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Singlet oxygen photosensitizing properties of bithiophene and terthiophene derivatives

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Abstract

An extensive set of thiophene derivatives has been evaluated to determine their sensitized quantum yields for singlet oxygen generation in solution. The values have been determined using laser excitation and time-resolved detection of the near-IR phosphorescence from singlet oxygen. Values determined in this work, cited in earlier publications and thesis dissertations, as well as those in the literature have been combined in an extensive set of tables providing an up-to-date compilation of these efficiencies. These values are independently being used to derive quantitative structure–activity relationships (QSARs) whereby an optimum set of physical parameters for the phototoxicity to a desired target organism may be ascertained.

Keywords: Singlet oxygen; Bithiophene derivatives; Terthiophene derivatives

1. Introduction

As part of an ongoing research project into the evaluation of the sensitizing and spectroscopic properties of α-terthienyl (α-T) and other thiophene derivatives, we have routinely carried out measurements involving the determination of quantum yields of singlet oxygen generation (Φ_Δ) for many of these compounds in solution. These values are currently being used to derive quantitative structure–activity relationships (QSARs) whereby an optimum set of physical parameters for their potential as light-activated insecticides towards a desired target organism may be ascertained [1,2]. The best parameter set is expected to serve as a guide for further synthesis of "tailored" photosensitizer molecules. In the course of this work a large number of data have been accumulated, since the quantitative structure–activity relationship analysis described above is statistical in nature and requires a fairly large database for each system.

Some of the singlet oxygen sensitization parameters have been reported earlier, while others have never been reported. Another group of measurements has been cited in work by some of the authors or their colleagues, but details of the determinations have never been published. As a result, much of the data are scattered in various publications, thesis dissertations and a few secondary publications. This paper aims at correcting this situation by providing a comprehensive set of data obtained by direct detection of the phosphorescence from singlet oxygen. Measurements by other techniques have historically played an important role e.g. [3–5] but are not covered here. A recent paper also reports on the determination of singlet oxygen yields for a series of related compounds [6]. These values have also been included in our tables in accordance with the criterion mentioned above.

To make the data more easily accessible to workers interested in this field, we give here the experimental details and results for $O_2(^1\Delta_g)$ sensitization by thiophene derivatives arising from time-resolved luminescence detection experiments to study directly the generation and reaction of $O_2(^1\Delta_g)$. Recently, thiophene oligomers and polymers have also been considered for the study and eventual manufacture of photoconducting devices [7–9]. The information reported here may prove useful in the understanding of these processes and in the eventual selection of the optimum substitution pattern.

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2. Experimental details

2.1. Preparation of samples

The syntheses of most of the samples listed in Tables 1–3 (see Section 3) can be found in the literature [3,10–14]. The sensitizers used were obtained from Aldrich, except for phenazine which was an Eastman Kodak product.

2.1.1. Terthiophenes 38–44

Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded on a Bomem MB100 spectrometer as solutions in methylene chloride. Low resolution (LRMS) and high resolution (HRMS) mass spectra were recorded using an AEIMS 9025 and a Kratos Concept 2H instrument respectively. UV spectra were recorded on a Hewlett–Packard (model 8451) UV spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Gemini instrument operating at 200 and 50 MHz for ^1H and ^{13}C NMR respectively or on a Varian XL300 instrument operating at 300 and 125 MHz for ^1H and ^{13}C NMR respectively. Samples were run as solutions in $CDCl_3$ unless otherwise stated. All chemical shifts (δ) are reported in ppm downfield from tetramethylsilane (TMS).

Column chromatography refers to flash column chromatography and was carried out using 230–400 mesh silica gel unless otherwise noted. Thin layer chromatography (TLC) was performed on Kieselgel 60 F_{254} precoated silica plates of 0.25 mm thickness.

Tetrahydrofuran (THF) was distilled over sodium under a nitrogen atmosphere and using benzophenone ketyl as an indicator. All amines except benzylamine were distilled from CaH_2 or KOH immediately prior to use. Benzylamine was used as received from Aldrich. Sulphuryl chloride and dimethylformamide (DMF) were distilled under a nitrogen atmosphere from CaH_2. Butyllithium (BuLi) was purchased from Aldrich and used after titration with diphenylacetic acid in THF at 0 °C. Unless otherwise noted, all reactions were carried out under an inert atmosphere in flame-dried glassware. Usual work-up refers to drying the organic solvent over anhydrous magnesium sulphate, filtration and evaporation of the solvent. All sulphonamides were prepared according to the general procedure given below for the *N*-benzyl sulphonamide.

