ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 110 (1997) 183–190

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A:CHEMISTRY

Photochemistry and photocuring activities of novel substituted 4′-(4-methylphenylthio)benzophenones as photoinitiators

Norman S. Allen [a,*], Michele Edge [a], Fernando Catalina [b], Teresa Corrales [b], Maria Blanco-Pina [b], Arthur Green [c]

[a] *Chemistry Department, Faculty of Science and Engineering, Manchester Metropolitan University, Chester Street, Manchester M1 5GD, UK*
[b] *Departamento de Fotoquimica de Polimeros, Instituto de Ciencia y Tecnologia de Polimeros, CSIC, 3 Juan de la Cierva, 28006 Madrid, Spain*
[c] *Great Lakes Fine Chemicals Ltd., Halebank Industrial Estate, Lower Road, Widnes, Cheshire WA8 8NS, UK*

Accepted 20 May 1997

Abstract

The photoinduced polymerization activities of 19 novel substituted 4′-(4-methylphenylthio)benzophenones (or 4′-(4-tolylthio)-benzophenones) were determined and compared with that of the unsubstituted derivative itself in different monomers and prepolymers using real-time infrared (RTFTIR) and pencil hardness methods. Absorption, fluorescence and phosphorescence analyses, as well as photoreduction/photolysis studies, were undertaken on the compounds, and the data were related to the photopolymerization activities. Solvent shift studies on the absorption maxima of all the compounds indicate the presence of a long-wavelength singlet $\pi\pi^*$ state with some $n\pi^*$ character. The absorption maxima of the bistolylthio, amino, chloro and nitro derivatives are more red shifted than those of the simpler alkyl, alkoxy, phenyl and phenoxy derivatives. Fluorescence and phosphorescence analyses indicate a high rate of intersystem crossing to the triplet state. The fluorescence emission maxima are markedly red shifted with increasing solvent polarity, indicating that the lowest excited singlet state exhibits a high degree of charge transfer character. The lowest excited triplet state of all the 4-substituted 4-tolylthiobenzophenones is essentially a $\pi\pi^*$ configuration, with some $n\pi^*$ character, as indicated by the phosphorescence lifetime data. The lowest excited triplet state of the unsubstituted derivative, on the other hand, is essentially $\pi\pi^*$ in character with a longer emission lifetime and a lower quantum yield. The emission maxima are independent of the nature of the substitution, indicating the presence of a rigid molecular structure. The latter is confirmed by the observation of very high phosphorescence quantum yields. The bistolylthio derivatives exhibit shorter phosphorescence emission lifetimes, indicating that their lowest excited triplet state is $n\pi^*$ in nature. The triplet $\pi\pi^*$ character of the amino derivatives is indicated by their increased emission lifetimes. The electron-withdrawing effect of the chloro and nitro groups markedly reduces the phosphorescence quantum yield. These effects are accounted for by the relative spacings of close-lying lowest excited singlet $\pi\pi^*$ and second excited triplet $n\pi^*$ states controlling the competitive processes of internal conversion and intersystem crossing. Compared with the unsubstituted 4-tolylthio derivative, all the alkyl-, alkoxy-, phenyl- and phenoxy-substituted derivatives exhibit higher activities as photoinitiators in the absence of an amine cosynergist. Lengthening or broadening of the alkoxy substituent also gives rise to an increased photoinitiation activity, whereas alkyl groups are less effective. The presence of an amine cosynergist enhances photocuring, giving rise to variable effects depending on the nature of the triplet exciplex interaction. The bistolylthio derivatives exhibit the highest photoinitiation activity, whereas the 4-nitro group has a marked deactivating effect. The presence of the 4-amino group also enhances the photoinitiation activity, but only by RTFTIR measurements. The photoreduction/photolysis rates of all the 4-substituted derivatives are greater than that of the unsubstituted derivative and show some relation to the nature of the lowest excited triplet state. The photophysical and photochemical data are discussed in relation to the relative photoactivities of the compounds as photoinitiators for curing acrylated multifunctional monomers. © 1997 Elsevier Science S.A.

Keywords: Methylphenylthiobenzophenones; Photochemistry; Photoinitiators; Photopolymerization

1. Introduction

The increasing market drive for better photoinitiators for coatings technology can be answered only by improving our knowledge of the mode of action of photoinitiators under various conditions [1,2]. Over the years, there has been considerable interest in aromatic carbonyl systems containing thio functionalities [3–9]. For example, the 4-methylthio derivative of benzophenone exhibits increased photocuring activity over that of benzophenone, which is associated with its red-shifted absorption and lower triplet state activity

---

* Corresponding author. Tel.: +44 161 247 1432; fax: +44 161 247 1438; e-mail: N.Allen@mmu.ac.uk

1010-6030/97/$17.00 © 1997 Elsevier Science S.A. All rights reserved
PII S1010-6030(97)00175-5

