LASER FLASH PHOTOLYSIS STUDY OF TRIPLETS OF CYCLOBUTANETHIONES

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Summary

Five cyclobutanethiones with different chromophores at the 3-position were examined for triplet state behaviour in benzene using laser excitation into their low lying $n\pi^{*1}$ band systems. A weak transient absorption attributable to the triplet state is observed in all these cases. Results concerning triplet lifetimes, intersystem crossing yields ($S_1 \rightarrow T_1$), self-quenching kinetics and kinetics of energy transfer to all-*trans*-1,6-diphenyl-1,3,5-hexatriene and oxygen and quenching by di-*t*-butyl nitroxide (DTBN) are presented. Intersystem crossing yields estimated with reference to *p,p'*-dimethoxythiobenzophenone are roughly unity in all five cases. Self-quenching rates are found to be less than diffusion limited and this is attributed to steric crowding at the α positions (dimethyl group). The rates of oxygen and DTBN quenching compare well with those reported for several other thiones in the literature. No transients other than the triplet were detected in the above cyclobutanethiones.

1. Introduction

The photophysics of thiocarbonyl compounds, the sulphur analogues of carbonyl compounds, has been overlooked for many years although that of the carbonyl compounds has been known since the beginning of this century. However, the past decade has witnessed a remarkable amount of activity in exploring the excited state behaviour of thiocarbonyl compounds. Recent photophysical studies of thiocarbonyl compounds have revealed that they possess many interesting excited state properties that are not displayed by their oxygen analogues [1]. Although a large amount of data has been collected on aromatic thiones [2 - 4], those on aliphatic thiones are still meagre. It is under these circumstances that we have carried out a flash photolysis study of the short-lived triplets of a number of cyclobutanethiones (1a - 1e,

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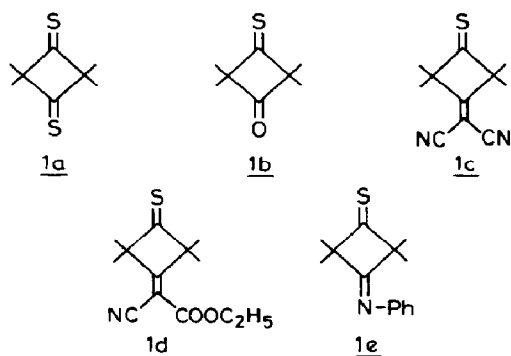
Fig. 1. The cyclobutanethiones investigated.

Fig. 1). We have also sought to identify the intermediates that result from α cleavage upon excitation to T_1 [5].

2. Experimental details

Thioketones were synthesized by following published procedures [6]. They were purified before use by performing chromatography on silica-gel columns. The solvents used were spectral grade from Aldrich. Di-t-butyl nitroxide (DTBN) (Eastman) and benzene (Aldrich, Gold Label) were used as received. p,p'-Dimethoxythiobenzophenone (Aldrich) and all-$trans$-1,6-diphenyl-1,3,5-hexatriene (DPH; Aldrich) were recrystallized from ethanol. For deoxygenation, high purity argon was bubbled through the solutions. In experiments where different concentrations of oxygen were necessary, mixtures of oxygen and nitrogen of known composition (Linde) were used for saturating the solutions. For most of the laser flash photolysis experiments, laser pulses at 337.1 nm (3 mJ, 8 ns, Molectron UV-400) or 532 nm (10 - 100 mJ, 6 ns, Quanta Ray Nd–YAG, second harmonic) were used for excitation at both right angle and front face geometries. The kinetic spectrophotometer and the computer-controlled data collection–processing system have been described previously [7]. Rectangular quartz cells of 2 mm and 3 mm path lengths were used for photolysis in a front face configuration. For measurement of T–T spectra a flow cell was used. Appropriate interference filters (Oriel) were placed in the path of the monitoring light in front of the analysing monochromator to minimize interference from the scattered light and were also placed before the photolysis cell to minimize photochemical deterioration of the solutions. Absorption and emission spectra were recorded using a Shimadzu UV–visible spectrophotometer (model UV-180) and a Shimadzu spectrofluorometer (model RF-540) respectively.