2,2':5',2"-Terthienyl-5-sulphonyl chloride. The sulphonyl chloride was prepared by adapting the procedure of Sone et al. [15]. To a cooled (0 °C) solution of DMF (1.66 g, 22.7 mmol) was added freshly distilled SO_2Cl_2 (3.06 g, 22.7 mmol) dropwise over 3 min. The resulting mixture was left at 0 °C for 1 h, during which time a white solid formed. A solution of α-terthiophene (5.02 g, 20.2 mmol) in $CHCl_3$ (100 ml) was then added and the resulting bright yellow solution was refluxed for 4 h, during which time the white SO_2Cl_2:DMF complex gradually dissolved and the solution changed from bright yellow to orange and finally red. The resulting red solution was stirred at room temperature (16 h) and then poured on to ice-cold water (75 ml) and extracted with CH_2Cl_2 until the aqueous phase was almost clear. Usual work-up afforded 3.96 g of the crude sulphonyl chloride and some remaining starting material as evident by TLC. The residue was dissolved in hot ethyl acetate and then crystallized by addition of hexanes. Filtration provided 1.31 g of the pure sulphonyl chloride and a second crop (0.68 g) of crystals was formed by reducing the mother liquor to half-volume and adding more hexanes. The resulting sulphonyl chloride had m.p. 120–122 °C; IR (cm^{-1}): 1380, 1176; EIMS *m/z* (%): 348 (2.3) (*M*+2), 346 (4.7) (*M*), 248 (100); ^1H NMR: 7.03 (dd, *J*=5.0, 3.6 Hz, 1H), 7.11 (t, *J*=3.6 Hz, 1H), 7.22 (dd, *J*=3.6, 1.0 Hz, 1H), 7.24 (d, *J*=3.8 Hz, 1H), 7.28 (dd, *J*=5.0, 1.0 Hz, 1H), 7.74 (d, *J*=4.1 Hz, 1H); ^{13}C NMR: 148.1, 140.3, 140.2, 136.1, 135.9, 132.4, 128.2, 127.6, 125.8, 124.9, 124.7, 122.8; HRMS for $C_{12}H_7S_4O_2Cl$: calc. 345.9017, found 345.9007.

N-Benzyl-2,2':5',2"-terthienyl-5-sulphonamide (38). To a cooled (0 °C) solution of benzylamide (41.5 mg, 0.39 mmol) and triethylamine (41.9 mg, 0.41 mmol) in CH_2Cl_2 (5 ml) was added dropwise a solution of sulphonyl chloride (101 mg, 0.29 mmol) in CH_2Cl_2 (10 ml). The resulting bright yellow solution was stirred at 0 °C for 1 h, then at room temperature overnight, after which time the resulting dark green solution was poured into CH_2Cl_2 (25 ml) and washed with 10% HCl (4×25 ml). Usual work-up followed by column chromatography (5:1 hexanes–ethyl acetate) afforded 68.2 mg (55.6%) of the sulphonamide as a pale yellow solid, m.p. 191–194 °C; IR (cm^{-1}): 3369, 1343, 1158; UV max. (CH_3CN): 370 nm (ϵ=11 270 M^{-1} cm^{-1}), 260 nm (ϵ=2860 M^{-1} cm^{-1}); EIMS *m/z* (%): 417 (13.4), 248 (100), 203 (34.8); ^1H NMR: 4.23 (d, *J*=8.0 Hz, 2H), 4.71 (t, *J*=8.0 Hz, 1H), 7.00–7.38 (m, 11H), 7.50 (d, *J*=4.1 Hz, 1H); ^{13}C NMR: 144.5, 139.2, 138.6, 137.0, 136.4, 134.3, 133.8, 129.4, 128.7, 128.6, 128.5, 126.9, 125.9, 125.1, 125.0, 123.6, 48.2; HRMS for $C_{19}H_{15}NO_2S_4$: calc. 416.9986, found 416.9981.