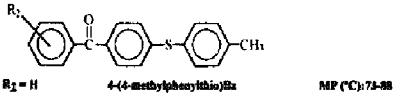
towards the monomer in terms of the hydrogen atom abstracting ability [8,9]. In addition to the hydrogen atom abstraction reaction to form a ketyl radical, these types of compound may undergo photolysis reactions at the C–S bond. These reactions are equally applicable to keto-sulphoxide derivatives [3] to produce alkyl and sulphoxide radicals. Direct scission at the aryl–S bond is also feasible to produce aryl and thio radicals [3]. Recently, we presented studies on the effect of different alkylthio and phenylthio groups on the photopolymerization activity of the benzophenone chromophore [10,11]. Increased absorption maxima and the formation of aryl and ketyl radicals were primarily responsible for the enhanced activities. The phenylthio derivatives were also found to exhibit strong synergism with a tertiary amine.

In view of the fact that the structure and electron density appear to play a crucial role in influencing the excited state activity for photocuring, we have examined the photopolymerization/photocuring activities of 19 novel substituted 4-methylphenylthio (or tolylthio) and bis(methylphenylthio)benzophenones. Here the phenyl group (or groups) is linked to the benzophenone chromophore via a freely rotating C–S bond. The structures are compared with the activities. The activities are related to the photochemical and spectroscopic properties, and the data are compared with those of the unsubstituted 4-(4-methylphenylthio)benzophenone as a reference system.

2. Experimental details

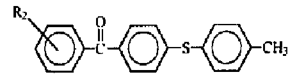
2.1. Materials

All solvents, diethylethanolamine, methyldiethanolamine, benzophenone and quinine sulphate were obtained from Aldrich Chemical Co. Ltd., UK and were of analar, spectroscopic or high performance liquid chromatography (HPLC) grade quality. The alkyl-, alkoxy-, phenyl- and phenoxy-substituted 4-methylphenylthiobenzophenones are shown in Scheme 1 (structures **1–12**), the three bis(tolyl)-benzophenones in Scheme 2 (structures **13–15**) and the amino-, chloro- and nitro-substituted 4-methylphenylthiobenzophenones in Scheme 3 (structures **16–20**). Two of the compounds, **5** and **20**, are not tolyl derivatives. These compounds were supplied by Great Lakes Fine Chemicals Ltd., Widnes, UK. All the compounds were chromatographically pure and had verified elemental C, H and S analysis.



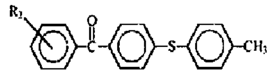
COMP 1	R_2 = H	4-(4-methylphenylthio)Bz	MP (°C):73-88
COMP 2	R_2 = i-Propyl	4-isopropyl-4'-tolylthioBz	MP (°C):97-98
COMP 3	R_2 = MeO	4-methoxy-4'-tolylthioBz	MP (°C):118-120
COMP 4	R_2 = 3-Me-4-MeO	3-methyl-4-methoxy-4'-tolylthioBz	MP (°C):88-91
COMP 5	R_2 = 3-MeO	3-methoxy-4'-phenylthioBz(not tolyl)	MP (°C):liquid
COMP 6	R_2 = EtO	4-ethoxy-4'-tolylthioBz	MP (°C):99-102
COMP 7	R_2 = n-PrO	4-n-propoxy-4'-tolylthioBz	MP (°C):106-107
COMP 8	R_2 = i-PrO	4-isopropoxy-4'-tolylthioBz	MP (°C):76-79
COMP 9	R_2 = AllO	4-allyloxy-4'-tolylthioBz	MP (°C):99-100
COMP 10	R_2 = i-AmylO	4-isoamyloxy-4'-tolylthioBz	MP (°C):80-83
COMP 11	R_2 = Phenyl	4-phenyl-4'-tolylthioBz	MP (°C):160-161
COMP 12	R_2 = Phenoxy	4-phenoxy-4'-tolylthioBz	MP (°C):119-120

Scheme 1. Structures **1–12**: 3- and 4-substituted 4'-tolylthiobenzophenones.



COMP 13	R_2 = 4-MePhS	Bis-(tolylthio)Bz	MP (°C):150-152
COMP 14	R_2 = 3-MePhS	Bis-(m-tolylthio)Bz	MP (°C):120-122
COMP 15	R_2 = 2-MePhS	Bis-(o-tolylthio)Bz	MP (°C):79-81

Scheme 2. Structures **13–15**: bistolylthiobenzophenones.



COMP 16	R_2 = di-iPr Amino	4-diisopropylamino-4'-tolylthioBz	MP (°C):166-167
COMP 17	R_2 = Piperidino	4-piperidino-4'-tolylthioBz	MP (°C):119-120
COMP 18	R_2 = Morpholino	4-morpholino-4'-tolylthioBz	MP (°C):160-161
COMP 19	R_2 = Chloro	4-chloro-4'-tolylthioBz	MP (°C):150-151
COMP 20	R_2 = Nitro	4-nitro-4'-phenylthioBz(not tolylthio)	MP (°C):151-152

Scheme 3. Structures **16–20**: 4-amino-, chloro- and nitro-substituted 4'-(4-methylphenylthio)benzophenones.