3. Results

In the spectral region 220 - 600 nm, the cyclobutanethiones 1a - 1e (Fig. 1) display three absorption band systems. The spectral data in

TABLE 1

Absorption spectral data of the cyclobutanethiones 1a - 1e in cyclohexane

Compound	S_1		S_2		S_3	
	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})
1a	500	30	298	409	227	21600
1b	530	11	328	110	228	8500
1c	503	11	301	376	229	3650
1d	496	8	301	376	229	2340
1e	518	13	312	312	226	4000

cyclohexane are summarized in Table 1. The weak $n\pi^{*1}$ bands of 1a - 1e are well separated from the intense band systems lying at higher energies (220 - 270 nm). In between these two bands, a band of medium intensity ($\epsilon \approx 100$) is also found. The transitions responsible for these bands have not yet been established. High intensity laser pulses at 532 nm (20 - 80 mJ pulse^{-1}; 6 - 8 ns at full width at half-maximum) were used to flash photolyse 1a - 1e into their $n\pi^{*1}$ bands. Under the conditions of our experiments, only 0.05% - 5% of the laser photons were absorbed by the compounds. An N_2 laser was used in a few experiments to excite thioketones into their second band. The extinction coefficients of the cyclobutanethiones at these two wavelengths differ by one to two orders of magnitude. The laser intensities were adjusted so that in experiments at different wavelengths the excited state and ground state concentrations were comparable with each other.

Short-lived transients assignable as triplets were observed upon 532 nm laser flash photolysis of benzene solutions (0.001 M) of 1a - 1e. The transient spectra obtained by averaging the kinetic traces from 20 - 30 laser shots at each monitoring wavelength are reproduced in Figs. 2 and 3. All five spectra show some similarity both in location and in appearance. The triplet assignment is based on efficient self-quenching and quenching by oxygen, DTBN and DPH. Using 532 nm excitation, the quenching behaviour of the thioketone triplets towards oxygen and DTBN was examined. The decay of the thioketone triplet was monitored under different quencher concentrations. The reciprocal of the observed lifetime was plotted against [Q] from which k_q was calculated. The quenching rates thus obtained are given in Table 2.

