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

Ralph S. Becker,*,†,‡ J. Seixas de Melo,†,§ António L. Maçanita,†,∥ and Fausto Elisei⊥

Instituto de Tecnologia Química e Biológica, Rua da Quinta Grande n°6, 2780 Oeiras, Portugal, Department of Chemistry, University of Arkansas, Fayetteville, AR, Departamento de Química, Universidade de Coimbra, 3000 Coimbra, Portugal, Departamento de Química do IST, Lisboa, Portugal, and Dipartimento di Chimica, Universitá di Perugia, Perugia, Italy

A large basis set of α-oligothiophenes with two to seven rings (α2−α7), also including thiophene, α1, 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 α2, α3 and α5, as well as calculations of transitions energies of the α-oligothiophenes. We have shown that the (l) ^{1}Bu state is the lowest singlet state for all α2−α7 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 α2−α7, ϕ_{IC} is small, k^0_F is approximately constant while k_{ISC} decreases significantly from α2 to α7. The decrease is 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 $^3O_2$ to produce $^1O_2$ is highly efficient for α2−α5. Based on all data, the first α*n* representative of α-polythiophene is α5.

Introduction

The α-oligothiophenes (designated α1, α2, α3, ... where *n* = 1, 2, 3, ..., respectively)
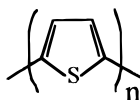
are currently of keen interest because (1) they are interesting analogues of polyenes, (2) they are good singlet oxygen sensitizers and biophotosensitizers, and (3) particularly those with higher *n* are important for their use in nonlinear optics applications, charge storage, and molecular electronics.

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, α2−α6 have been studied[2,3] relative to ϕ_F and ϕ_F for α2−α6 and ϕ_Δ for α3−α6.[4] Other scattered data exist for some α*n*'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, expecially regarding torsional (inter-ring) barriers, ΔH of trans and cis conformers, and

energy of states, but again, these have been limited essentially to α2−α3, particularly α2. 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 ^{1}Bu and ^{1}Ag ones within C_{2h} symmetry, and this notation, or ^{1}B and ^{1}A, 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 α2, in solution the (1)^{1}Bu-like state is the lowest where the (2)^{1}Ag-like state has been located above it by two-photon spectroscopy,[5] and this (2)^{1}Ag-like state also has been located above the (1)^{1}Bu-like state in a *crystalline film* of α6[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 ^{1}Ag and ^{1}Bu states energies of some polythiophene oligomers, and the difference in state energies expected for α6 in the crystalline state vs alkane solution, the (2)^{1}Ag state was assigned *below* the (1)^{1}Bu state for α6 *and* all other polythiophene oligomers with more than six rings (α6, α7, ...).[7] We will show that this is not the case.

Other calculations[8] predict the (2)^{1}Ag state already below the (1)^{1}Bu state at α2−α4, with crossing occurring between α4 and α5. However, by restriction of the CI (which seems to have no real rational justification as was also done before),[7] the (1)^{1}Bu state was now predicted to be lowest for all α*n*'s through α6, α7. Still other calculations[9−11] on α2 and some higher α*n*'s in

† Instituto de Tecnologia Química e Biológica.
‡ University of Arkansas.
§ Universidade de Coimbra.
∥ Departamento de Química do IST.
⊥ Universitá di Perugia.

some cases give varying results regarding the relative ordering of the states for α2 and place the $(2)^1Ag$ state lowest for α3 and α4.[9]

We will show that despite any theoretical and/or comparative experimental data to the contrary, *the $(1)^1Bu$ state is the lowest excited singlet state in all* α-oligothiophenes from α2 *to and including* α7. We will also determine the following in *five* solvents for α2−α7: (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^0_F, k_{ISC} (intersystem crossing), k_{IC} (internal conversion), and k_{NR} (nonradiative), (4) absorption (and ϵ values) and fluorescence spectra (and phosphorescence for α1) at 298 and 77 K, (5) singlet oxygen quantum (ϕ_Δ) yields of α2−α5 and α7, (6) τ_F and ϕ_F as a function of temperature for α3 and α7, (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 α2, α3, α5, (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 α1−α5, 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 α1−α7.

Experimental Section

Thiophene was purchased from Riedel de Häen 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 ($Ni[C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Cl_2$) synthesized as elsewhere reported (and dried with $SOCl_2$).[12] The final product, α5, was recrystallized from dichloromethane.

All the solvents were of spectroscopic or equivalent grade, except for methylcyclohexane (which was purified over a mixture of H_2SO_4/HNO_3, then distilled, and finally chromatographed on an Al_2O_3/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 cyclohexane[13]). 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−Berg[14] equation

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

with

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

using the integrated first absorption band and the fluorescence band. For thiophene, since there is no fluorescence, the use of the equation of Förster[15] was needed:

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

Fluorescence decays were obtained using a time-correlated single-photon-timing technique with a home-built apparatus as previously described[16] 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 α2−α5 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 equation[20]

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

was used where the acceptor A = αn 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 M^{-1} 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