2.2. Spectroscopic measurements

Absorption spectra were obtained using a Perkin–Elmer Lambda 7 absorption spectrometer. Fluorescence and phosphorescence excitation and emission spectra were obtained using a Perkin–Elmer LS-50B luminescence spectrometer. Fluorescence quantum yields were obtained by the relative method using quinine sulphate in 0.05 M sulphuric acid as a standard [12]. The quantum yield of quinine sulphate was assumed to be 0.55. Phosphorescence quantum yields were obtained in ethanol at 77 K in liquid nitrogen using the relative method with benzophenone as a standard, assuming a quantum yield of 0.74 in ethanol [12]. Clear glasses were obtained in absolute ethanol. All spectra were corrected using a Perkin–Elmer IBM-compatible GEM package with an appropriate built-in correction factor for this purpose for the photoresponse of the photomultiplier and optics. Blank measurements were obtained on the solvents alone to correct for Raman scatter and were subtracted from the original sample spectra. Phosphorescence lifetime measurements were obtained under the same conditions (77 K) using benzophenone as a standard for lifetime comparison (6.0 ms). In these conditions, the influence of oxygen diffusion will be insignificant. Measurements were obtained using GEM software and by electronically gating the emission signal decay, taking into account the phosphorescence lifetime and delay/gate widths in the data acquisition.

2.3. Photoreduction quantum yields

The absolute quantum yields of photolysis (ϕ_r) of the initiators were determined in acetonitrile at 10^{-5} M using an irradiation wavelength of 365 nm, selected from a Philips high-pressure Hg lamp (HB-CS 500 W) and a Kratos GM252 monochromator. Sample cells were thermostatically controlled at 30 °C and the solutions were nitrogen (less than 5 ppm O_2) saturated. The absorbed light intensity was measured using an International Light model 700 radiometer previously calibrated with Aberchrome 540 [13,14]. During the early stages of irradiation, because of the interference of product formation with the quantum yield measurements, only subsequent photolysis rates could be measured against the light intensity for the range of compounds.

2.4. *Real-time infrared (RTFTIR) measurements*

The initiators were dissolved in a minimum quantity (2–3 cm^3) of tetrahydrofuran, followed by mixing with a prepolymer, Actilane 420 (ethoxylated bisphenol-A-dimethacrylate) (Akcros Chemicals, Eccles, Manchester, UK) (0.001 M). Traces of solvent were then removed by flushing with argon for 30 min, followed by the addition of 1% w/w of the co-initiator *p*-ethyl-4-(dimethylamino)benzoate (EDB) (Great Lakes, Widnes, UK).

The resin was placed between pieces of low-density polyethylene using a separator to give a film thickness of 100 μm. The polyethylene holder was placed on a specular reflectance unit directing the sample beam into the grating system. Two polyethylene film samples were used as reference. The decrease in absorbance at 1638 cm^{-1} of the vinyl absorption band was monitored with a Nicolet FTIR spectrometer in real-time mode during irradiation using a fibre optic arrangement (8 mm aperture). The irradiation source used was a Macam 100 W high-pressure Hg lamp. Plots of percentage conversion vs. time were obtained, from which second plots of moles per litre vs. time in seconds were obtained. From the initial slopes of the second plots, R_p values (mol l^{-1} s^{-1}) were obtained.

2.5. *Commercial curing*

The photoinitiators (2% w/w) and methyldiethanolamine (3% w/w) were dissolved in a resin formulation made up of 55% Photomer 3148 (epoxy acrylate oligomer), 20% tripropylene glycol diacrylate and 25% trimethylol propane triacrylate from Akcros Chemicals Ltd., Manchester, UK. The cure speeds of the formulations, coated at 12 μm thickness on glass slides and cured to give a pencil hardness of 2H, were assessed using a single 80 W cm^{-1} tube Minicure Unit (Jiga and Lamps Ltd., UK). This is a simple test whereby the coating is cured such that it is able to be scored by a 2H grade pencil [1,2]. The cure rates were assessed by the belt speed for effective cure.

3. Results and discussion

3.1. *Photocuring and photopolymerization*

The photopolymerization and photocuring data using RTFTIR and pencil hardness for compounds **1–12**, **13–15** and **16–20** are shown in Tables 1–3 respectively. In the first instance, for RTFTIR in the absence of an amine, it can be seen that all the substituted 4-methylphenylthio derivatives (**2–12**) exhibit a higher photoactivity than that of the unsubstituted derivative (**1**) (Table 1). This trend is also reflected in the photocuring data from the pencil hardness results. Under RTFTIR conditions, the addition of a tertiary amine results in enhanced synergism, except for the ethoxy (**6**) and iso-amyloxy (**10**) derivatives. Lengthening or broadening of the alkoxy substituent also gives rise to an increased photoinitiation activity, whereas alkyl groups are less effective. The former effect is associated with the enhanced solubility of the compounds in the resins. In Table 2, the bistolylthio derivatives exhibit the highest photoinitiation activity under both photocuring conditions. Substitution by 4-amino groups also

