplet lifetimes in a variety of solvents that were not vacuum degassed (but N_2 bubbled) at room temperature (vs temperature on the order of 10 K for the supersonic jet experiment), where intermolecular interactions must be more plentiful than in the supersonic jet experiment. These considerations make us very doubtful of the assignment of the T_1 triplet state (of $\alpha 2$) as the state to be associated with the 550 ns lifetime.

Recall that thiophene itself, $\alpha 1$, did show a weak phosphorescence but “no” fluorescence ($\phi_F \leq 5 \times 10^{-4}$). We do not know whether phosphorescence is weak because ϕ_T is low (ϕ_{IC} is high) or because the nonradiative process from T_1 is high. Nonetheless, phosphorescence does exist at a level greater than any other αn so far examined ($\alpha 2-\alpha 4$, $\alpha 6$). Given that it would be reasonable to expect ϕ_T to be quite high because of matrix elements of the type described in the previous section above (thiophene also has a large amount of charge transfer going from $S_0 \rightarrow S_1$, Table 8), we would expect ϕ_P to be high. Thus, the reason phosphorescence is weak is very likely because of a

highly efficient nonradiative process out of T_1 . This is supported by the short τ_T (1 μ s) compared to those of all other αn 's.

Singlet Oxygen Formation by Energy Transfer. In Table 1, it can be seen that the ϕ_Δ decreases with an increase in the number of rings. Note that for $\alpha 3$, the efficiency of triplet energy transfer to produce 1O_2 , $S_\Delta = \phi_\Delta/\phi_T$, is 0.85 while for $\alpha 2$, $\alpha 4$, and $\alpha 5$ it is near 1. These results clearly indicate energy transfer is highly efficient from many oligothiophenes to ground state oxygen. Although we are not totally confident about the ϕ_Δ for $\alpha 7$ (or ϕ_T), it appears to be in the 0.2–0.3 range, giving a S_Δ that is relatively low (~ 0.5). This may be because of the presence of two *n*-butyl groups preventing efficient encounter transfer and the fact that the triplet is expected to be quite low for $\alpha 7$ ($9\text{--}12\,000\text{ cm}^{-1}$). The situation for $\alpha 6$ is unclear, although based on ϕ_T data in two solvents for $\alpha 5$ and one for $\alpha 7$, it seems that ϕ_T for $\alpha 6$ should be in the 0.5 area. If true, the S_Δ is definitely lower than for the others except possibly for $\alpha 7$, based on the literature value (Table 1) of 0.36⁴ for ϕ_Δ . There are several literature values for the ϕ_Δ of $\alpha 3$: 0.15,²⁶ ~ 0.8 ,^{1,4} ~ 0.8 ,⁴⁸ 0.73³⁰ (which was believed to be more accurate than an earlier 0.86 value determined by some of the same authors), and 0.6 or 0.86 depending on the technique used⁴⁹ compared with our values of 0.81 in benzene and 0.74 in acetonitrile. We believe the 0.15²⁶ value is very probably incorrect for $\alpha 3$. On the basis of all the data available, we believe ϕ_Δ for $\alpha 3$ is 0.75 ± 0.05 .

The ϕ_Δ values of other αn 's have been given to be⁴ ~ 0.7 for $\alpha 4$, ~ 0.5 for $\alpha 5$, and ~ 0.36 for $\alpha 6$, where both $\alpha 4$ and $\alpha 5$ (as well as $\alpha 3$) are close to our values (see Table 1). Elsewhere,²⁶ a value of 0.24 has been determined for $\alpha 4$. We believe this value of 0.24²⁶ is quite probably incorrect for $\alpha 4$ based on our value of ϕ_T of ~ 0.7 . Furthermore, we and others⁴ find a value of ~ 0.7 for ϕ_Δ of $\alpha 4$ and, of course, ϕ_Δ cannot be greater than ϕ_T as it would be if $\phi_T = 0.24$.²⁶ The ϕ_Δ values of some substituted bithiophenes (acetylenic, olefinic) are known,⁵⁰ and these all seem to be quite low, ~ 0.05 , compared to what we obtain for bithiophene itself, ~ 0.97 (Tables 1 and 2).