α-Oligothiophenes

J. Phys. Chem., Vol. 100, No. 48, 1996 **18685**

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 (μs)
α2	0.026	0.046	0.55	21[e]	0.99	0.96	0.11[c]	22	104
α3	0.07	0.16	0.44	5.8[e]	0.95	0.81[d]	0.03[c]	5.9	88
α4	0.18	0.44	0.41	1.9	0.73	0.72	0.20	1.7	38
α5	0.34	0.82	0.41	0.81	0.59	0.56	0.098	0.72	24
α6	0.44	0.97	0.45	0.58		~0.36[f]			≥17[g]
α7	0.36	0.82	0.43	0.79	≤0.6	h	0.049	0.73	21

[a] Solutions degassed with nitrogen or argon by bubbling. k's are 10^9 s^{-1}, and α7 is the di-*n*-butyl-substituted α7. [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 $^1O_2$. In acetonitrile a value of 0.74 was obtained by measuring $^1O_2$ 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 μs in dichloromethane and also α4 = 35 μs. [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 α*n* was obtained by the laser energy effect on the change of absorbance of an α*n* 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 α*n*'s was then calculated from the $\epsilon_T\phi_T/\epsilon_T$ ratio.

For α7, 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 technique[21] 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 α7 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 α*n*'s were determined by measuring the emission of $^1O_2$ 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 α*n*'s was obtained from a ratio of the slopes and the known ϕ_Δ of phenalenone.

Results

Table 1 presents comprehensive photophysical data of α1−α7 (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 α6 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_F^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 α2−α7 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 α2 and α3. 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 α4−α7 (Figure 3). If α2 and α3 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 α2 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 α2, and even α3, are not yet legitimate representatives of a polythiophene and that such a representation seemingly begins with α4. Actually, additional consideration of all the photophysical data indicates that *the first true representative of a polythiophene is α5.*

On the basis of the plot of $1/n$ vs absorption maxima of α4−α7 (corrected for the presence of two *n*-butyl groups), we can predict the expected maxima for α8−α13 and α∞: α8, 456 nm; α9, 466 nm; α10, 473 nm; α11, 480 nm; α12, 485 nm; α13, 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 α1−α7. If you plot ϵ values for α3−α5 vs $1/n$ and n, both plots are very linear. If you then use these to predict the extinction coefficients of α6 and α7 by extrapolation, the results are excellent from the $1/n$ plot (ϵ of α6 predicted to be 47 400 compared to the experimental 47 910; ϵ of α7 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 α7 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 α*n*. 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] l

Methylcyclohexane

cpd	ϕ_F	τ_F (ns)	k_F^0	k_{NR}
α2	0.014	≤0.1	≥0.14	≥9.9
α3	0.057	0.19	0.30	5.0
α4	0.18	0.49	0.37	1.7
α5	0.33	0.83	0.39	0.81
α7	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 (μs)
α2	0.014	0.04	0.046[b]	0.35	~21	1.0	0.10	~21	100
α3	0.054	0.12	0.19	0.28	5.0	0.96	0.03[c]	5.1	91
α4	0.18	0.18	0.52	0.34	1.6	0.70	0.23	1.3	43
α5	0.32	0.34	0.88	0.36	0.77				20
α7	0.29	0.28	0.82	0.35	0.87	≤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 (μs)
α2	0.013	≤0.1	≥0.133	≥10.1	0.93	0.98	≥0.6	≥9.5	124
α3	0.056	0.18	0.311	5.1	0.90	0.74	0.24	5.0	62
α4	0.16	0.48	0.33	1.8	0.71	0.72	0.27	1.5	40
α5	0.33	0.90	0.37	0.74	0.63	0.50	0.011	0.70	20
α7	0.30	0.90	0.33	0.78	≤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 (μs)
α2	0.017	0.046[b]	0.37	21	0.94	0.93	20	146
α3	0.066	0.21	0.31	4.5	0.93	0.019	4.4	108
α4	0.18	0.49	0.36	1.7	0.67	0.31	1.4	48
α5	0.36	0.82	0.44	0.78	0.6[d]	0.05	0.73	29
α6[e]	0.41	1.0	0.41	0.55				
α7	0.34	0.85	0.40	0.78	≤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 α7 is the di-*n*-butyl-substituted α7. The lifetime of thiophene (α1) is ~1 μs (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] α6 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	ϵ/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]
α1	231	8340[c]	0.33[d]			305
			0.023[d]			
α2	303	12440		0.22[e]	362	385
				0.38[e]		
α3	354	22080[f]	0.30	0.31	407, *426*	460
α4	392	31560[g]	0.34	0.36	437, *478*	*560*, 700
α5	417	42670	0.38	0.44	*482*, 514	630
α6	436	47910		0.41	*502*, 537	685
α7[h]	441	50500	0.39	0.40	*522*, 560	720

[a] T–T maxima in other solvents vary by only 10 nm at the maximum. The α1 datum is with acetonitrile. [b] The italicized wavelength is the band maximum. The other one is another distinct band (see Figure 4). The α1 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] ϵ(benzene) = 22 540 M^{-1} cm^{-1}, ϵ(acetonitrile) = 24 215 M^{-1} cm^{-1} and ϵ(ethanol) = 23 590 M^{-1} cm^{-1} at their maxima of 354, 352, and 355 nm, respectively. [g] ϵ(acetonitrile) is 34 700 at its maximum. [h] For the di-*n*-butyl-substituted α7.

as well—for example, ϕ_F and ϕ_T of α3−α5 vs n if used to predict α2, α6, and α7.