Table 1
Photopolymerization (RTFTIR) (in Actilane 420) and photocuring (in epoxy acrylate) data with 3- and 4-substituted 4′-tolylthiobenzophenones as initiators

Compound	Photocuring^a (m min^{-1})	Photopolymerization (RTFTIR) R_p^{b} (mol dm^{-3} s^{-1})	
		Without amine	With amine
1	3.7	0.86	3.77
2	4.7	1.93	6.91
3	7.7	1.71	3.92
4	5.2	0.91	4.53
5	4.7	1.33	5.11
6	7.7	1.63	3.00
7	5.4	1.34	5.57
8	6.2	1.77	6.45
9	7.7	1.98	4.39
10	4.7	1.49	2.81
11	6.9	2.03	4.83
12	7.7	2.13	3.85

[a] 2% w/w methyldiethanolamine (data ± 0.2).
[b] 1% w/w *p*-ethyl-4-(dimethylamino)benzoate (EDB) (data ± 0.05).

Table 2
Photopolymerization (RTFTIR) (in Actilane 420) and photocuring (in epoxy acrylate) data with bistolylthiobenzophenones as initiators

Compound	Photocuring^a (m min^{-1})	Photopolymerization (RTFTIR) R_p^{b} (mol dm^{-3} s^{-1})	
		Without amine	With amine
13	8.9	2.32	3.74
14	8.9	3.36	3.38
15	7.7	2.00	3.88

[a] 2% w/w methyldiethanolamine (data ± 0.05).
[b] 1% w/w *p*-ethyl-4-(dimethylamino)benzoate (EDB) (data ± 0.2).

Table 3
Photopolymerization (RTFTIR) (in Actilane 420) and photocuring (in epoxy acrylate) data with 4-amino-, chloro- and nitro-substituted 4′-(4-methylphenylthio)benzophenones as initiators

Compound	Photocuring^a (m min^{-1})	Photopolymerization (RTFTIR) R_p^{b} (mol dm^{-3} s^{-1})	
		Without amine	With amine
16	3.3	1.95	4.65
17	2.4	1.52	1.82
18	3.7	2.21	2.75
19	3.0	4.95	5.46
20	< 1.0	0.22	0.91

[a] 2% w/w methyldiethanolamine (data ± 0.05).
[b] 1% w/w *p*-ethyl-4-(dimethylamino)benzoate (EDB) (data ± 0.2).

Table 4
Absorption properties of 3- and 4-substituted 4′-tolylthiobenzophenones in different solvent media

Compound	Cyclohexane		Chloroform		Ethanol		Acetonitrile	
	λ_{max}	log ϵ	λ_{max}	log ϵ	λ_{max}	log ϵ	λ_{max}	log ϵ
1	313	4.23	319	4.13	315	4.23	311	4.22
2	313	4.28	317	4.26	314	4.00	311	4.29
3	307	4.27	317	4.25	313	4.33	313	4.32
4	303	4.32	309	4.31	313	4.35	307	4.25
5	313	4.31	318	4.29	316	4.21	312	4.34
6	304	4.37	315	4.25	313	4.43	307	4.31
7	304	4.33	313	4.24	313	4.33	306	4.42
8	304	4.36	313	4.25	313	4.30	307	4.60
9	304	4.22	299/313	4.31/4.32	313	4.38	302	4.31
10	305	4.33	313	4.40	313	4.34	307	4.25
11	313	3.92	305/317	4.34/4.35	313	3.81	313	4.43
12	313	4.32	300/313	4.27/4.31	313	4.26	310	4.33

Log ϵ is ±0.01.

Table 5
Absorption properties of bistolylthiobenzophenones in different solvent media

Compound	Cyclohexane		Chloroform		Ethanol		Acetonitrile	
	λ_{max}	log ϵ	λ_{max}	log ϵ	λ_{max}	log ϵ	λ_{max}	log ϵ
13	320	4.36	329	4.48	327	4.39	320	4.61
14	317	4.41	324	4.27	321	4.31	317	4.34
15	320	4.39	328	4.28	325	4.19	321	4.49

Log ϵ is ±0.01.

Table 6
Absorption properties of 4-amino-, chloro- and nitro-substituted 4′-(4-methylphenylthio)benzophenones in different solvent media

Compound	Cyclohexane		Chloroform		Ethanol		Acetonitrile	
	λ_{max}	log ϵ	λ_{max}	log ϵ	λ_{max}	log ϵ	λ_{max}	log ϵ
16	317	4.31	322	4.39	320	4.29	314	4.28
17	334	4.36	313/355	4.22/4.45	312/359	4.07/4.35	351	4.37
18	326	4.38	339	4.23	340	4.36	337	4.44
19	317	4.01	324	4.24	321	3.93	314	4.43
20	329	4.13	335	4.01	331	4.09	324	4.14

Log ϵ is ±0.01.

enhances photocuring, but only under RTFTIR conditions (Table 3). On the other hand, substitution by a 4-nitro group strongly deactivates the molecule towards photoinitiation activity for curing.

