Deactivation of the S_2 and Two Lowest Triplet States of 4*H*-1-Benzopyran-4-thione and Its Alkyl Derivatives in Methanol Solution

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Spectral and photochemical properties of three aromatic thioketones, 4*H*-1-benzopyran-4-thione and its two alkyl derivatives, in their second excited singlet and two lowest triplet states have been a subject of stationary and time-resolved studies. Quantum yields of emissions from the above-mentioned states as well as lifetimes of these states have been measured. The results indicate an important role of intermolecular solvent-induced processes in deactivation of the excited states of the thioketones studied. The possible mechanism of these processes involves hydrogen atom abstraction and/or formation of exciplex. For relatively high thione concentrations, the contribution of self-quenching in deactivation of the triplet states becomes significant. The effect of the alkyl chain in a thione molecule on deactivation parameters is discussed.

INTRODUCTION

Aromatic thioketones have attracted considerable interest due to their intriguing spectral, photophysical, and photochemical properties. The energy gaps between the second and the lowest excited singlet states of their molecules are sufficiently large to inhibit radiationless relaxation of the S_2 state, so that a radiative process, S_2 fluorescence, can compete with radiationless deactivation processes of the S_2 efficiently enough for the S_2 fluorescence to be readily detected [1–7]. Another relatively strong room-temperature emission is phosphorescence from the two lowest thermally equilibrated triplet states [1,8–12]. Photochemical reactions can occur from the second excited singlet [1,13,14], the triplet states of thione molecules [1,15,16], and, more seldom, the lowest excited singlet state [17]. Extensive stationary and time-resolved investigations of the deactivation of the excited states of thiocarbonyl compounds have shown the high reactivity of the S_2 state [6,7,18–22] and, to some extent, also the triplet states [12,23,24]. This property of thioketones is the reason that, in all common solvents except perfluoro-alkanes and perfluorocycloalkanes (PF), intermolecular processes connected with interaction of an excited thioketone molecule with a solvent are the dominating pathways of deactivation of the S_2 state [25]. The contribution of a solvent in deactivation of the triplet states depends on their energy [26], the kind of solvent [12,23], and the concentration of the thioketone [12,23,24,27]. One of the most interesting processes involving thione triplet is its

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quenching by molecules of the same kind in the ground state (self-quenching, concentration quenching) occurring at diffusion-controlled rates [12,23,27–31]. In PF and alkanes at concentrations higher than $1 \cdot 10^{-5}$ *M*, this bimolecular process is the most important deactivation pathway of the T_1 state. Despite the high reactivity of the excited states of thioketone molecules, photochemical reactions often occur at small quantum yields because of the efficient fast processes involving primary products leading to a chemically unchanged thioketone molecule [7,12,32–34]. The S_1 state is very short-lived due to the highly efficient fast decay to T_1, and hence no prompt fluorescence from this state can be observed [35,36]. At sufficiently high temperatures the S_1 state can be populated via back-intersystem crossing, and in the case of aromatic thiones, thermally activated fluorescence from this state in some solvents has been observed [37–39]. Spectral properties of thioketones (particularly the position of the $S_0 \rightarrow S_1$ absorption band) depend strongly on the environment. The strong dependence of the spectral as well as the photophysical properties of thioketones on the environment permitted their use as convenient probe in studies of microorganized media [22,40–43].

Most studies of photophysics of aromatic thioketones have been carried out in PF and alkanes. The aim of this investigation was to describe the properties of one of the most thoroughly studied thioketones, 4*H*-1-benzopyran-4-thione (benzopyrantion; BPT), and its two alkyl derivatives (Fig. 1), in a more polar and strongly interactive solvent—methanol. The two derivatives differ from each other in having an alkyl chain of different length at position 2. The alkyl chain in a 2-decyl-4*H*-1-benzopyran-4-thione (BPTC$_{10}$) molecule, contrary to that in 2-butyl-4*H*-1-benzopyran-4-thione (BPTC$_4$), is long enough for direct interaction between the alkyl group and the reactive thiocarbonyl group to take place. The alkyl substituent can influence the properties of an excited thione molecule in a threefold way. First, an electron-donor alkyl group modifies by induction effect the electron density distribution, in particular, perhaps increasing
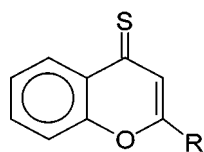
BPT - R = H
BPTC$_4$ - R = n-C$_4$H$_9$
BPTC$_{10}$ - R = n-C$_{10}$H$_{21}$