The room temperature solution fluorescence of α2−α7 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 α2, less for α3, and continuing to be less as the number of rings increases to α4 and on to α7. 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 α4 on) and between room- and low-temperature (77 K) bands for a given αn—for example, see α4 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
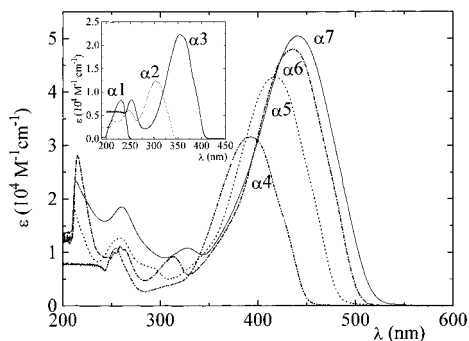
α-Oligothiophenes

J. Phys. Chem., Vol. 100, No. 48, 1996 **18687**

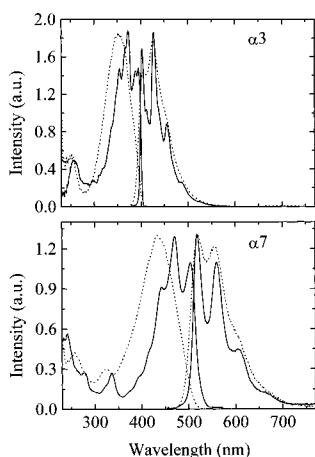**Figure 1.** Room temperature absorption spectra of α1−α7 in dioxane.

Figure 2. Absorption and fluorescence at room temperature (···) and fluorescence and fluorescence excitation spectra (−) at 77 K for α3 and α7 in ethanol.
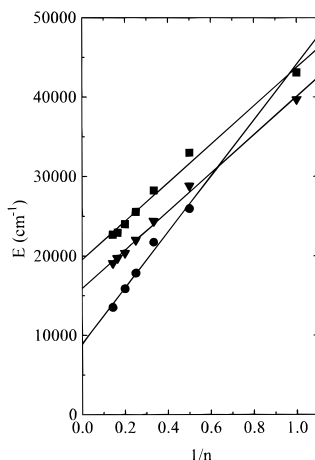

Figure 3. $E_{T_1-T_n}$(max) ●, $E_{S_0-S_1}$(max) ■, and $E_{S_0-S_1}$(0−0) ▼ vs 1/n.

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

Figure 5. Room- (- - -) and low-temperature (77 K) (−) fluorescence spectra of α2−α7 in ethanol, except for α6 where the solvent is 2-methyltetrahydrofuran.

including an aliphatic hydrocarbon, ethanol, and one containing 10% ethyl iodide, and others could not see phosphoresecence for α3 and α4.[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 α6, α7, and longer ones.[27] However, it has been reported[29] that α3 (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 α3 seems very strange particularly from the point of view that it is at the same wavelength as a multithiophene component polymer—surely the
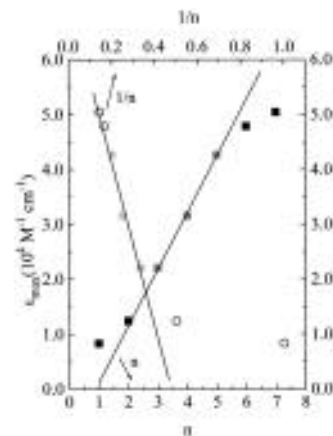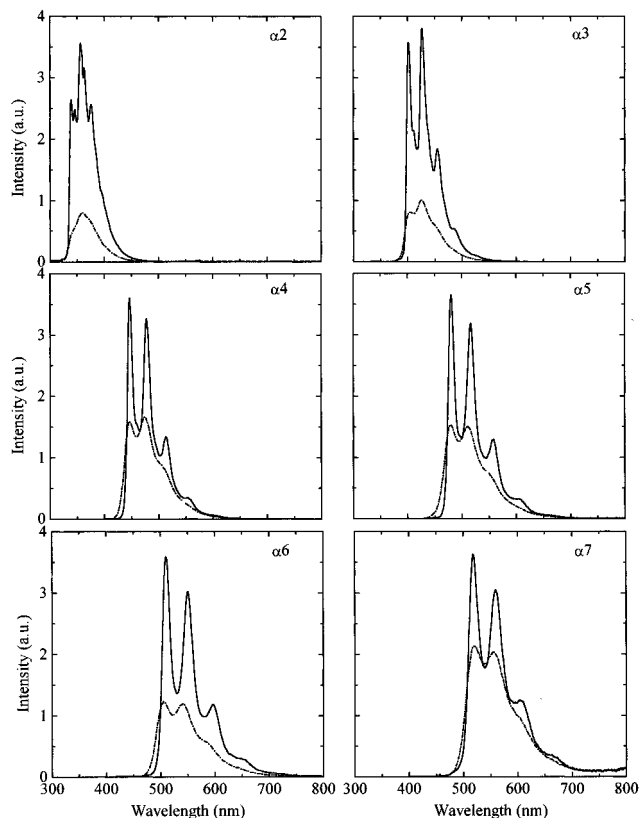
triplet energies could not be the same. Furthermore, there is some published evidence that the lowest triplet of α3 is near 720 nm (0−0)[30] and we have evidence that it may be at still lower in energy at ∼788 nm (0−0) based on photoacoustical experiments. Presumably, α3 could possibly have a maximum 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*, α*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 cm^{-1}. This would give a singlet−triplet (S_1-T_1) separation of close to 12 300 cm^{-1}. For α3 using 720 nm[30] (∼13 900 cm^{-1}) as the origin of T_1, there is a S_1-T_1 separation of 10 800 cm^{-1},
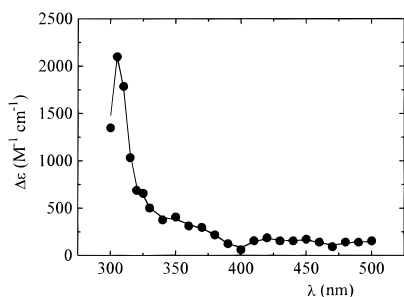
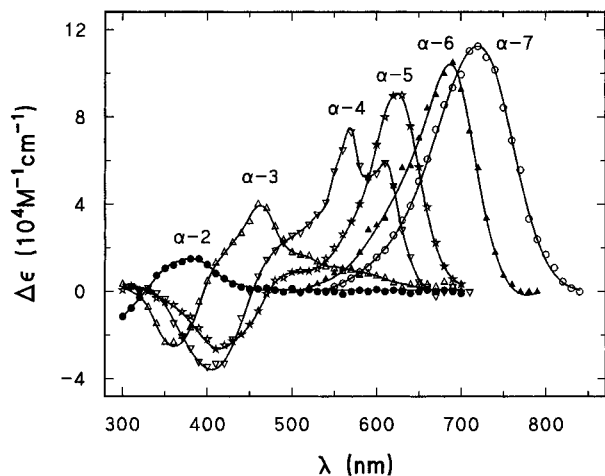**Figure 6.** Triplet−triplet absorption spectrum of α1 at room temperature in benzene.