Comparison of Solution and Film Data. Recall that there is great interest in oligothiophenes regarding their application in nonlinear optical charge storage and molecular electronics devices. In most of these applications, the solid phase is the phase of most interest. However, because of film quality, thickness, homogeneity, and crystallinity, as well as the ambient conditions, the absorption, fluorescence, and other photophysical properties truly intrinsic to a particular αn are not well defined. Therefore, a study as carried out here can provide intrinsic properties at the molecular level, and these can then be used as a reference to better understand and interpret solid state absorption and photophysical results.

For films of the oligothiophenes, assignment of the lowest excited state varies. Studies of films and solutions⁴ showed that the ϕ_F of ultrathin and thin films were considerably less in general than those in solutions ($10\text{--}10^3$ times) and that the absorption maximum was strongly blue-shifted⁵¹ (although absorption could continue to near the same onset). Also, fluorescence decay curves of films are strongly nonexponential,⁵¹ in contrast to our work in solution. This indicates considerable inhomogeneity in the surroundings of the oligomers. The lowest excited state was assigned as $(2)^1A_g$ for all oligothiophenes including $\alpha 2\text{--}\alpha 8$.³ However, although this assignment for all was repeated again,⁵¹ there was some question about how unambiguous it was. Others⁴⁵ have assigned the lowest excited state for films $\alpha 6$ as $(1)^1B_u$, which was noted to be some 900 cm^{-1} below the $(2)^1A_g$ (comparing lowest exciton levels of each exciton band). The fluorescence (radiative)

lifetime was given as shorter than 600 ps. Recall that our work in solutions clearly defines the lowest excited state of the oligomers $\alpha 2\text{--}\alpha 7$ as $(1)^1B_u$.

Absorption data for a single crystal of $\alpha 6$ indicated that the maximum was red-shifted compared to the solution data,⁴⁵ whereas for oriented thin films, it was blue-shifted.⁵¹ Other studies on thin films of $\alpha 6$ found the excited singlet state lifetime to be ~ 40 ps and a triplet–triplet (sharp) absorption near 790 nm with a lifetime of 4 ns for the triplet state.⁵² The singlet lifetime is very short compared to that in solution (24-fold), but in general ϕ_F values are also much lower, so some quenching mode exists. The short 4 ns triplet lifetime is at least partially explained by the presence of air.

Thin polycrystalline films of $\alpha 4\text{--}\alpha 6$ showed transient absorptions that were assigned as $T_1 \rightarrow T_n$ absorption.⁵³ Lifetimes of 310 ns ($\alpha 6$), 550 ns ($\alpha 5$), and 1.3 μ s ($\alpha 4$) were reported (presumably in the presence of air). These are 40–50 times shorter than ours in degassed solutions (see Tables 1 and 2). In a crystalline film (at 5–10 Torr) the τ_T of $\alpha 6$ ($\sim 170\ \mu$ s) is very much longer than that found above (4 ns)⁵² and even much longer than in degassed solutions ($\sim 17\ \mu$ s, Table 1). The lifetimes of a film of $\alpha 7$ ($\sim 100\ \mu$ s) is also much longer than that in degassed solution (21 μ s, Table 1).

Summary/Conclusions

1. Based on the k_F^0 of $\alpha 2\text{--}\alpha 7$ in any and all five solvents, the lowest excited singlet state is $(1)^1B_u$ (π,π^*).

2. There is a significant shift ($\sim 1600\text{ cm}^{-1}$) of the absorption maxima of $\alpha 2\text{--}\alpha 7$ upon going from 295 to 77 K, but much smaller shifts occur for the 0–0 band ($200\text{--}400\text{ cm}^{-1}$). We interpret this to be largely due to an increase in the overall planarity of the ground state among the existing conformers (or virtual molecule) at 77 K. That is, the potential energy minima of S_0 and S_1 are more vertically aligned such that the vertical transition is to a lower vibronic level of S_1 (but the actual state energy difference is little changed).