3.2. *Spectroscopic properties*

The absorption maxima and extinction coefficients (logarithmic) of compounds **1–12**, **13–15** and **16–20** are given in Tables 4–6 respectively for a range of solvents. The absorption maxima of the 3- and 4-substituted 4′-tolylthiobenzophenones are similar and not significantly influenced by the nature of the substitution. The wavelength maxima exhibit high logarithmic values (above 4.0) and undergo a small red shift from cyclohexane to chloroform and then a blue shift in ethanol and acetonitrile. This is indicative of a $\pi\pi^*$ transition with strong $n\pi^*$ character. The extinction coefficients of compounds **2**–**12** are higher than that of compound **1** in chloroform and acetonitrile. In relation to a UV curable formulation, this effect may contribute to the higher photoactivity of compounds **2–12** compared with that of compound **1**. Substitution of another 4-methylphenylthio group into the adjacent ring of benzophenone to give a bistolylthio structure leads to a red shift in the main absorption maximum above 317 nm due to increased electron donation via the sulphur atom. This accounts for the increased photoinitiation activity during photocuring compared with compounds **1–12**. There is again a variable red/blue shift in the absorption maxima with increasing solvent polarity, indicative of a strongly

Table 7
Fluorescence properties of 3- and 4-substituted 4′-tolylthiobenzophenones in different solvents

Compound	Cyclohexane		Ethanol		Acetonitrile	
	λ_{max}	ϕ_F	λ_{max}	ϕ_F	λ_{max}	ϕ_F
1	343	0.0007	-	-	491	0.0013
2	344	0.0008	488	0.0049	505	0.0015
3	345	0.0008	490	0.0016	485	0.0012
4	345	0.0011	480	0.0015	465	0.0020
5	344	0.0006	469	0.0017	469	0.0007
6	345	0.0006	485	0.0009	483	0.0017
7	344	0.0007	484	0.0015	489	0.0008
8	345	0.0009	497	0.0019	491	0.0006
9	345	0.0006	497	0.0012	499	0.0014
10	345	0.0007	485	0.0015	438	0.0017
11	361	0.0120	489	0.0068	506	0.0031
12	345	0.0009	490	0.0021	499	0.0017

ϕ_F: ±0.0001.

Table 8
Fluorescence properties of bistolylthiobenzophenones in different solvents

Compound	Cyclohexane		Ethanol		Acetonitrile	
	λ_{max}	ϕ_F	λ_{max}	ϕ_F	λ_{max}	ϕ_F
13	362	0.0006	492	0.0021	505	0.0013
14	386	0.0006	475	0.0018	487	0.0024
15	386	0.0015	478	0.0013	495	0.0015

ϕ_F: ±0.0001.

Table 9
Fluorescence properties of 4-amino-, chloro- and nitro-substituted 4′-(4-methylphenylthio)benzophenones in different solvents

Compound	Cyclohexane		Ethanol		Acetonitrile	
	λ_{max}	ϕ_F	λ_{max}	ϕ_F	λ_{max}	ϕ_F
16	345	0.0009	508	0.0020	507	0.0038
17	467	0.0092	497	0.0040	503	0.0011
18	447	0.0013	458	0.0034	504	0.0009
19	386	0.0045	490	0.0077	510	0.0018
20	383	0.0030	394	0.0020	380	0.0005

ϕ_F: ±0.0001.

mixed $n\pi^*$–$\pi\pi^*$ state. The extinction coefficients of compounds **13–15** are slightly higher than those of the substituted tolylthio derivatives **1–12**. The 4-amino-, chloro- and nitro-substituted compounds **16–20** also exhibit absorption maxima red shifted relative to that of the unsubstituted and substituted compounds **1–12** (Table 6). For the amino and chloro derivatives, this contributes to their enhanced photoinitiation activity by RTFTIR. In the presence of an amine cosynergist, the effects are complicated by intermolecular competition for triplet exciplex formation with the benzophenone chromophore. The inactivity of the 4-nitro-substituted compound (**20**) may be associated with the introduction of a weak, low-lying, charge transfer state, which influences the relative positions of the singlet and triplet energy levels, thereby affecting the intersystem crossing rate.

Luminescence analysis of the 4-methylphenylthiobenzophenone structures **1–12**, **13–15** and **16–20** indicates weak fluorescence, as shown in Tables 7–9 respectively. This indicates a high rate of intersystem crossing to the triplet state or rapid internal conversion. For all the compounds, except the 4-nitro derivative (**20**), the fluorescence emission maxima are markedly red shifted with increasing solvent polarity, indicating that the lowest excited singlet state exhibits a high degree of charge transfer character. The emission maxima of the 4′-bistolylthio (**13–15**) and 4-amino and 4-chloro (**16–19**) derivatives are red shifted from those of compounds **1–**

12 due to the strong electron-donating effects of the substituents. The fluorescence quantum yields of compounds **16–19** are also marginally higher. The fluorescence emission maximum of the 4-nitro derivative is blue shifted from those of the 4-amino derivatives and insensitive to the solvent polarity. This may be associated with the formation of a rigid charged donor–acceptor structure.