Figure 7. Triplet−triplet absorption spectra of α2−α7 at room temperature in benzene.

Figure 8. ϕ_F (dark symbols) and ϕ_T (open symbols) vs n for α2−α7 in four solvents.

Figure 9. k_F (▽), k_{ISC} (□), and k_{IC} (○) vs $1/n$ for α2−α7 in benzene.

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

Triplet−Triplet Absorption. Our triplet−triplet absorption data are shown in Figure 6 for α1 and in Figure 7 for α2−α7. 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 α3 and α4 clearly have band shoulders (bands for α4) at wavelengths both shorter and longer than that of the main maximum. Also, the *onset* of the 460 nm band maximum of α3 is at an unusually long wavelength, essentially equal to that of α5 (where the maximum is at 630 nm). It appears that for α3 there must be more than one T → T$_n$ transition in the broad absorption region of ~700−460 nm, and probably for α4 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 α9 and α11, 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 α5 to α7 (also see Figure 8). The τ_F values are also quite *solvent in*dependent, *but* clearly, the τ_F increases as the *number of rings increase,* becoming essentially constant from α5 to α7. 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
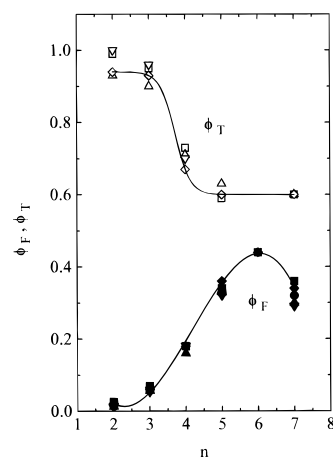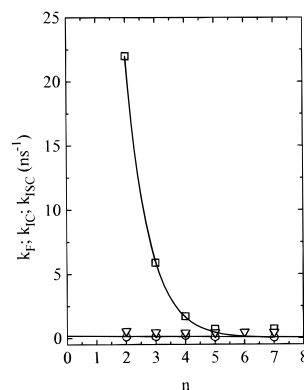
number of rings except perhaps for α2. Also, for α3, k_F^0 (in Table 2) seems somewhat different (lower) than for α4−α7, except for perhaps benzene and acetonitrile. The k_F^0 values in benzene generally appear larger than in the other solvents (Tables 1 and 2). Despite this, it is generally valid that 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 α5 to α7*. 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 α5 to α7. The trend in k_{IC} is much more difficult to discern, but from α2 to α5−α7, there is a decrease in k_{IC} with the data for acetonitrile, while the other solvents produce a scatter on the way from α2 to α5−α7. 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 α2 and α3. Moreover, the error in ϕ_T is ±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 ($\phi_T = \pm15\%$, only ~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 α3−α6[2−4] are within a few percent to 10% of ours.[2] Other data[33] for α3 and α6 are ~30% shorter than ours (theirs in dichloromethane), and for others[34] the α3 is some 30% longer than ours while α4 is close to ours. The

α-Oligothiophenes

J. Phys. Chem., Vol. 100, No. 48, 1996 **18689**

α5 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 α2 are missing, and there is no data on α7. Our ϕ_F and τ_F data are given in Tables 1 and 2. The ϕ_F values of α3−α6 have been determined by Chosrovian et al.[2] and Colditz et al.[3] (α2−α6), 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 α3 and α4, which are certainly not correct (see later discussion). Others[3,4] have measured ϕ_F of α2−α6, and except for α2, these were also within 10% of our values. Moreover, ϕ_F data[33] are available on α2−α4 and α6 and all agree with ours except for α6 (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 α3 is similar to ours and others[26,30,34] but α4 is noticeably lower[34] than ours *and* that of others[2−4,26] (and τ_F's are reasonably similar to ours).