The triplet yields, the rate of energy transfer to DPH and the rate of self-quenching were measured indirectly by energy transfer to DPH. This is necessitated by the fact that the signals due to T–T absorption were weak and deterioration of the sample occurred upon absorption of a large number of laser pulses. The procedure adopted was based on monitoring the transient absorbance due to DPH triplets at 420 - 430 nm (this method is described in detail in a previous paper [4]). With each thioketone, the following two sets of experiments were carried out in benzene under 532 nm laser excitation. First, with [TK] = 0.001 M, the k_{obs} (the pseudo-first-order
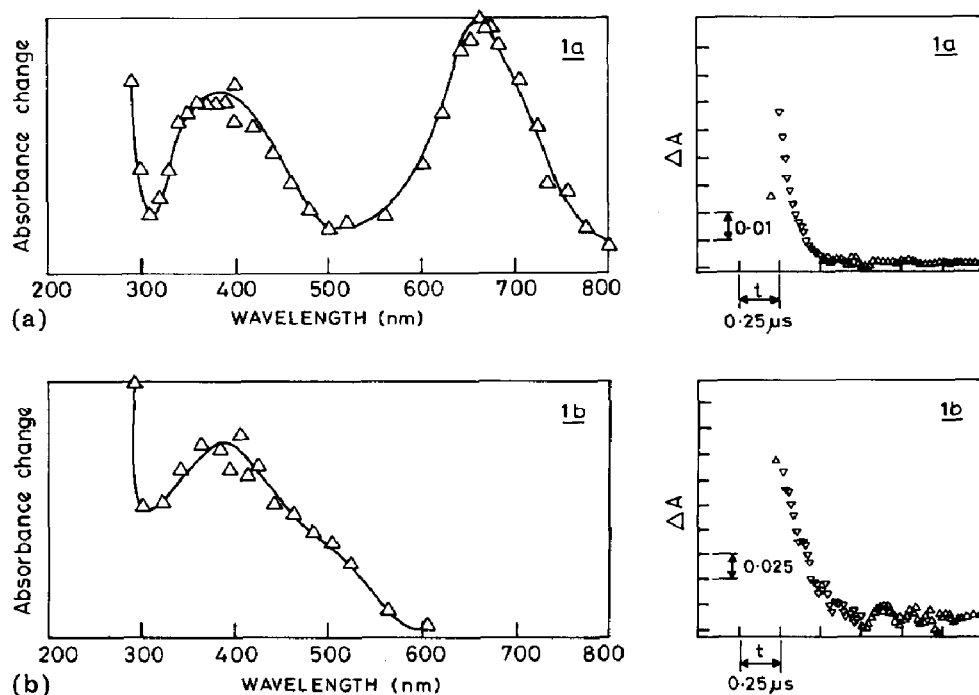
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Fig. 2. Transient absorption spectra observed upon 532 nm laser flash photolysis in deoxygenated benzene of (a) 1a and (b) 1b.
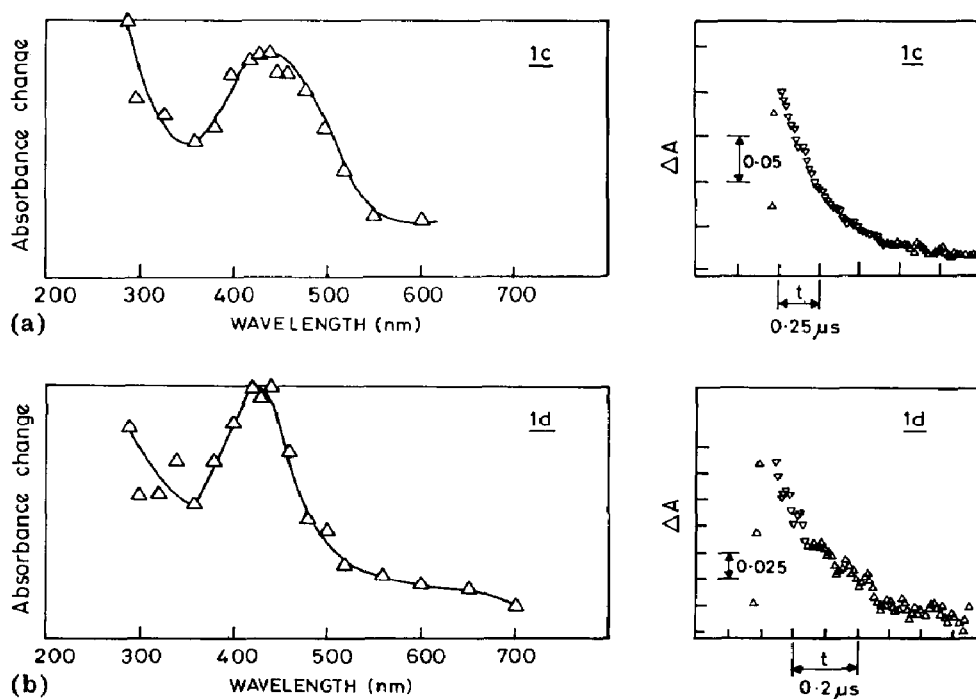

Fig. 3. Transient absorption spectra observed upon 532 nm laser flash photolysis of (a) 1c and (b) 1d.