N,N-Diethyl-2,2':5',2"-terthienyl-5-sulphonamide (39). Bright yellow powder, m.p. 121–124 °C; IR (cm^{-1}) 1012, 1149.2, 1346; UV max. (CH_3CN): 370 nm (ϵ=27 580 M^{-1} cm^{-1}), 260 nm (ϵ=3520 M^{-1} cm^{-1}); EIMS *m/z* (%): 383 (75.1), 263 (53.3), 248 (100), 247 (60.3), 203 (74.5); ^1H NMR: 1.18 (t, *J*=7.1 Hz, 6H), 3.25 (1, *J*=7.1 Hz, 4H), 7.01–7.25 (m, 6H), 7.41 (d, *J*=4.0 Hz, 1H); ^{13}C NMR: 143.5, 138.9, 138.8, 137.0, 134.5, 132.7, 128.7, 126.6, 125.8, 125.0, 124.9, 123.5, 43.3, 14.9; HRMS for $C_{16}H_{17}NO_2S_4$: calc. 383.0142, found 383.0143.

N-Allyl-2,2':5',2"-terthienyl-5-sulphonamide (40). Bright yellow solid, m.p. 118–121 °C; IR (cm^{-1}): 3370, 1158, 1342; UV max. (CH_3CN): 370 nm (ϵ=45 730 M^{-1} cm^{-1}), 260 nm (ϵ=13 270 M^{-1} cm^{-1}); EIMS *m/z* (%): 367 (74.2), 248 (100), 203 (53.0); ^1H NMR: 0.85 (t, *J*=8.0 Hz, 3H), 1.20–1.60 (m, 4H), 3.05 (m, 2H), 4.45 (t, *J*=8.0 Hz, 1H), 6.95–7.29 (m, 6H), 7.48 (d, *J*=4.0 Hz, 1H); ^{13}C NMR: 144.1, 139.1, 138.9, 137.0, 134.4, 133.4, 128.6, 126.8,

125.8, 125.1, 125.0, 123.6, 43.9, 32.1, 20.3, 14.2; HRMS for $C_{15}H_{13}NO_2S_4$: calc. 366.9829, found 366.9802.

N-Butyl-2,2':5',2"-terthienyl-5-sulphonamide (41). Pale green powder, m.p. 130–131 °C; IR (cm^{-1}): 3367, 1339, 1156; UV max. (CH_3CN): 370 nm ($\epsilon = 33\,866\ M^{-1}\ cm^{-1}$), 260 ($\epsilon = 10\,543\ M^{-1}\ cm^{-1}$); EIMS *m/z* (%): 383 (100), 263 (35), 248 (99.4) 247 (46.3); ^1H NMR: 0.85 (t, $J = 8.0$ Hz, 3H), 1.20–1.60 (m, 4H), 3.05 (m, 2H), 4.45 (t, $J = 8.0$ Hz, 1H), 6.95–7.29 (m, 6H), 7.48 (d, $J = 4.0$ Hz, 1H); ^{13}C NMR: 144.1, 139.1, 138.9, 137.0, 134.4, 133.4, 128.6, 126.8, 125.8, 125.1, 125.0 123.6, 43.9, 32.1, 20.3, 14.2; HRMS for $C_{16}H_{17}NO_2S_4$: calc. 383.0142, found 383.0164.

5-Benzyl-2,2':5',2"-terthienyl sulphide (42). To a cooled (−78 °C) solution of α-T (5.02 g, 20.25 mmol) in THF (150 ml) was added dropwise a solution of "BuLi (8.6 ml (2.35 M in hexanes), 20.21 mmol). The resulting bright yellow solution was stirred at this temperature for 30 min, after which time a solution of benzyl disulphide (4.9771 g, 20.20 mmol) in THF (35 ml) was added via cannula. The resulting green solution was allowed to warm to ambient temperature over 12 h. The resulting dark red solution was poured into water (150 ml) and extracted with ethyl acetate (6×100 ml). Usual work-up afforded 7.42 g (99%) of a yellow–orange solid. Trituration with ether and filtration afforded 4.78 g (64%) of the pure sulphide as a yellow solid, m.p. 148–151 °C; EIMS *m/z* (%): 370 (35.1), 279 (100), 246 (27.1); ^1H NMR: 3.95 (s, 2H), 6.78 (d, $J = 3.4$ Hz, 1H), 6.90–7.06 (m, 4H), 7.12–7.28 (m, 7H); HRMS for $C_{19}H_{14}S_4$: calc. 369.9998, found 369.9987.