The phosphorescence emission maxima, quantum yields and lifetimes for compounds **1–12**, **13–15** and **16–20** are shown in Tables 10–12 respectively. The lowest excited triplet state of all the 4-substituted 4-tolylthiobenzophenones in Table 10 (**2–12**) is essentially a $\pi\pi^*$ configuration with some $n\pi^*$ character, as indicated by the phosphorescence lifetime data. The lowest excited triplet state of the unsubstituted derivative, on the other hand, is essentially $\pi\pi^*$ in character with a longer emission lifetime and lower quantum yield; hence its lower photoinitiation activity for curing. The emission maxima are independent of the nature of the substitution, indicating the presence of rigid molecular structures. The latter is confirmed by the observation of very high phosphorescence quantum yields, which in the case of compound **4** approach unity. The bistolylthio derivatives (Table 11) exhibit shorter phosphorescence emission lifetimes, indicating that their lowest excited triplet state is essentially $n\pi^*$ in nature, and this is consistent with their enhanced photoinitiation activity. The triplet $\pi\pi^*$ character of the amino derivatives is indicated by their increased emission lifetimes, with intermolecular exciplex formation with themselves being responsible for the increased activity in the absence of an amine cosynergist. The electron-withdrawing effects of the chloro and nitro groups markedly reduce the phosphorescence quantum yields. The increased photoinitiation activity of the 4-chloro derivative may be associated with competitive photolysis reactions involving, for example, dehalogenation.

The above phosphorescence data can be accounted for by the relative spacings of close-lying lowest excited singlet $\pi\pi^*$ and second excited triplet $n\pi^*$ states controlling the competitive processes of internal conversion and intersystem crossing. By constructing an energy level diagram with the aid of earlier data on benzophenone [15], and taking compound **4** as a case in point, it is noted from Fig. 1 that the level of the $^3n\pi^*$ state is just below that of the $^1\pi\pi^*$ state. In this case, rapid deactivation from the first excited $^1\pi\pi^*$ state by intersystem crossing to the $^3n\pi^*$ state is strongly favoured by two factors: (a) the small size of the potential energy gap between the two states and (b) the fact that the crossing involves states of differing configuration. This accounts for the very low fluorescence quantum yields of these compounds. Following efficient intersystem crossing to the $^3n\pi^*$ state, further rapid deactivation occurs within the triplet manifold to the $^3\pi\pi^*$ state. At this point, however, further radiationless deactivation to the ground state is inefficient on both multiplicity and configuration grounds [16], and explains the substantial quantum yields and relatively long lifetimes of phosphorescence of these derivatives. In the case of the 4-chloro and 4-nitro derivatives, the energy of the lowest $^1\pi\pi^*$ state is reduced and, for compound **20** in Fig. 2, is seen to be isoenergetic with the corresponding $^3n\pi^*$ state. In this case, the rate of intersystem crossing is significantly reduced and deactivation is more likely to occur via internal conversion from the $^1\pi\pi^*$ state.

Table 10
Phosphorescence properties of 3- and 4-substituted 4′-tolylthiobenzophenones in ethanol

Compound	λ_{max}	$\phi_P{}^a$	τ (ms)^b
1	443, 470	0.14	68.9
2	443, 468	0.31	20.4
3	443, 467	0.49	25.8
4	441, 463	0.99	34.7
5	445, 469	0.23	33.1
6	439, 464	0.18	23.2
7	441, 463	0.88	23.0
8	445, 469	0.32	24.4
9	442, 464	0.90	29.3
10	443, 466	0.62	23.9
11	448, 469	0.66	25.7
12	445, 467	0.80	23.0

[a] ±0.01.
[b] ±0.1.

Table 11
Phosphorescence properties of bistolylthiobenzophenones in ethanol

Compound	λ_{max}	$\phi_P{}^a$	τ (ms)^b
13	444, 474	0.30	14.2
14	451, 476	0.17	19.6
15	440, 470, 505	0.56	11.0

[a] ±0.01.
[b] ±0.1.

Table 12
Phosphorescence properties of 4-amino-, chloro- and nitro-substituted 4′-(4-methylphenylthio)benzophenones in ethanol

Compound	λ_{max}	$\phi_P{}^a$	τ (ms)^b
16	449, 476	0.37	20.1
17	494	0.46	72.3
18	466, 485	0.24	49.3
19	445, 472, 506	0.03	27.8
20	445, 469	0.01	35.0

[a] ±0.01.
[b] ±0.1.