TABLE 2

Kinetic data for cyclobutanethione triplets in benzene at 296 K

Compound	τ_0[a] (μs)	Quenching data[b]				Φ_{ISC}[c]
		k_{O_2} ($\times 10^{-9}$ M^{-1} s^{-1})	k_{O_2} ($\times 10^{-9}$ M^{-1} s^{-1})	k_{DTBN} ($\times 10^{-9}$ M^{-1} s^{-1})	k_{DPH} ($\times 10^{-9}$ M^{-1} s^{-1})	
1a	0.60 (0.30)	7.2	2.5	3.0	7.4	1.0
1b	0.50 (0.30)	3.5	3.3	2.9	7.7	1.0
1c	0.20 (0.50)	3.3	3.3	2.3	5.7	1.2
1d	0.50 (0.30)	4.0	3.7	2.7	5.8	1.1
1e	0.50 (0.80)	2.0	1.5	4.0	6.5	1.0

[a]Lifetime ($\pm 20\%$) estimated from the plots of k_T^{obs} versus [TK] and k_T^{obs} versus [DPH]; the numerals in parentheses correspond to the latter.
[b]$\pm 15\%$.
[c]$\pm 25\%$.

rate constants for the growth of DPH triplet absorption as a result of energy transfer from thioketone triplets to DPH) were measured for a series of solutions containing different concentrations of DPH in the range 0.0005 - 0.004 M. Representative plots of k_{obs} versus [DPH] are shown in Fig. 4. The slopes of these plots give the bimolecular rate constants $k_{q, DPH}$ for energy transfer from thioketone triplets to DPH while the intercepts give estimates of the thioketone triplet lifetimes at a concentration of 0.001 M. Second, with [DPH] = 0.001 M, the k_{obs} were obtained for a series of solutions containing different thioketone concentrations in the range 0.0005 - 0.005 M. Again the linear plots of k_{obs} against [TK] gave k_{sq} as the slope. Representative plots
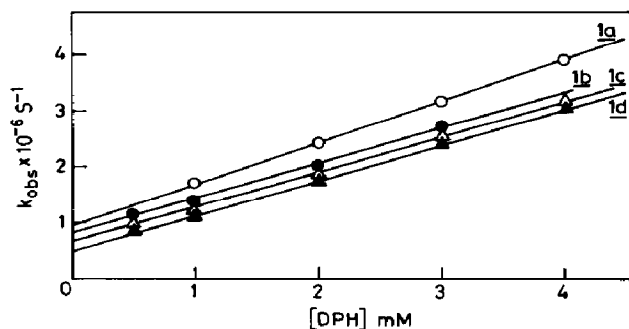

Fig. 4. Typical plots of the observed pseudo-first-order rate constant for the growth of DPH triplet absorption vs. DPH concentration.
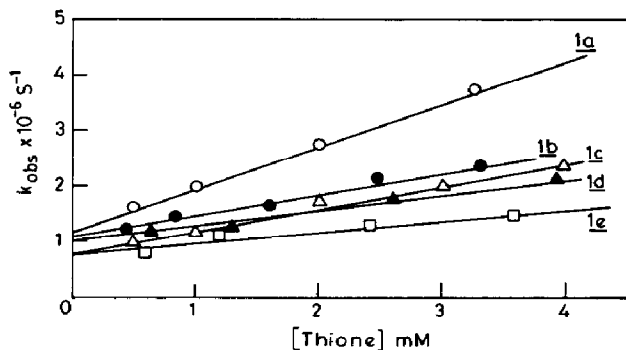
Fig. 5. Typical plots of the observed pseudo-first-order rate constant for the growth of DPH triplet absorption *vs.* thioketone concentration.

are shown in Fig. 5. The data concerning $k_{q, DPH}$ and k_{sq} are summarized in Table 2. The intrinsic triplet lifetime τ_0 of 1a - 1e can be obtained from the intercepts of these two plots. The results thus estimated are shown in Table 2 and a fair agreement is noticeable between the two sets of values. The small disagreement between the two sets of values is a reflection of the large errors associated with the way in which they are measured. In spite of this, both sets suggest submicrosecond lifetimes (intrinsic) for all five thioketones. Also, the direct monitoring of the transient absorption at [TK] = 1 mM using a 532 nm laser gave lifetimes in reasonable agreement with those measured from DPH quenching.