5-Benzyl-2,2':5',2"-terthienyl sulfoxide (43). To a cooled (−55 °C) solution of sulphide **42** (998.0 mg, 2.7 mmol) in $CHCl_3$ (200 ml) was added dropwise over 1 min a solution of *m*-chloro-perbenzoic acid (*m*-CPBA; 0.81 g, 2.4 mmol) in $CHCl_3$ (2 ml). The resulting bright yellow solution was stirred at −55 °C for 30 min and then washed with 5% $NaHCO_3$ (4×100 ml). Usual work-up afforded 0.80 g of the crude sulphoxides as a bright yellow solid. Recrystallization from $CHCl_3$–Et_2O afforded 0.68 g (65%) of the sulphoxide as a golden powder. The resulting sulphoxide has m.p. 191–194 °C; EIMS *m/z* (%): 386 (5.7), 370 (30.3), 295 (100), 279 (80.7); ^1H NMR. 4.12 (d, $J = 13.2$ Hz, 1H), 4.38 (d, $J = 13.2$ Hz, 1H), 6.90–7.30 (m, 12H); HRMS for $C_{19}H_{14}S_4O$: calc. 385.9928, found 385.9918.

5-Benzyl-2,2':5',2"-terthienyl sulphone (44). To a cooled (−78 °C) solution of sulphide **42** (145.7 mg, 0.38 mmol) in ethyl acetate (100 ml) was added dropwise over 1 min a solution of *m*-CPBA (346.7 mg, 0.76 mmol). The resulting yellow solution was stirred at −78 °C for 1 h, then warmed to room temperature and stirring was continued for 12 h. The resulting green solution was washed with 5% $NaHCO_3$ (4×100 ml), dried over $MgSO_4$, filtered and concentrated, affording the crude product (120 mg) as a green solid. Recrystallization from ether–hexanes afforded 80.0 mg of the sulphone as dark green plates. The resulting sulphone had m.p. 196–198 °C; EIMS *m/z* (%): 402 (75.1), 338 (17.1), 247 (33.0), 91 (100); ^1H NMR: 4.40 (s, 2H), 7.00–7.35 (m, 12H); HRMS for $C_{19}H_{14}S_4O_2$: calc. 401.9877, found 401.9867.

2.2. Spectroscopic measurements

Acetonitrile (Omnisolv, BDH) and dichloromethane (Fisher) were of spectroscopic grade and used as received. The time-resolved IR emission detection apparatus used to monitor the kinetics of the relaxation of singlet oxygen, $O_2(^1\Delta_g)$, is based on the detection of luminescence using a germanium photodiode as previously described in the literature [16,17]. Our particular set-up [18] employed pulses from a Molectron UV-24 nitrogen laser ($\lambda = 337.1$ nm, 10 ns pulse, 5 mJ or less per pulse) or a Lumonics excimer laser ($\lambda = 308$ nm, 10 ns pulse, 35 mJ or less per pulse) to excite oxygenated samples contained in a quartz fluorescence cuvette of 10×10 mm path length. Detection of the phosphorescent emission from $O_2(^1\Delta_g)$ was carried out at right angles to the direction of the excitation beam, with an anti-reflection-coated silicon filter 3 mm thick (CVI Laser Corp.) placed between the sample and the detector to remove interfering light of lower wavelengths due to fluorescence or laser scattering. The detector used was an EG&G Judson J16 8SP ROM5 (5 mm) germanium photodiode mounted on a modified BNC connector. Signals were amplified using a Judson PA100 voltage preamplifier (about 500 gain), with further amplification (×10) obtained through the use of a home-made amplifier. The preamplifier was operated under a small reverse bias voltage in order to improve the rise time of the detection. In later experiments a Stanford Research Systems low noise preamplifier (model SR560) was used. Amplified signals were captured by either a Transiac 2001 or a Tektronix 2440 digitizer. Computer control of the experiment and data acquisition were similar to those used in laser flash photolysis work [19,20].

In order to determine accurate quantum yields (Φ_Δ) of singlet oxygen sensitization from thiophene derivatives, a comparative method was used whereby the energy dependence of the initial $O_2(^1\Delta_g)$ luminescence intensity (I_0) was measured for optically matched samples under study and for a reference compound for which the Φ_Δ value is accurately known in the same solvent. By direct comparison of the slopes of the power dependence plots, the Φ_Δ value for the sample may be obtained. Laser energies were varied using a series of calibrated sets of neutral density filters. Up to 50 shots were averaged (for the lowest laser excitation energy) for each data point. In many cases a non-linear plot was obtained owing to competitive absorption by the thiophene triplet states formed during the laser pulse. In these cases a second-order polynomial fit was carried out to determine the slope at zero dose (and hence at zero triplet concentration). We anticipate that under conditions of oxygen saturation at least 95% of the thiophene triplets will decay by oxygen quenching for lifetimes (under nitrogen) in excess of about 600 ns.