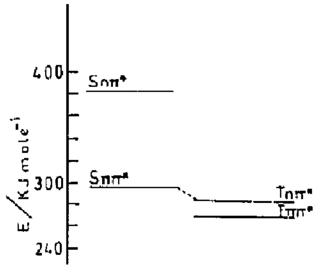


Fig. 1. Energy level diagram for compound 4 in ethanol.

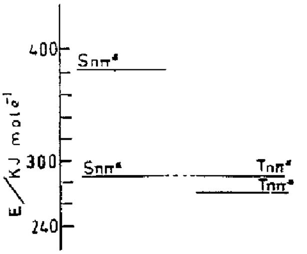


Fig. 2. Energy level diagram for compound **20** in ethanol.

3.3. Photoreduction/photolysis

The photolysis of the compounds in acetonitrile in the presence of an amine (diethylethanolamine) leads to product formation which interferes in the initial absorption measurements. However, during the later stages of irradiation, the photolysis rates can be measured and these are compared in Figs. 3–5. It is interesting to note that a number of compounds undergo rapid photolysis, with the substituted compounds **2**–**12** being more readily photolysed than compound **1**. This correlates with their increased photoinitiation activities during curing and is consistent with their more active $^3n\pi^*$ states. Compounds **13**–**15** photolyse at a much faster rate than **1**–**12**, with the rates following the trend **15** > **13** > **14** (Fig. 4). The latter correlates closely with the corresponding phosphorescence lifetimes (**15** < **13** < **14**) and is consistent with the increasing $^3n\pi^*$ character of the lowest excited triplet state. Compounds **16** and **19** also exhibit short lifetimes and high photolysis rates, whereas compounds **18** and **17** have longer phosphorescence lifetimes and slower photolysis rates (Fig. 5). These derivatives, like the alkylthio derivatives, can therefore undergo direct photolysis via the excited singlet state to give 4-methylphenylthio and aryl radicals [3]. Weak ketyl radical formation has also been observed, but to a much lesser extent than that for benzophenone [10,11].

4. Conclusions

Absorption spectra and solvent shift studies of the compounds under investigation indicate the presence of a long-

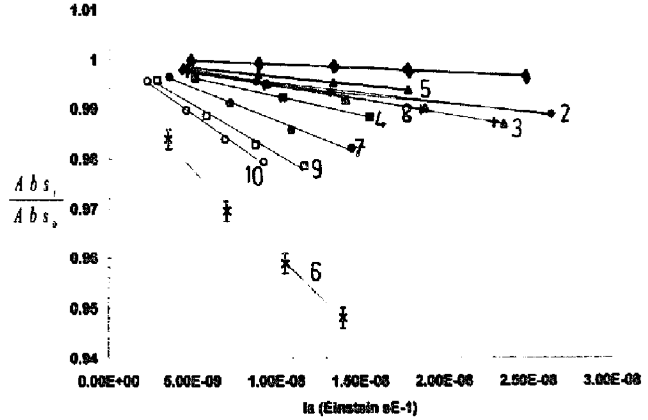


Fig. 3. Relative photolysis rates (absorbance change) of compounds **1**–**12** at 365 nm (einstein s^{-1}) in acetonitrile solvent (10^{-5} M) in the presence of *N*,*N*-diethylethanolamine (10^{-4} M).

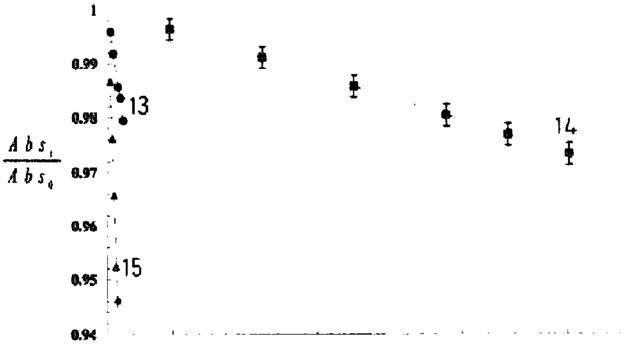


Fig. 4. Relative photolysis rates (absorbance change) of compounds **13**–**15** at 365 nm (einstein s^{-1}) in acetonitrile solvent (10^{-5} M) in the presence of *N*,*N*-diethylethanolamine (10^{-4} M).

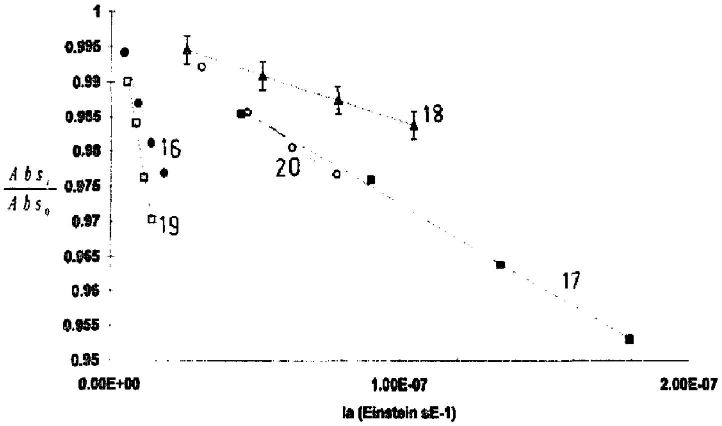


Fig. 5. Relative photolysis rates (absorbance change) of compounds **16–20** at 365 nm (einstein s^{-1}) in acetonitrile solvent (10^{-5} M) in the presence of *N,N*-diethylethanolamine (10^{-4} M).