The triplet yields Φ_T of thioketones 1a - 1e in benzene under 532.1 nm laser excitation were determined indirectly by energy transfer to DPH. 4,4'-Dimethoxythiobenzophenone in benzene ($\Phi_T \approx 1$) [2] was used as the reference and the optical density of the solutions at 532 nm was matched at 0.01 in 2 mm cells. Using thioketone solutions (1a - 1e and 4,4'-dimethoxythiobenzophenone) with optical densities matched at 532 nm, the maximum absorbance changes ΔOD_{DPH} due to DPH triplets at 420 nm were measured at DPH concentrations ranging from 0.0025 to 0.02 M. The intercepts of the plots of $1/\Delta OD_{DPH}$ *versus* $1/[DPH]$ (Fig. 6) gave the reciprocal of the relative intersystem crossing efficiencies. Knowing the value of Φ_T for 4,4'-dimethoxythiobenzophenone (1.00) enabled those of the others to be estimated. The intersystem crossing efficiencies thus estimated are within ±20% of unity.

Since cyclobutanethiones 1a - 1e are known to undergo the process of α cleavage [5], attempts were made to detect the diradicals which were presumed to result: 1b and 1c were flash photolysed at 532, 337 and 266 nm and a careful search was made for intermediates other than triplets. Under all these circumstances, absorptions attributable to triplets alone were observed. 1a - 1e exhibit phosphorescence in 3-methylpentane glass at 77 K. No fluorescence either from S_1 or S_2 was detected. Phosphorescence in all cases is due to the thiocarbonyl chromophore and no emission due to the second chromophore present in all of these systems is observed.
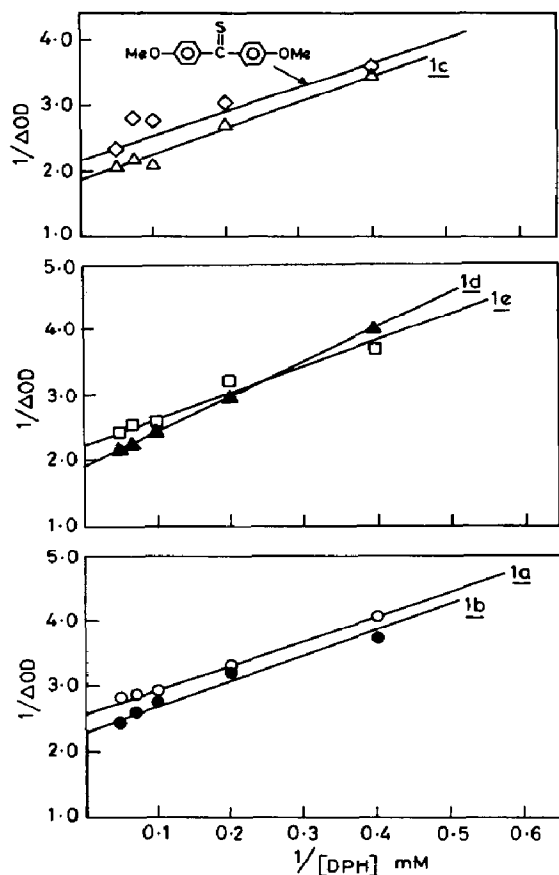
Fig. 6. Double reciprocal plots of the absorbance change due to DPH triplet at 420 nm *vs.* DPH concentration (solvent, benzene).

4. Discussion

On the basis of the phosphorescence spectra in 3-methylpentane at 77 K, the triplet energies of 1a - 1e are estimated to be in the range 48 - 50 kcal mol^{-1}. Therefore, quenching by DPH ($E_T \approx 35$ kcal mol^{-1}) at a near-diffusion-controlled rate is expected. The rates of energy transfer to DPH, as anticipated, do not show any dependence on the structures of 1a - 1e. Thioketones are generally recognized to have intersystem crossing yields close to unity [1]. Our results based on laser flash photolysis with excitation into S_1 corroborate this for cyclobutanethiones. Therefore, it is clear that the intersystem crossing efficiency of the thiocarbonyl moiety is independent of the molecular framework in which it is present. Thus this phenomenon has to be understood solely on the basis of this chromophore. The self-quenching rate constants for the cyclobutanethiones 1a - 1e are rather large. The rates are roughly similar in all cases (1b - 1e) except for 1a. The rate for 1a is twice that of the others; this is understandable as there are two thiocarbonyl chromophores in this molecule. Generally, the rates of self-quenching for