Fig. 1. Structures of BPT (4*H*-1-benzopyran-4-thione), BPTC$_4$ (2-butyl-4*H*-1-benzopyran-4-thione), and BPTC$_{10}$ (2-decyl-4*H*-1-benzopyran-4-thione).

the electron density on the thiocarbonyl group, leading to a possible change in reactivity of the thiocarbonyl group. Second, the substitution can change the positions of molecular energy levels, which can affect both intra- and intermolecular deactivation of an excited thione molecule. Third, the interaction between the alkyl and the thiocarbonyl group of an excited thioketone molecule provides the possibility for a new inter- and, more importantly, intramolecular channel of deactivation of excited states to appear [44]. This additional intramolecular process is possible only in the derivative with the longer substituent.

EXPERIMENTAL

BPT, BPTC$_4$, and BPTC$_{10}$ were synthesized and purified by methods described elsewhere [12,45]. UV/VIS absorption spectra were taken on an M40 Specord (Carl Zeiss, Jenna) and UV-VIS-550 (Jasco), whereas fluorescence and phosphorescence spectra were recorded on a modified MPF-3 (Perkin–Elmer) spectrofluorimeter. The modifications introduced enabled a single-photon counting detection, computer control, and data processing using a dual-photon counting set (Light Scan). The spectrofluorimeter was also equipped with a reference quantum counter, which measured the intensity of incident light, directly in front of the sample. Emission measurements were carried out upon excitation to the S_2 state on air-equilibrated (fluorescence) and deoxygenated (phosphorescence) samples. Deoxygenation was carried out by bubbling oxygen-free helium through the solutions. All emission spectra given here were corrected for the photomultiplier tube response, and the background due to solvent impurities and scattering was subtracted. To avoid overestimation of Raman scattering in the sample, which is lower than in the pure solvent, the contribution due to Ramman scattering in the solvent was multiplied by transmittance of the sample for excitation wavelength. Quantum yields of emission ϕ were measured using the relative method, taking into account appropriate solution refractive index corrections [46]. Quinine bisulfate in 0.05 *M* H$_2$SO$_4$, $\phi_F = 0.52$, was used as a standard [47]. The S_2-fluorescence lifetimes τ_{S_2} were measured using a TCSPC spectrometer, FWHM $\sim$ 30 ps (Fig. 2), described in detail elsewhere [48]. It is characterized by the exceptional work stability of the whole system, which ensures the IRF constant (changes only within <0.5 ps). Consequently, picosecond lifetimes can be measured to a high accuracy and at a high repeatability [49]. Triplet lifetimes τ_T were measured using a laser flash photolysis system of nanosecond resolution [50].
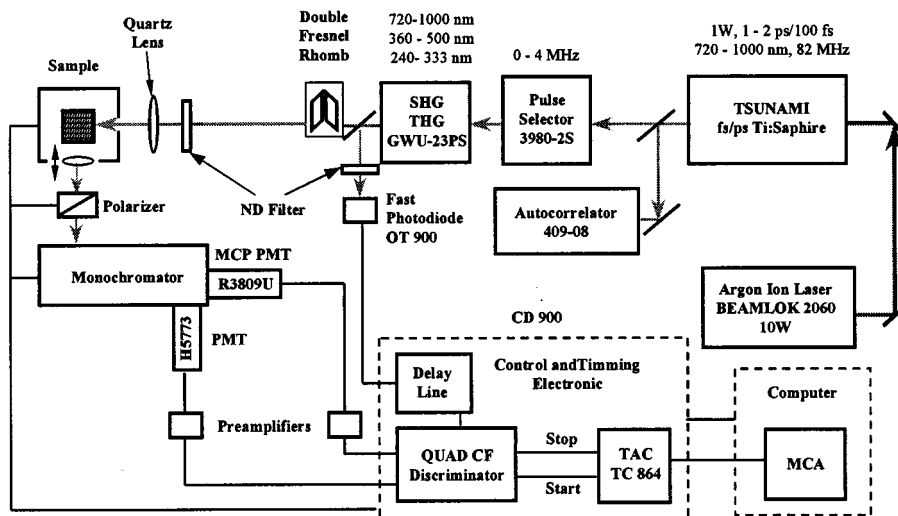
Fig. 2. A schematic diagram of the TCSPC system.