3. Results

As an example of the comparative method used, sulphonamide **38** listed in Table 1 is used for demonstration purposes. Fig. 1 shows a typical luminescence decay trace for $O_2(^1\Delta_g)$ emission centred at 1.27 μm. The initial amplitude of this signal is proportional to the yield of singlet oxygen, since under oxygen saturation we expect over 95% of the sensitizer triplets to decay by interaction with oxygen. Under our experimental conditions, using low sensitizer concentrations, the decay of this signal which reflects the lifetime of $O_2(^1\Delta_g)$ was consistent with that reported in the literature in the same solvents [21]. A typical energy dependence plot obtained is presented in Fig. 2. The phenazine plot has a measured slope of 15.2 V J^{-1}, while the sample has a slope of 13.9 V J^{-1}. The ratio of these slopes corresponds to the ratio of singlet oxygen generation quantum yields and gives a calculated Φ_Δ value of about 0.76 using 0.83 as the quantum yield of singlet oxygen produced by phenazine in acetonitrile. When taking into account the errors in the fits, the overall uncertainty associated with this technique is typically only about 10%.

The results of this study are given in Tables 1–3, the sensitizers being categorized on the basis of their molecular structure into terthiophenes, bithiophenes and miscellaneous thiophene photosensitizers. Owing to the limited solubility of some thiophene derivatives, a variety of different solvents were employed in this study, thus requiring a reference compound for each particular solvent. The references used and their respective Φ_Δ values for each solvent are listed in Table 4.

All the compounds studied demonstrated observable singlet oxygen sensitizing ability ranging from 0.15 to close to 0.9. Halogen substitution, especially iodine, causes a significant decrease in efficiency. Conjugation beyond the terthienyl moiety (as in the case of **29**) can also cause some reduction of the yield. It is unclear why methoxy substitution in the case of **8** causes such a significant decrease. We note that changes in yield can reflect intrinsic changes in efficiency for singlet oxygen generation or a reduced quantum yield for intersystem crossing. We further note that the naturally occurring bithiophene (**48–54**) and terthiophene (**1, 2**) sensitizers

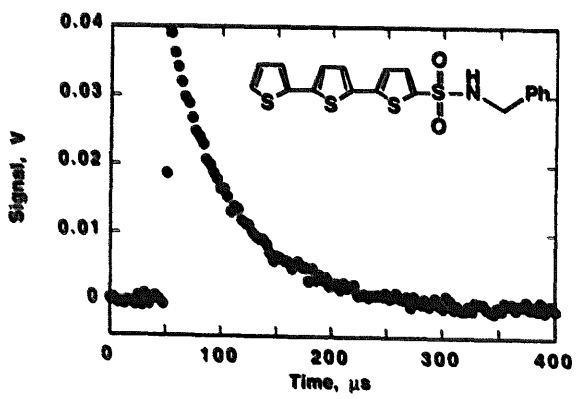


Fig. 1. Decay trace for $O_2(^1\Delta_g)$ emission centred at 1.27 μm generated from compound **38**.