3. Significant changes in atomic charge occur on sulfur and the α -carbons of all αn 's when comparing S_1 to S_0 (and T_1) but not when comparing T_1 to S_0 ($\alpha 2$). These are compatible with geometry changes between S_0 and S_1 but not between S_0 and T_1 (also see items 4–6, below).

4. On the basis of absorption spectral shape, charge density calculations of the ground and first excited states, and existing literature,⁴² we believe the excited singlet state, S_1 , has a quinoidal-like form and therefore is essentially planar while the ground state is twisted for all αn 's.

5. There is almost no shift ($100\text{--}200\text{ cm}^{-1}$) of the fluorescence maxima of $\alpha 2\text{--}\alpha 7$ (in contrast to absorption). We interpret this as the result of a combination of circumstances, including a quinoidal-like planar S_1 state, a twisted ground state, and the presence of (at 295K) or absence of (at 77 K) of solvent reorientation.

6. The small magnitude of ϕ_{IC} (≤ 0.1) is interpreted to be the result of small coupling between modes of the planar (quinoidal) S_1 state and the essentially single-bonded (inter-ring bond) twisted S_0 state.

7. The decrease in k_{ISC} as one proceeds from $\alpha 2$ to $\alpha 7$ (with plateauing at/near $\alpha 5$, is believed to be the result of the decrease in magnitude of matrix elements of the type

$$\langle {}^1\Psi_{CT} | H' | {}^3\Psi_i \rangle$$

which may be caused by a decrease in the overlap of the electron donor–electron acceptor orbitals. In any event, the classical heavy atom effect alone is not able to explain this observation.

8. The increase in ϕ_F with increasing n ($\alpha 2$ – $\alpha 7$) arises primarily because of a decrease in k_{isc} (see item 7 above) and not from an increase in k_F^0 (k_F^0 is essentially constant over all αn 's).

9. "No" phosphorescence has been observed by us or others^{26–28} for $\alpha 2$ – $\alpha 4$, although the ϕ_T is very high (0.70–1.0). This is believed to be the result of a large radiationless rate constant.

10. There is a dramatic decrease in τ_T from $\alpha 2$ to $\alpha 7$ (≥ 100 to 20 μ s). This is interpreted based on the premise that the lifetimes represent essentially the radiationless ones. The change in τ_T would then be expected, since the lifetimes should decrease as the T_1 – S_0 energy gap decreases because of a significant increase in the Franck–Condon factors between T_1 and S_0 upon which the radiationless rate depends.

11. All ϕ_F , ϕ_T , k_{isc} , and τ_T reach a plateau at or near $\alpha 5$. These results, coupled with some absorption and fluorescence data, are interpreted as indicating that $\alpha 5$ acts as the first representative of an " α -polythiophene".

12. Triplet αn 's can transfer energy to 3O_2 to produce 1O_2 with high efficiency where the ϕ_Δ values are essentially the same as ϕ_T for $\alpha 2$, $\alpha 4$, and $\alpha 5$ and only 15% lower than ϕ_T for $\alpha 3$. It appears that the efficiency for $\alpha 6$ and $\alpha 7$ is less, which could be caused by the low energy of the triplets (and possibly also steric factors for the dibutyl-substituted $\alpha 7$).

13. Up to 10 different methods of calculations have been used to explore the most stable geometric forms of $\alpha 2$ – $\alpha 5$ (twisting S–C–C–S angles) and the ΔH between the *all-trans* and *all-cis* forms. These include three levels of *ab initio*. In general MOPAC and MNDO93,PM3 predicted a most stable geometry of *all-cis* that disagreed with all other calculation methods that predicted *all-trans* (the former of which is certainly incorrect). For $\alpha 2$ – $\alpha 5$, the *all-trans* conformer is predicted to be the most stable from among *all* possible conformers (2 for $\alpha 2$, 3 for $\alpha 3$, and 10 for $\alpha 5$). For $\alpha 3$, MOPAC,MM2, DGauss, and *ab initio* STO3G indicate a near planar structure for the *tt* conformer. For $\alpha 5$, *ab initio* STO3G alone indicates a near *t* planar structure for the *tttt* conformer.