RESULTS AND DISCUSSION

Absorption spectra of BPT and $BPTC_{10}$ are shown in Fig. 3, the spectrum of $BPTC_4$ is very similar to that of $BPTC_{10}$. The strong band in the near UV is assigned to the electric-dipole allowed $S_0 \rightarrow S_2$ ($\pi \rightarrow \pi^*$) transition, while the much weaker one in the visible to the electric-dipole forbidden $S_0 \rightarrow S_1$ ($n \rightarrow \pi^*$) transition [1, 9, 51]. Perhaps the latter overlaps the band corresponding to the $S_0 \rightarrow T_1$ transition, which is observable as a distinct band in PF and alkanes [12, 52]. The $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ bands are stronger for the two alkyl derivatives than for the unsubstituted compound as shown in

Table I. A change of the solvent from very weakly interactive PF to methanol results in a loss of vibrational structure in absorption spectra of the three thioketones (only for BPT can very weak traces of vibrational structure in the $S_0 \rightarrow S_2$ band be observed). Excitation at the region of the $S_0 \rightarrow S_2$ band results in two emissions, S_2 fluorescence and phosphorescence, as shown in Fig. 4.

Since the measured quantum yields of photochemical decomposition of BPT in both PF and methanol on excitation to the S_2 state are not higher than $1 \cdot 10^{-3}$ and the highest S_2-fluorescence quantum yield for the thiones studied is as low as 0.025 [for deoxygenated BPT solution in perfluoro(tetradecahydrophenantrene)] [53], the radia-
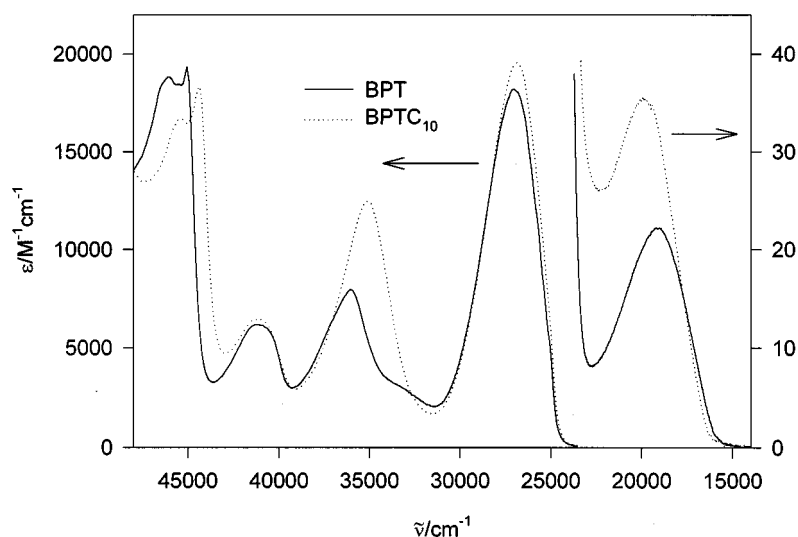

Fig. 3. Absorption spectra of BPT and $BPTC_{10}$ in methanol.

Table I. Spectral Properties of BPT, BPTC$_4$, and BPTC$_{10}$ in Methanol

Thioketone	$\epsilon_{max}(S_0 \to S_1)$ (M^{-1} cm^{-1})	$\tilde{\nu}_{max}(S_0 \to S_1)$ (cm^{-1})	$\epsilon_{max}(S_0 \to S_2)$ (M^{-1} cm^{-1})	$\tilde{\nu}_{max}(S_0 \to S_2)$ (cm^{-1})
BPT	22.2 ± 0.7	19,010	$18,220 \pm 60$	27,030
BPTC$_4$	33.6 ± 0.9	19,900	$19,550 \pm 80$	26,850
BPTC$_{10}$	35.4 ± 1.3	19,920	$19,550 \pm 110$	26,850

tionless processes constitute a dominating pathway of the decay of the S$_2$ state in inert as well as reactive solvents. In the present study the decay of this state was investigated by monitoring temporal evolution of thione emission in the picosecond time range by TCSPC and by stationary emission measurements. No additional emission bands were observed in the fluorescence spectra on the solvent change from PF to methanol. All emission