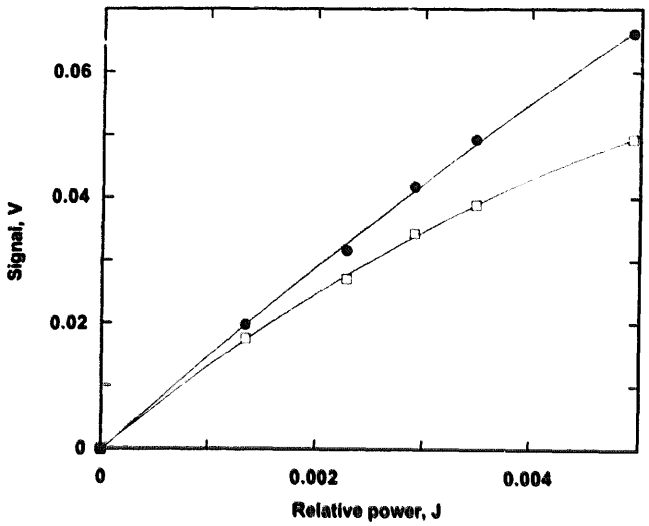


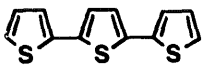
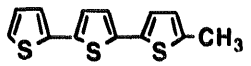
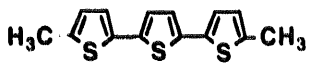
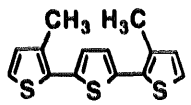
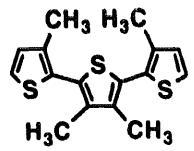
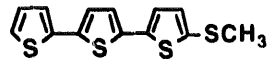
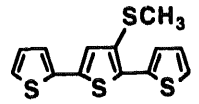
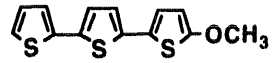
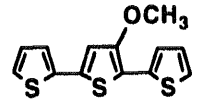
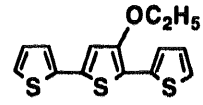
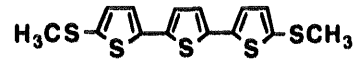
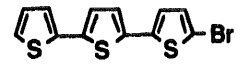
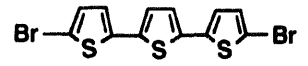
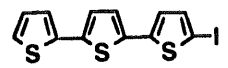
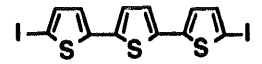
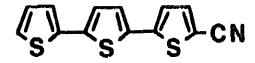
Fig. 2. Typical power dependence plot obtained from the same sample as in Fig. 1 (□) and a standard, phenazine (●) (excitation at 308 nm; solvent, acetonitrile).

all have high Φ_Δ values (greater than 0.5), which is consistent with their role as light-activated defences of plants of the *Asteraceae* family that synthesize them.

It is immediately apparent that under natural sunlight the rate of singlet oxygen generation by any one of these sensitizers will be dependent not only on its Φ_Δ value but also on the extent of overlap between its absorption spectrum and the solar spectrum, i.e. a molecule with high Φ_Δ value but little spectral overlap may be less effective than one in which a lower Φ_Δ value is combined with more favourable spectral characteristics. The observed variable thiophene phototoxicity to various organisms such as mosquito larvae [2], brine shrimps [1] and viruses [12] has been successfully predicted for 14 or more compounds using QSAR models. These models are linear regressions based on the calculation of the total rate of singlet oxygen generation (i.e. the product of Φ_Δ and the number of photons absorbed) and the calculated partition coefficient of the compounds in water–octane. For each of the organisms both terms are significant in a bilinear model which explains greater than 80% of the variation in thiophene phototoxicity. The significance of the present data set on 44 thiophenes is that it gives an immediate assessment of the contribution of singlet oxygen generation to phototoxicity and provides a much wider range of compounds than originally considered in the published QSAR models for the prediction of toxicity.

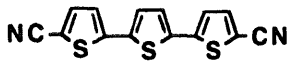
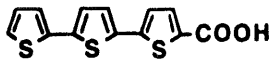
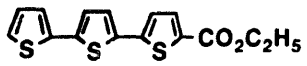
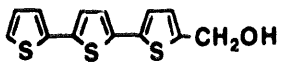
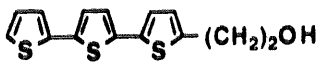
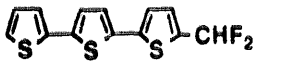
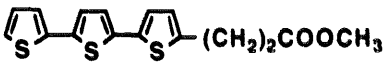
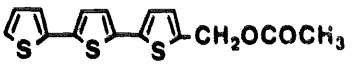
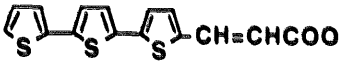
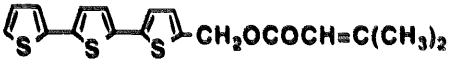
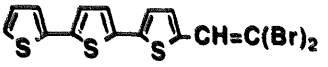
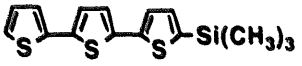
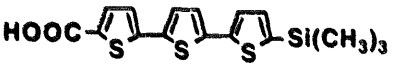
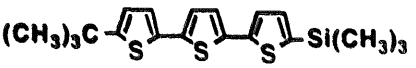
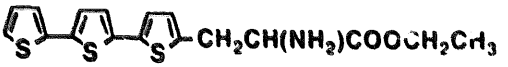
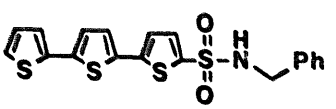
The phototoxicity of several of these compounds exhibiting similar spectral and sensitizing properties proved to be widely different when tested as photo-activated insecticides. One possible phenomenon which could lead to a reduced phototoxic effect would be reaction of the sensitized singlet oxygen with the thiophene sensitizer. This possibility was tested by studying the effect of α-T concentration on the lifetime of singlet oxygen. To facilitate this study, the absorbance of the solution was varied between 0.1 and 1.5 (at 337 nm) for each sample in deuterated acetonitrile (CD_3CN),