a large number of thiocarbonyls have been reported to be near the diffusion limit [1, 8]. However, a few examples are known in which the rates are lower than the diffusion value [4, 9]. A typical example is di-t-butyl thioketone wherein the self-quenching rate is roughly one hundredth of the diffusion limit. Therefore, unlike the intersystem crossing efficiency, the self-quenching rate is dependent on the nature of the framework in which the thiocarbonyl chromophore is present. In cyclobutanethiones the self-quenching rates are lower than those in aromatic thiones but higher than that of di-t-butylthione. This is consistent with the assumption that steric crowding around the thiocarbonyl chromophore plays a significant role in the self-quenching mechanism. Cyclobutanethiones 1a - 1e wherein the methyl groups are held back by the cyclobutyl ring skeleton have less steric crowding around the thiocarbonyl chromophore than in di-t-butylthione. Therefore a rate of self-quenching higher than that in di-t-butylthione is expected and is indeed observed.

The observed quenching rates of the thiones 1a - 1e by DTBN are lower than the diffusion value ($3 \times 10^9 \, \text{M}^{-1} \, \text{s}^{-1}$) but are similar to those for the DTBN quenching of aromatic thione and di-t-butylthione triplets [2, 4]. Based on literature reports [10] on the quenching of aromatic triplets by DTBN, an energy transfer process is expected to dominate during the quenching of triplets of 1a - 1e by DTBN. However, in aromatic thione systems, energy transfer is not expected and the quenching is attributed to an electron-exchange process. Although a lower than diffusion-limited value is not unprecedented for a sterically restricted triplet–triplet energy transfer process, the closely similar quenching rates observed with thiones having different triplet energies and steric hindrances suggest that the principal mechanism of DTBN quenching of thiocarbonyl triplets is an electron-exchange process; this is represented by

$$\text{TK}^{*3} + \text{DTBN}^2 \rightleftharpoons (\text{TK}^* \cdots \text{DTBN})^2 \longrightarrow \text{TK}^1 + \text{DTBN}^2 \qquad (1)$$
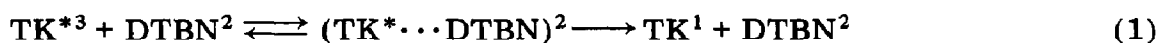
The oxygen quenching data in Table 2 show that k_{O_2} for the triplets of the cyclobutanethiones 1a - 1e is $(2/9)k_{\text{diff}}$ where k_{diff} ($1.6 \times 10^{10} \, \text{M}^{-1} \, \text{s}^{-1}$) is the rate constant for diffusion in benzene. Generally, the rate constants for triplet quenching by oxygen are predicted on the basis of spin-statistical considerations to have a value of about $(1/9)k_{\text{diff}}$. However, values ranging from $(1/9)k_{\text{diff}}$ to $(4/9)k_{\text{diff}}$ have been reported for the oxygen quenching of thione triplets [1]. The rates of oxygen quenching for most aliphatic and aromatic thiones lie in a similar range $((2.5 - 4.0) \times 10^9 \, \text{M}^{-1} \, \text{s}^{-1})$. The slightly higher rates observed for Michler's thiones ($0.97 \times 10^{10} \, \text{M}^{-1} \, \text{s}^{-1}$) and N-methylthioacridone ($1.2 \times 10^{10} \, \text{M}^{-1} \, \text{s}^{-1}$) may be due to the presence of an amino group which is also known to participate in the quenching process. Two possible explanations for the observation of $k_{O_2} > (1/9)k_{\text{diff}}$ have been offered. These are a charge transfer quenching mechanism and a spin–spin interaction mechanism [11]. If the charge transfer mechanism operates (partial electron transfer from thiocarbonyl triplets to oxygen) one would expect a linear correlation between the quenching rate and the ionization