Fig. 4. (a) Emission spectra of BPT and BPTC$_{10}$ in methanol normalized to the same intensity of absorbed light; $\lambda_{exc} = 360$ nm; thione concentration, ca. $1.7 \cdot 10^{-5}$ M. (b) Emission spectra of BPT in water and in hexane; $\lambda_{exc} = 360$ nm; BPT concentration, ca. $1.2 \cdot 10^{-5}$ M.

decays can be treated as monoexponential. However, careful analysis of emission decays shows a very small contribution of emission of a longer lifetime. This may originate from the S$_2$ exciplex. This problem will be the subject of further studies.

The solvent can influence the rate of intramolecular and intermolecular processes responsible for deactivation of the S$_2$ state. The main intramolecular process from the S$_2$ state is S$_2$~>S$_1$ transition [54]. Measurements of the lifetimes of several rigid aromatic thioketones in very weakly interactive PF, in which the decay of the S$_2$ is entirely intramolecular, have shown that the logarithm of the rate constant of this process depends linearly on the energy gap between the second and the lowest excited singlet states [$\Delta E(S_2 S_1)$] according to the energy gap law [6]. Spectral studies of BPT in various solvents have demonstrated that the S$_2$S$_1$ energy gap clearly depends on the solvent becoming narrower in solvents characterized by a high polarity and the ability to form a hydrogen bond with the thione molecule [55]. Since the S$_2$~>S$_1$ transition takes place between relaxed states [21], information about energies of the S$_2$ and S$_1$ states involved in this transition was obtained from emission and absorption spectra, respectively. Values of the solvent-dependent rate constant of the S$_2$~>S$_1$ internal conversion process ($k_{nr\ intra}$) in methanol for the three thioketones could be estimated from the relation between the S$_2$S$_1$ energy gap and this rate constant determined for a series of rigid aromatic thioketones in PF. The values obtained for BPT and its alkyl derivatives in methanol by this method are given in Table II. Although these values are indeed significantly higher than those determined in PF, it is not an increase in the rate of intramolecular decay but interaction with the solvent that is the main factor (especially for BPT) leading to a strong shortening of the S$_2$ lifetimes observed in methanol. The quenching of S$_2$ fluorescence of thiones by various quenchers in PF has been extensively studied by stationary [20] and time-resolved studies [7,18,19,56]. It has been well established that for a wide range of quenchers, the rate constants of the process are high, often close to those of diffusion-controlled processes. More detailed investigations have demonstrated a significant contribution of the transient effect connected
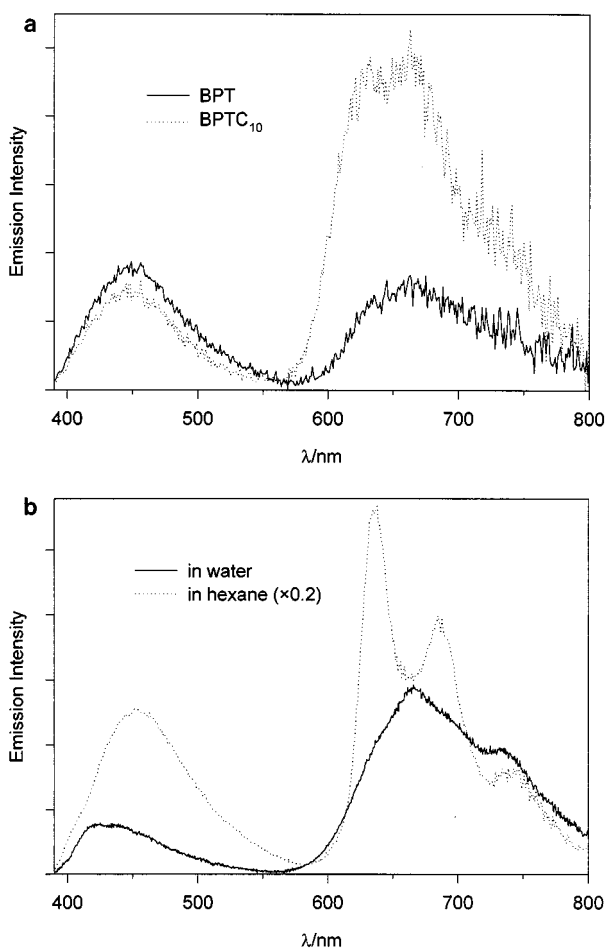
Table II. Photophysical Properties of the S_2 State of BPT, BPTC$_4$, and BPTC$_{10}$ in Perfluoro-1-Methyldecaline[a] and Methanol