Triplet yields for α3 of 0.2,[26] ≥0.9,[30] and 0.95[35] exist vs our values of 0.90−0.96 (Tables 1 and 2). Based on all available data, a ϕ_T for α3 of 0.2 cannot be correct. For α4, 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_Δ for α4 (0.69),[4] we believe the value of ∼0.2 for ϕ_T of α4 is not correct.

In Tables 1 and 2 our triplet state lifetimes are shown. Some other data also exist: for α3, a value of 30 μs 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 μs (dioxane) (Table 2). For α3 and α4, others[26] report a value of 57 (α3) and 45 μs (α4) in ethanol vs our values of 91 (α3) and 43 μs (α4) in the same solvent. The lifetime of α5 in dioxane in nitrogen has been given[4] to be 7.7 μs (0.24 μs 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 α3 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 α6, α7, α9, and α11 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 μs for α6, 350−380 μs for α7, 300 μs for α9, and 250 μs for α11. The trend to shorter lifetimes with increasing number of rings is the same as what we find for α2−α7 (Tables 1 and 2). An interesting case is that of α2 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 μs (∼225-fold) at room temperature in fluid solution. This also seems to be very short for a triplet of an isolated, cold molecule (of α2) (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 α2 (Table 4), as well as α3−α5 (Table 5). In Table 4, for α2 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 α3 and α5, since their was very little or no significant data on these latter α-oligothiophenes. It can be seen in Table 4 that for α2, the two experimental ΔH values are quite different from one

TABLE 4: Relative Stabilities of Cis and Trans Conformers of α2 by Various Theoretical Approximations[a]

method	result (kcal/mol)	ref/footnote
exptl	t < c, 1.16 ± 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
ab initio STO 3G	t < c, 1.3	c
ab initio STO 3G	t < c, 1.20	d
ab initio 3-21G*	t < c, 0.64	e
ab initio RHF/DPZ	t < c, 0.8	f
plus electron correlation	t < c, 0.4	f
ab initio 3-21G	t < c, 1.9	f
ab initio 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)
α2	MOPAC	c < t	0.46
	MM2	t < c	1.04
	AMPAC/AM1	t < c	0.16
	exptl	t < c	1.16 ± 0.13;[c] 0.2
α3	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
	ab initio STO 3G	tt < cc	2.41
	ab initio 6−311 G	tt < cc	2.22
	ab initio 6−31 G(d)	tt < cc	1.47
α4	AMPAC/AM1	ttt < ccc	2.73
α5	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
	ab initio 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 α2, 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 experiments[42] 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 $\sim 21°$ 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 proposed[41] 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 beween 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 configuration[44] 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 ^{1}H 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, reinvestigation[44] 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)	
	AMPAC/AM1	t	345	302 (303)
		c	325	
tri-	MOPAC	all-t	398 (1.07)	350 (354)
		all-c	397 (1.09)	
	AMPAC/AM1	all-t	373	350 (354)
		all-c	354	
tetra-	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 date of α,ω-dithienylpolyenes, calculations, and some extrapolated data, the $(2)^1$Ag state was assigned below the $(1)^1$Bu for oligothiophenes of $n = 6$ and greater.[7] For $\alpha 2$, two-photon spectroscopy[5] has located the ^{1}Ag above the ^{1}Bu. Theoretically, it has been predicted[8] that the ^{1}Ag state would be below the ^{1}Bu 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 ^{1}Bu state being lowest from $\alpha 2$ to$\alpha 7$ (others predicted ^{1}Ag to be lowest for $\alpha 6$ and longer chain). Also, more recent calculations[9] for $\alpha 1-\alpha 4$ predicted that the ^{1}Ag state (0 level) would be below the ^{1}Bu state (0 level). They believed the ^{1}Ag state observed was the $(3)^1$Ag 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

	exptl[b]		theoretical	
	λ	ϵ	λ	
cpd	(nm)	(M^{-1} cm^{-3})	(nm)	f
thiophene	232	8340	227	0.26 (PPP)[d]
			211	0.27
			170, 169	1.5
di-	303 (302)[c]	12440	311	0.83 (PPP)[d]
	247	6200	257	0.39
	205		204	0.19
tri-	354 (350)[c]	22100	342	1.40 (PPP)[d]
			276	0.02
	252	8600	250, 245	0.24
	221		234	0.15
	205		222	0.22
quater-	391 (386)[c]	31560		
	308 (sh)	4300		
	252	10700		
	205			
quinque-	417 (410)[c]	42650	405	1.56 (ZINDO)
	~340 (sh)			
	290	7300	286	0.12
	256	12700	256, 260	0.06
	207–214		236	0.10
			196	1.71
sexi-	436	47910		
	314			
	259			
septa-	441 (433)[c]	50460		
	361 (sh)			
	325	10900		
	282, 298 (sh)			
	256	18200		
	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 (α1) place the (2)$^1A_1$ state below the $^1B_2$.[46] More recently, *ab initio* calculations[11] (multi-CI) for α2 give a ^1Bu state below the ^1Ag state and, in fact, predicts two ^1Bu states below the lowest ^1Ag. Very recent calculations[3] 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, α2–α7, 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 α4–α7. 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 (others[3] 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 earlier[1], k_F^0 values calculated based on the Strickler–Berg (SB) equation over the first absorption band for α2–α5 and α7 *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 α2–α7 is of allowed character and is (1)^1Bu and not (2)^1Ag. This was noted earlier[1] for α2–α5 and α7 in benzene, but we can now *include* α6 as well and, moreover, safely conclude that this *order is independent of the solvent for* α2–α7.