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References and Notes

- Becker, R. S.; Seixas de Melo, J.; Maçanita, A. L.; Elisei, F. *Pure Appl. Chem.* **1995**, *67*, 9.
- Chosrovian, H.; Rentsch, S.; Grebner, D.; Dahn, D. U.; Birchner, E. *Synth. Met.* **1993**, *60*, 23.
- Colditz, R.; Grebner, D.; Hebig, M.; Reutsch, S. *Chem. Phys.* **1995**, *201*, 309.
- Oelkrug, D.; Egelhaaf, H.-I.; Wilkinson, F. *J. Fluoresc.*, in press.
- Birnbaum, D.; Fichou, D.; Kohler, B. E. *J. Chem. Phys.* **1992**, *96*, 165.
- Periasamy, N.; Daneli, R.; Ruani, G.; Zamboni, R.; Talani, C. *Phys. Rev. Lett.* **1992**, *68*, 919.
- Birnbaum, D.; Kohler, B. E. *J. Chem. Phys.* **1992**, *96*, 2492.
- Belijonne, D.; Shuai, Z.; Bredas, J. L. *J. Chem. Phys.* **1993**, *98*, 8819.
- Negri, F.; Zgierski, M. Z. *J. Chem. Phys.* **1994**, *100*, 2571.
- Soos, Z. B.; Galvão, D. S. *J. Phys. Chem.* **1994**, *98*, 1029.
- Rubio, M.; Merchán M.; Ortí, E.; Roos, B. Personal communication.
- Van Hecke, G. R.; Horrocks, De W., Jr. *Inorg. Chem.* **1966**, *5*, 1968.]
- Seixas de Melo, J.; Becker, R. S.; Maçanita, A. L. *J. Phys. Chem.* **1994**, *98*, 6054.
- Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, *37*, 814.
- Förster, Th. *Fluoreszenz Organischer Verbindungen*; Vandenhoeck und Ruprecht: Göttingen, Germany, 1951.
- Maçanita, A. L.; Costa, F. P.; Costa, S. M.; Melo, E. C.; Santos, H. *J. Phys. Chem.* **1989**, *93*, 336.
- Stricker, G. In *Effective Implementation of Modulation Functions in Deconvolution and Reconvolution of Analytical Signals*; Bouchy, M., Ed.; University Press: Nancy, France, 1982.
- Elisei, F.; Aloisi, G. G.; Görner, H. *J. Phys. Chem.* **1991**, *95*, 4225.
- Aloisi, G. G.; Elisei, F.; Latterini, L. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2139.
- Dawe, E. A.; Long, D. A.; Land, E. J. *J. Chem. Soc., Faraday Trans. 1*, **1977**, *73*, 1319.
- Charmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.
- Murov, S.; Charmichael, I.; Hug, G. L. *Handbook of Photochemistry*; M. Dekker Inc.: New York, 1993.
- Medinger, T.; Wilkinson, F. *Trans. Faraday Soc.* **1965**, *61*, 620.
- Horrocks, A. R.; Wilkinson, F. *Proc. R. Soc., Ser. A* **1968**, *306*, 257.
- Hurley, J. K.; Sinai, N.; Linschitz, H. *Photochem. Photobiol.* **1983**, *38*, 9.
- Wilkinson, F.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1993**, *22*, 113.
- Reyftman, J. P.; Kagan, J.; Santus, R.; Morliere, P. *Photochem. Photobiol.* **1985**, *41*, 1.
- Janssen, R. A.; Smilowitz, L.; Sariciftci, N. S.; Moses, D. *J. Chem. Phys.* **1994**, *101*, 1787.