Table 1
Photosensitizing properties of terthiophenes

No.	Structure	Φ_Δ	Solvent	Ref.
1		0.75	C_6H_6	[18]
		0.67	$CHCl_3$	[18]
		0.73	$CDCl_3$	[18]
		0.75	CH_2Cl_2	[18]
		0.68	CH_3CN	[18]
		0.67	CD_3OD	[18]
		0.70	CD_3OD	[18]
		0.59	CH_3CH_2OH	[6]
		~0.8	C_6H_6	[22]
2		0.79	C_6H_6	Cited in [1]
3		0.66	C_6H_6	Cited in [1]
4		0.58	CH_3CH_2OH	[6]
5		0.64	CH_3CH_2OH	[6]
6		0.81	C_6H_6	Cited in [12]
7		0.64	CH_3CH_2OH	[6]
8		0.26	CH_3CH_2OH	[6]
9		0.63	CH_3CH_2OH	[6]
10		0.56	CH_3CH_2OH	[6]
11		0.52	C_6H_6	Cited in [1]
12		0.52	C_6H_6	Cited in [12]
		0.58	CH_3CH_2OH	[6]
13		0.63	CH_3CH_2OH	[6]
14		0.26	CH_3CN	This work
15		0.22	CH_3CN	Cited in [12]
16		0.61	C_6H_6	Cited in [12]

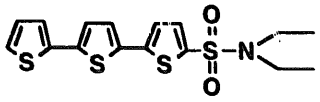
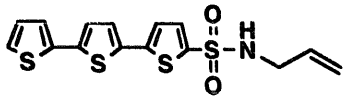
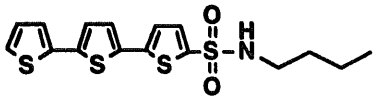
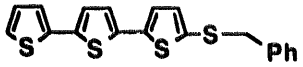
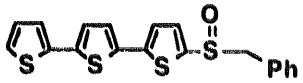
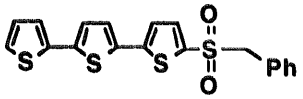
(continued)

Table 1 (*continued*)

No.	Structure	Φ_Δ	Solvent	Ref.
17		0.79	CH_3CN	Cited in [12]
18		0.71	CH_3CN	Cited in [12]
19		0.64	CH_3CH_2OH	[6]
20		0.65	C_6H_6	Cited in [12]
21		0.65	C_6H_6	Cited in [12]
22		0.62	CH_3CH_2OH	[6]
23		0.60 0.57	C_6H_6 CH_3CH_2OH	This work [6]
24		0.76	CH_2Cl_2	Cited in [1]
25		0.73	CH_2Cl_2	Cited in [1]
26		0.60	CH_3CH_2OH	[6]
27		0.42	C_6H_6	Cited in [1]
28		0.61	CH_3CH_2OH	[6]
29		0.31	C_6H_6	Cited in [12]
30		0.64	CH_3CH_2OH	[6]
31		0.77	C_6H_6	This work
32		0.76	CH_3CN	This work
33		0.15	C_6H_6	Cited in [1]
34		0.84	C_6H_6	Cited in [12]
35		0.86	C_6H_6	Cited in [12]
36		0.57	C_6H_6	This work
37		0.58	CH_2Cl_2	This work
38		0.76	CH_3CN	This work

(*continued*)

Table 1 (*continued*)

No.	Structure	Δ_Δ	Solvent	Ref.
39		0.77	CH_3CN	This work
40		0.68	CH_3CN	This work
41		0.65	CH_3CN	This work
42		0.44	CH_2Cl_2	This work
43		0.30	CH_2Cl_2	This work
44		0.60	CH_3CN	This work

the deuterated solvent being chosen because the longer lifetime (much greater than 300 μs) of singlet oxygen allows potentially a larger range in the determined quenching rate constant k_q to be studied. An almost 20-fold increase in concentration from 4.1×10^{-6} to 7.7×10^{-5} M resulted in little change in the rate constant of $O_2(^1\Delta_g)$ decay, i.e. from 2.19×10^3 to only 2.57×10^3 s^{-1}. This is less than a 15% decrease in the lifetime for $O_2(^1\Delta_g)$. This allows us to estab-