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. Others[3] 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 α2–α7 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 α2 and α3, ~300 cm^{-1} for α4, and ~400 cm^{-1} for α5 and α7. 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 S_0 and S_1. 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 α5–α7 and perhaps for α4.

There are clear indications that α2 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 α2 undergo the most dramatic increase in vibrational resolution as a function of temperature compared with all other αn's (see Figure 5 and ref l). However, the red shift of the absorption maxima at low temperature is essentially the same as for α3–α5 (~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 α2 the ground state becomes more planar, as it is for all αn's, and a greater population of a more singular conformer exists for α2 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
α1			1.84		2.52	
	S5	+0.02		−0.22		
	C1, C2 (α-C)	−0.14		+0.03		
	C3, C4 (β-C)	−0.03		−0.01		
α2			0.007		0.009	
	S5, S13	+0.004 (+0.58)		−0.15 (+0.38)		(+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		
α3			1.84		1.77	
	S5, S20	+0.004		−0.14		
	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		
α5			2.11		2.16	
	S26, S34	+0.02		−0.12		
	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 α2, 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 (α2) in a supersonic jet [42] where there is a clear indication that in S_1 the α2 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 multiminima *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 α1−α3 and α5 and atomic charges in T_1 for α2, 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
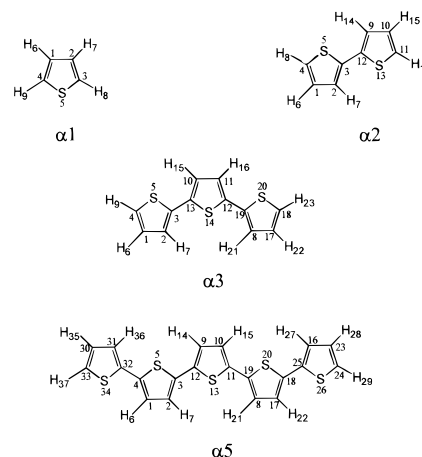

Figure 10. Numbering of atoms of various oligothiophenes for reference to atomic charges given in Table 8.

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 (∼0.07e). One obvious important implication of this is that the lowest energy transition (longest wavelength one) now clearly established to be

$$^1A \rightarrow (1)^1Bu$$

α-Oligothiophenes

J. Phys. Chem., Vol. 100, No. 48, 1996 **18693**
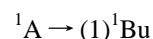
has some charge transfer character. Secondly, with such large changes in atomic charges there must be an accompanying change in the geometry of the excited singlet state (as previously noted, based simply on the Franck−Condon forbidden shape of the first transition). A quinoidal-like structure is compatible 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 αC−αC torsional coordinate found in supersonic jet experiments[42] where for α2, the inter-ring αC−αC 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 α2 and α3 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 (α4−α7)*. Others[35] also found a very similar change for α3 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 α3 and found little or no change over the range 290−140 K. Others[35] 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 ^1B_u state is the lowest for all αn's from α2 to α7, and moreover, this order is solvent independent.

In general, the k_F^0 is quite constant (∼20%) as a function of the number of rings (α2−α7) 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 α2 and α5 and a leveling of k_{ISC} occurs from α5 to α7. 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 (±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 α2 to α5 and than a leveling from α5 to α7 (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 ($\phi_{IC} \approx 0.1-0.0$).

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 effect[47] of the sulfur. Nonetheless, ϕ_T and k_{ISC} show a progressive *decrease* from α2 to α5 and then a leveling off (while ϕ_F shows a progressive *increase* from α2 to α5 and then a leveling off from α2 to α7). We believe that most of the spin−orbit coupling is not due to the classical heavy atom effect[47] but that this coupling is mediated by charge transfer (CT) mixing involving matrix elements of the type

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

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 $^1\psi_{CT}$ 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 α2 to α5, which becomes essentially constant from α5 to α7.

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 α2 to α7 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 (α2−α7) 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 α2. Some two-photon photoionization experiments[37] 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 α2, 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 α2 in the supersonic jet experiment above[37] 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 α2) as the state to be associated with the 550 ns lifetime.

Recall that thiophene itself, α1, 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 (α2−α4, α6). 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 μs) 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 ($\sim$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 $\alpha 7$ (9–12 000 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 0.36[4] for ϕ_Δ. There are several literature values for the ϕ_Δ of $\alpha 3$: 0.15,[26] $\sim$0.8,[1,4] $\sim$0.8,[48] 0.73[30] (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 used[49] compared with our values of 0.81 in benzene and 0.74 in acetonitrile. We believe the 0.15[26] 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 $\pm$ 0.05.