- Evans, C.; Weir, D.; Scaiano, J. C.; MacEachern, A.; Arnason, J. T.; Morand, P.; Hallebone, B.; Leitch, L. C.; Philogene, J. R. *Photochem. Photobiol.* **1986**, *44*, 441.
- Xu, B.; Holdcroft, S. *J. Am. Chem. Soc.* **1993**, *115*, 8447.
- Scaiano, J. C.; Redmond, R. W.; Mehta, B.; Arnason, J. T. *Photochem. Photobiol.* **1990**, *52*, 655.
- Van Veen, E. H. *Chem. Phys. Lett.* **1976**, *41*, 535.
- Flicker, W. M.; Mosher, O. R.; Kuppermann, A. *Chem. Phys. Lett.* **1976**, *38*, 489.
- Garcia, P.; Pernaut, P.; Hopiat, P.; Wintgens, V.; Valat, P.; Garnier, F.; Delabouglise, D. *J. Phys. Chem.* **1993**, *97*, 513.
- Rossi, R.; Carpita, A.; Ciofalo, M.; Houben, J. L. *Gazz. Chim. Ital.* **1990**, *120*, 793.
- Rossi, R.; Ciofalo, M.; Carpita, A.; Ponterini, G. *J. Photochem. Photobiol., A* **1993**, *70*, 59.
- Charra, C.; Fichou, D.; Nunzi, J. M.; Pfeffer, N. *Chem. Phys. Lett.* **1992**, *192*, 566.
- Buma, W. J.; Kohler, B. E.; Shaler, T. A. *J. Phys. Chem.* **1994**, *98*, 4990.
- Visser, G. J.; Heeres, G. J.; Wolters, J.; Vos, A. *Acta Crystallogr. B* **1968**, *24*, 467.
- Samdal, S.; Samuelson, E. J.; Volden, H. *Synth. Met.* **1993**, *59*, 259.
- Bucci, P.; Longeri, M.; Veracini, C. A.; Lunazzi, L. *J. Am. Chem. Soc.* **1974**, *96*, 1305.
- Chadwick, J. E.; Kohler, B. E. *J. Phys. Chem.* **1994**, *98*, 3631.
- Takayanagi, M.; Gejo, T.; Hanazaki, F. *J. Phys. Chem.* **1994**, *98*, 12893. Hanazaki, F. Personal communication.
- Van Bolhuis, F.; Wynberg, H.; Havinga, E. E.; Meijer, E. W.; Staring, E. G. I. *Synth. Met.* **1989**, *30*, 381.
- De Witt, L.; Blanchard, G. J.; Le Goff, E.; Benz, M. E.; Liao, J. H.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 12158. Blanchard, G. J. Personal communication.
- Taliani, C.; Danieli, R.; Lazzaroni, R.; Periasamy, N.; Ruani, G.; Zamboni, R. *Synth. Met.* **1993**, *55–57*, 4714.
- Andres, L. S.; Merchan, M.; Fulscher, M.; Roos, B. O. *Chem. Phys. Lett.* **1993**, *211*, 125.
- Becker, R. S. *Theory and Interpretation of Fluorescence and Phosphorescence*; Wiley-Interscience: New York, 1969.
- Foote, C. S. *Light Activated Pesticides*; Heitz, J. R., Downum, K. R., Eds.; ACS Symposium Series 339; American Chemical Society: Washington, DC, 1987; p 36.
- Ciofalo, M.; Ponterini, G. *J. Photochem. Photobiol., A* **1994**, *83*, 1.
- D'Auria, M.; D'Onofrio, F. *Gazz. Chim. Ital.* **1988**, *118*, 633.
- Egelhaaf, H.-I.; Oelkrug, D. *SPIE*, in press.
- Nunzi, J. M.; Pfeffer, N.; Charra, F.; Fichou, D. *Chem. Phys. Lett.*, in press.
- Cheng, X.; Ichimura, K.; Fichou, D.; Kobayashi, T. *Chem. Phys. Lett.* **1991**, *185*, 286.