potential of the n electrons (although the electron shared is from the π^* orbital of the thione one can roughly estimate the energy of the π^* orbital from the energies of the n orbital and the $n\pi^*$ transition). However, no such correlation is observed. For example, di-*t*-butylthione and **1a**, which have a similar $n\pi^*$ energy gap, have a significant difference in their n-orbital energies (7.8 eV and 8.32 eV respectively [12]). However, the quenching rates are close ($4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ respectively). This becomes all the more evident when one compares thiobenzophenone with **1a**. Thiobenzophenone, with an n-electron energy of 8.0 eV [13] and an $n\pi^*$ energy gap of only 42 kcal mol^{-1}, is quenched by oxygen at $2.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Therefore, we tentatively conclude that the charge transfer mechanism may not be solely responsible for the slightly large quenching rates by oxygen. Yet another possible mechanism involves spin–spin interaction. In a first-order approximation, the charge transfer mechanism would result in a lower yield of O_2^{*1} whereas the spin–spin interaction mechanism would result in unit efficiency. All the thiones so far studied exhibit quantitative production of singlet oxygen [2, 4, 14]. High values of singlet oxygen production and large k_{O_2} favour the spin–spin interaction mechanism over the alternative charge transfer mechanism for oxygen quenching of thione triplets.

It is interesting to compare the T–T spectra of thiocarbonyl compounds. Aromatic thiones (thiobenzophenone, *p,p'*-dimethoxythiobenzophenone, Michler's thiones, xanthione and thioxanthione) possess T–T absorptions in the region 280 - 650 nm [2]. However, negative absorbances are observed for some of these compounds in the range 380 - 440 nm because of ground state depletion in the spectral region corresponding to the $S_0 \rightarrow S_2$ transition. No reports on arylalkylthione triplets have appeared. However, a few reports on aliphatic thiones have been published [3, 4]. For example, the triplet of adamantanethione absorbs in the region 280 - 350 nm and presumably also at shorter wavelengths. Another example is di-*t*-butylthione. With the di-*t*-butylthione triplet a very weak absorption is observed in the region 280 - 400 nm. A similar weak absorption is also noticed for several [2.2.1] bicyclic thiones [15]. The cyclobutanethiones **1a** - **1e** investigated here can be classified as aliphatic thiones. The T–T spectra of **1b** - **1e** are very similar and they show absorption in the region 280 - 600 nm. In addition to the presence of a possible maximum below 280 nm, another maximum is seen in the region 400 - 450 nm in all these cases. It is important to note that such a transition is absent in di-*t*-butylthione and adamantanethione. At this stage, it is not clear whether such a transition can be attributed to the possible interaction of the thiocarbonyl chromophore with the other chromophore present at the 3-position of the cyclobutyl skeleton. An interesting observation has been made in the case of 1,3-cyclobutanedithione (**1a**). The T–T spectrum consists of three bands in the spectral region 280 - 800 nm. Three absorption maxima are observed: one below 280 nm, the second at 400 nm and the third at 680 nm. In this compound it has been established through an ultraviolet photoelectron spectroscopy (UVPES) study [16] that there is an interaction in the

ground state between the two thiocarbonyl chromophores. The He–I photoelectron spectrum of **1a** shows the two sharp bands of the thiocarbonyl group at 8.32 eV and 8.74 eV indicating an n-orbital splitting of 0.42 eV. Such an interaction is even seen in the electronic absorption spectrum. The $n\pi^*$ band of **1a** exhibits two distinct bands around 427 nm and 492 nm in methanol, showing a separation of 0.4 eV, probably corresponding to the n-orbital splitting found in UVPES. It is quite likely that the presence of an additional band at 670 nm in the T–T spectra of **1a** is due to the presence of additional states resulting from 1,3-interaction.

Acknowledgment

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