The ϕ_Δ values of other αn's have been given to be[4] $\sim$0.7 for $\alpha 4$, $\sim$0.5 for $\alpha 5$, and $\sim$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 0.24[26] is quite probably incorrect for $\alpha 4$ based on our value of ϕ_T of $\sim$0.7. Furthermore, we and others[4] find a value of $\sim$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, $\sim$0.05, compared to what we obtain for bithiophene itself, $\sim$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, homogeniety, 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 solutions[4] showed that the ϕ_F of ultrathin and thin films were considerably less in general than those in solutions (10–10^3 times) and that the absorption maximum was strongly blue-shifted[51] (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 inhomogeniety in the surroundings of the oligomers. The *lowest excited state* was assigned as (2)^{1}Ag for all oligothiophenes including $\alpha 2$–$\alpha 8$[3]. However, although this assignment for all was repeated again,[51] there was some question about how unambiguous it was. Others[45] have assigned the lowest excited state for *films* $\alpha 6$ as (1)^{1}Bu, which was noted to be some 900 cm^{-1} below the (2)^{1}Ag (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 $\alpha 2$–$\alpha 7$ as (1)^{1}Bu.

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 $\sim$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 $\alpha 4$–$\alpha 6$ 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 μs ($\alpha 4$) 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$170 μs) is very much longer than that found above (4 ns)[52] and even much longer than in degassed solutions ($\sim$17 μs, Table 1). The lifetimes of a film of $\alpha 7$ ($\sim$100 μs) is also much longer than that in degassed solution (21 μs, Table 1).

Summary/Conclusions

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

2. There is a significant shift ($\sim$1600 cm^{-1}) of the absorption maxima of $\alpha 2$–$\alpha 7$ upon going from 295 to 77 K, but much smaller shifts occur for the 0–0 band (200–400 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 (100–200 cm^{-1}) of the fluorescence maxima of $\alpha 2$–$\alpha 7$ (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} ($\leq$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.

α-Oligothiophenes

J. Phys. Chem., Vol. 100, No. 48, 1996 **18695**

8. *The increase in ϕ_F with increasing n* (α2−α7) 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 abserved by us or others[26−28] for α2−α4, 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 α2 to α7 (≥ 100 to 20 μs). 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 signficant increase in the Franck−Condon factors between T_1 and S_0 upon which the radiationless rate depends.

11. All ϕ_F, ϕ_F, k_{isc}, and τ_T reach a plateau at or near α5. These results, coupled with some absorption and fluorescence data, are interpreted as indicating that α5 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 α2, α4, and α5 and only 15% lower than ϕ_T for α3. It appears that the efficiency for α6 and α7 is less, which could be caused by the low energy of the triplets (and possibly also steric factors for the dibutyl-substituted α7).

13. Up to 10 different methods of calculations have been used to explore the most stable geometric forms of α2−α5 (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 α2−α5, the *all*-trans conformer is predicted to be the most stable from among *all* possible conformers (2 for α2, 3 for α3, and 10 for α5). For α3, MOPAC,MM2, DGauss, and *ab initio* STO3G indicate a near planar structure for the tt conformer. For α5*, ab initio* STO3G alone indicates a near t planar structure for the tttt conformer.

References and Notes

(1) Becker, R. S.; Seixas de Melo, J.; Maçanita, A. L.; Elisei, F. *Pure Appl. Chem.* **1995**, *67*, 9.

(2) Chosrovian, H.; Rentsch, S.; Grebner, D.; Dahn, D. U.; Birchner, E. *Synth. Met.* **1993**, *60*, 23.

(3) Colditz, R.; Grebner, D.; Hebig, M.; Reutsch, S. *Chem. Phys.* **1995**, *201*, 309.

(4) Oelkrug, D.; Egelhaaf, H.-I.; Wilkinson, F. *J. Fluoresc.,* in press.

(5) Birnbaum, D.; Fichou, D.; Kohler, B. E. *J. Chem. Phys.* **1992**, *96*, 165.

(6) Periasamy, N.; Daneli, R.; Ruani, G.; Zamboni, R.; Talani, C. *Phys. Rev. Lett.* **1992**, *68*, 919.

(7) Birnbaum, D.; Kohler, B. E. *J. Chem. Phys.* **1992**, *96*, 2492.

(8) Belijonne, D.; Shuai, Z.; Bredas, J. L. *J. Chem. Phys.* **1993**, *98*, 8819.

(9) Negri, F.; Zgierski, M. Z. *J. Chem. Phys.* **1994**, *100*, 2571.

(10) Soos, Z. B.; Galvão, D. S. *J. Phys. Chem.* **1994**, *98*, 1029.

(11) Rubio, M.; Merchán M.; Orti, E.; Roos, B. Personal communication.

(12) Van Hecke, G. R., Horrocks, De W., Jr. *Inorg. Chem.* **1966**, *5*, 1968.]

(13) Seixas de Melo, J.; Becker, R. S.; Maçanita, A. L. *J. Phys. Chem.* **1994**, *98*, 6054.

(14) Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, *37*, 814.

(15) Förster, Th. *Fluoreszenz Organischer Verbindungen*; Vandenhoeck und Ruprecht: Göttingen, Germany, 1951.