Table 2
Photosensitizing properties of bithiophenes

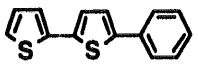
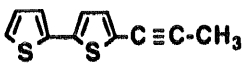
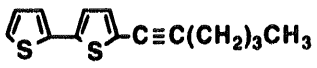
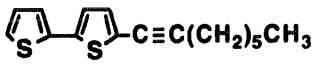
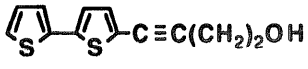
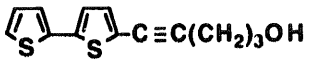
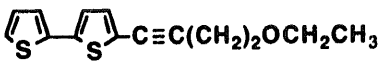
No.	Structure	Φ_Δ	Solvent	Ref.
45		0.60	C_6H_6	Cited in [14]
46		0.47	C_6H_6	Cited in [14]
47		0.80	CH_3CN	This work
48		0.62	C_6H_6	This work
49		0.52	C_6H_6	This work
50		0.70	CH_3CN	This work
51		0.51	C_6H_6	This work
52		0.73	CH_3CN	This work
53		0.63	C_6H_6	Cited in [14]
54		0.72	C_6H_6	Cited in [14]

Table 3
Photosensitizing properties of miscellaneous thiophene sensitizers

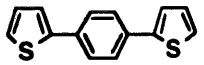
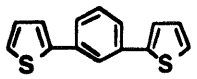
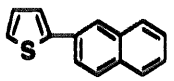
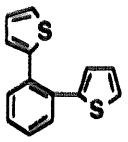
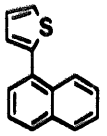
No.	Structure	Φ_Δ	Solvent	Ref.
55		0.31	C_6H_6	Cited in [1]
56		0.56	C_6H_6	Cited in [1]
57		0.27	C_6H_6	Cited in [1]
58		0.58	C_6H_6	Cited in [1]
59		0.23	CH_3CN	This work
60		0.58	C_6H_6	Cited in [1]

Table 4
Singlet oxygen standards used

Standard	Φ_Δ	Solvent	Ref.
Phenazine	0.83	C_6H_6	[23]
	0.84	$CHCl_3$	[24]
	0.84	$CHCl_3$	[25]
	0.89	CH_2Cl_2	[24]
	0.83	CH_3CN	[26]
Acridine	0.82	CH_3CN	[24]
Anthracene	0.55	CD_3OD	[25]
$Ru(bipy)_3$	0.86	CD_3OD	[27]

lish an upper limit for the reactivity of singlet oxygen with α-T of less than $10^6\ M^{-1}\ s^{-1}$. Thus we can conclude that in this case, and probably in general, scavenging of $O_2(^1\Delta_g)$ by reaction with its thiophene precursor is unlikely to account for the reduced phototoxicity observed for some derivatives. In spite of the low quantum yield for singlet oxygen scavenging by α-T, under prolonged irradiations this reaction leads to considerable α-T depletion.

Acknowledgments

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References

[1] R.J. Marles, R.L. Compadre, C.M. Compadre, C. Soucy-Breau, R.W. Redmond, F. Duval, B. Mehta, P. Morand, J.C. Scaiano and J.T. Arnason, *Pest. Biochem. Physiol., 41* (1991) 89.
[2] R.J. Marles, J.T. Arnason, R.L. Compadre, C.M. Compadre, C. Soucy-Breau, P. Morand, B. Mehta, R.W. Redmond and J.C. Scaiano, *Recent Adv. Phytochem., 25* (1991) 371.
[3] J.C. Scaiano, A. MacEachern, J.T. Arnason, P. Morand and D. Weir, *Photochem. Photobiol., 46* (1987) 193.
[4] J.P. Reyftmann, J. Kagan, R. Santus and P. Morliere, *Photochem. Photobiol., 41* (1985) 1.
[5] J. Kagan, M. Bazin and R. Santus, *J. Photochem. Photobiol. B: Biol., 3* (1989) 165.
[6] M. Ciofalo and G. Ponterini, *J. Photochem. Photobiol. A: Chem., 83* (1994) 1.
[7] J.V. Caspar, V. Ramamurthy and D.R. Corbin, *J. Am. Chem. Soc., 113* (1991) 600.
[8] B. Xu and S. Holdcroft, *J. Am. Chem. Soc., 115* (1993) 8447.
[9] M.S.A. Abdou and S. Holdcroft, *Chem. Mater., 6* (1994) 962.
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