wavelength singlet $\pi\pi^*$ (charge transfer) state with some $n\pi^*$ character. Compared with the unsubstituted 4-tolylthio derivative, all the alkyl-, alkoxy-, phenyl- and phenoxy-substituted derivatives exhibit higher activity as photoinitiators in the absence of an amine cosynergist. Lengthening or broadening of the alkoxy substituent gives rise to increased photoinitiation activity, but alkyl groups are less effective. The presence of an amine cosynergist enhances photocuring, giving rise to variable effects depending on the nature of the triplet exciplex interaction. The bistolylthio derivatives exhibit the highest photoinitiation activity, whereas the 4-nitro group has a marked deactivating effect. The presence of the 4-amino group also enhances the photoinitiation activity. The fluorescence emission maxima are markedly red shifted with increasing solvent polarity, indicating that the lowest excited singlet state exhibits a high degree of charge transfer character. The lowest excited triplet state of all the 4-substituted 4-tolylthiobenzophenones is essentially a $\pi\pi^*$ configuration, with some $n\pi^*$ character, as indicated by the phosphorescence lifetime data. The lowest excited triplet state of the unsubstituted derivative, on the other hand, is essentially $\pi\pi^*$ in character, explaining its reduced photoactivity. The phosphorescence emission maxima are independent of the nature of the substitution, indicating the presence of rigid molecular structures. The latter is confirmed by the observation of very high phosphorescence quantum yields, with compound 4 approaching unity. The bistolylthio derivatives exhibit shorter phosphorescence emission lifetimes, indicating that their lowest excited triplet state is $n\pi^*$ in nature. The electron-withdrawing effects of the chloro and nitro groups markedly reduce the phosphorescence quantum yields. These effects are accounted for by the relative spacings of the close-lying lowest excited singlet $\pi\pi^*$ and second excited triplet $n\pi^*$ states, controlling the competitive processes of internal conversion within the singlet manifold and intersystem crossing within the triplet manifold. The photoreduction/photolysis rates of all the 4-substituted derivatives are greater than that of the unsubstituted derivative, and show some relation to the nature of the lowest excited triplet state.

Acknowledgements

The authors wish to thank the Comunidad Autonoma de Madrid (CAM) for financial support of Teresa Corrales.

References

[1] K. Dietliker, in: J.P. Fouassier, J. Rabek (Eds.), Radiation Curing in Polymer Science and Technology, Part III: Photoinitiating Systems, Elsevier Applied Science Publishers, London, 1993, Chapter 3, p. 155.
[2] A.W. Green, A.W. Timms, P.N. Green, Proc. Conf. Radtech Europe, Edinburgh, 1991, p. 636.
[3] J.P. Fouassier, D.J. Lougnot, L. Avar, Polymer 36 (1995) 5005.
[4] J.P. Fouassier, D. Lougnot, J. Polym. Commun. 31 (1990) 417.
[5] H. Tomioka, Y. Takimoto, M. Kawabata, M. Harada, J.P. Fouassier, D.J. Ruhlmann, J. Photochem. Photobiol. A: Chem. 53 (1990) 359.
[6] H.J. Hageman, F.P.B. Ban der Maeden, P.C.G.M. Jansen, Makromol. Chem. 180 (1979) 2531.
[7] J.P. Fouassier, D.J. Lougnot, J.C. Scaiano, Chem. Phys. Lett. 160 (1989) 335.
[8] D. Ruhlmann, J.P. Fouassier, Eur. Polym. J. 27 (1991) 991.
[9] D. Ruhlmann, J.P. Fouassier, Eur. Polym. J. 28 (1992) 591.
[10] N.S. Allen, T. Corrales, M. Edge, F. Catalina, M. Blanco-Pina, C. Peinado, A. Green, Eur. Polym. J., in press.
[11] N.S. Allen, T. Corrales, M. Edge, F. Catalina, M. Blanco-Pina, A. Green, Polymer, in press.
[12] J.N. Demas, G.A. Crosby, J. Phys. Chem. 75 (1971) 991.
[13] H.G. Heller, J.R. Lanagan, J. Chem. Soc., Perkin Trans. I (1981) 341.
[14] H.G. Heller, British Patent 7/1464603.
[15] N.S. Allen, E. Lam, J.L. Kotecha, W.A. Green, A. Timms, S. Navaratnam, B.J. Parsons, J. Photochem. Photobiol. A: Chem. 54 (1990) 367.
[16] M. Kasha, Rad. Res. Suppl. 2 (1960) 243.