(16) Maçanita, A. L.; Costa, F. P.; Costa, S. M.; Melo, E. C.; Santos, H. *J. Phys. Chem.* **1989**, *93*, 336.

(17) Stricker, G. In *Effective Implementation of Modulation Functions in Deconvolution and Reconvolution of Analytical Signals*; Bouchy, M., Ed.; University Press: Nancy, France, 1982.

(18) Elisei, F.; Aloisi, G. G.; Görner, H. *J. Phys. Chem.* **1991**, *95*, 4225.

(19) Aloisi, G. G.; Elisei, F.; Latterini, L. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2139.

(20) Dawe, E. A.; Long, D. A.; Land, E. J. *J. Chem. Soc., Faraday Trans. 1*, **1977**, *73*, 1319.

(21) Charmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.

(22) Murov, S.; Charmichael, I.; Hug, G. L. *Handbook of Photochemistry*; M. Dekker Inc.: New York, 1993.

(23) Medinger, T.; Wilkinson, F. *Trans. Faraday Soc.* **1965**, *61*, 620. Horrocks, A. R.; Wilkinson, F. *Proc. R. Soc., Ser. A* **1968**, *306*, 257.

(24) Hurley, J. K.; Sinai, N.; Linschitz, H. *Photochem. Photobiol.* **1983**, *38*, 9.

(25) Wilkinson, F.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1993**, *22*, 113.

(26) Reyftman, J. P.; Kagan, J.; Santus, R.; Morliere, P. *Photochem. Photobiol.* **1985**, *41*, 1.

(27) Janssen, R. A.; Smilowitz, L.; Sariciftci, N. S.; Moses, D. *J. Chem. Phys.* **1994**, *101*, 1787.

(28) 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.

(29) Xu, B.; Holdcroft, S. *J. Am. Chem. Soc.* **1993**, *115*, 8447.

(30) Scaiano, J. C.; Redmond, R. W.; Mehta, B.; Arnason, J. T. *Photochem. Photobiol.* **1990**, *52*, 655.

(31) Van Veen, E. H. *Chem. Phys. Lett.* **1976**, *41*, 535.

(32) Flicker, W. M.; Mosher, O. R.; Kuppermann, A. *Chem. Phys. Lett.* **1976**, *38*, 489.

(33) Garcia, P.; Pernaut, P.; Hopiat, P.; Wintgens, V.; Valat, P.; Garnier, F.; Delabouglise, D. *J. Phys. Chem.* **1993**, *97*, 513.

(34) Rossi, R.; Carpita, A.; Ciofalo, M.; Houben, J. L. *Gazz. Chim. Ital.* **1990**, *120*, 793.

(35) Rossi, R.; Ciofalo, M.; Carpita, A.; Ponterini, G. *J. Photochem. Photobiol., A* **1993**, *70*, 59.

(36) Charra, C.; Fichou, D.; Nunzi, J. M.; Pfeffer, N. *Chem. Phys. Lett.* **1992**, *192*, 566.

(37) Buma, W. J.; Kohler, B. E.; Shaler, T. A. *J. Phys. Chem.* **1994**, *98*, 4990.

(38) Visser, G. J.; Heeres, G. J.; Wolters, J.; Vos, A. *Acta Crystallogr. B.* **1968**, *24*, 467.

(39) Samdal, S.; Samuelson, E. J.; Volden, H. *Synth. Met.* **1993**, *59*, 259.

(40) Bucci, P.; Longeri, M.; Veracini, C. A.; Lunazzi, L. *J. Am. Chem. Soc.* **1974**, *96*, 1305.

(41) Chadwick, J. E.; Kohler, B. E. *J. Phys. Chem.* **1994**, *98*, 3631.

(42) Takayanagi, M.; Gejo, T.; Hanazaki, F. *J. Phys. Chem.* **1994**, *98*, 12893. Hanazaki, F. Personal communication.

(43) Van Bolhuis, F.; Wynberg, H.; Havinga, E. E.; Meijer, E. W.; Staring, E. G. I. *Synth. Met.* **1989**, *30*, 381.

(44) 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.

(45) Taliani, C.; Danieli, R.; Lazzaroni, R.; Periasamy, N.; Ruani, G.; Zamboni, R. *Synth. Met.* **1993**, *55−57*, 4714.

(46) Andres, L. S.; Merchan, M.; Fulscher, M.; Roos, B. O. *Chem. Phys. Lett.* **1993**, *211*, 125.

(47) Becker, R. S. *Theory and Interpretation of Fluorescence and Phosphorescence*; Wiley-Interscience: New York, 1969.

(48) 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.

(49) Ciofalo, M.; Ponterni, G. *J. Photochem. Photobiol., A* **1994**, *83*, 1.

(50) D'Auria, M.; D'Onofrio, F. *Gazz. Chim. Ital.* **1988**, *118*, 633.

(51) Egelhaaf, H.-I.; Oelkrug, D. *SPIE*, in press.

(52) Nunzi, J. M.; Pfeffer, N.; Charra, F.; Fichou, D. *Chem. Phys. Lett.*, in press.

(53) Cheng, X.; Ichimura, K.; Fichou, D.; Kobayashi, T. *Chem. Phys. Lett.* **1991**, *185*, 286.