Thioketone	Solvent	$\Delta E(S_2 S_1)$ (cm^{-1})	ϕ_{fl} (10^{-2})	τ_{S2} (ps)	k_{fl} (10^8 s^{-1})	$k_{nr\ intra}$ (10^{10} s^{-1})	k_s (10^{10} s^{-1})
BPT	PFMD[d]	8590	2.5[b]	180[b]	1.4	0.55	—
	Methanol	6370	0.062	7	0.9	2.6	12
	Methanol-d$_1$	—[c]	0.079	8	1.0	2.6	10
	Methanol-d$_4$	—[c]	0.14	13	1.1	2.6	5.4
BPTC$_4$	PFMD	8050	1.4[b]	101[b]	1.4	0.99	—
	Methanol	5830	0.055	7	0.8	3.8	10
BPTC$_{10}$	PFMD	8050	1.3[b]	97[b]	1.3	1.0	—
	Methanol	5830	0.053	7	0.8	3.8	10

[a] Taken from Ref. 53.
[b] For deoxygenated solution.
[c] Assumed the same as for methanol.
[d] Perfluoro-1-methyldecaline, k_{fl} was calculated from $\phi_{fl} = k_{fl} \times \tau_{S_2}$.

with time evolution of the quencher concentration around a donor molecule in the quenching process due to the relatively short lifetime of the latter [57]. The quenching process in PF spiked with a quencher can be divided into two stages: diffusion of a quencher molecule to a donor, resulting in formation of an encounter complex at a rate constant k_{diff}, and a reaction leading to a chemically distinct product, namely, a radical or an exciplex, occurring at a rate constant k_r. These products must be nonemissive since no new emission bands could be observed under these conditions. In a pure solvent acting as a quencher the diffusion stage is not needed for the quenching process to take place. Thus, the rate constant of quenching by pure solvent k_s can be compared to the rate constant of the chemical stage of the quenching process k_r. The values of k_s given in Table II can be determined assuming that $1/\tau_{S_2}$ is given as $k_{fl} + k_D + k_{nr\ intra} + k_s$, where k_D is a negligibly small decomposition rate constant from the S_2 state. Because only a small fraction of thione molecules undergoing intramolecular radiationless decay from the S_2 state bypasses the S_1 state [54], it is reasonable to use the values of $k_{nr\ intra}$ applying the energy gap law as described above. A few interesting conclusions can be drawn from analysis of the values given in Table II. Methanols of any isotopic composition are very efficient quenchers of the S_2 states, which is indicated by the much lower quantum yields of S_2 fluorescence and much shorter lifetimes of the S_2 state in these solvents in comparison with those measured in PF and, most evidently, by the very high k_s, of the order of 10^{11} s^{-1}. Because of the high k_s, the intermolecular decay is the main path of the thione molecules in their S_2 state decay, probably through an S_2-exciplex, to lower-lying electronic states [58]. The S_2 states of BPT and its derivatives are extremely reactive to methanol, and this accounts for the fact that k_s for all the three thioketones take similar values. To address the

issue of the mechanism of quenching of the S_2 state, the values of τ_{S_2}, ϕ_{fl}, and k_s for BPT in methanol and its deuterated analogues should be compared. The parameters of deactivation of the S_2 state given in Table II indicate that the efficiency of intermolecular deactivation decreases with increasing degree of deuteration. This strong isotopic effect observed on deuteration of methyl group shows that an important process responsible for the decay of the S_2 state is interaction with a C–H (or C–D) bond, leading to its weakening or even breaking. This process must be almost entirely reversible as in alkanes since excitation to the S_2 state results in very little net photochemistry. Because radiationless deactivation of the S_2 state of BPT in methanol is distinctly faster than in alkanes (τ_{S_2} = 24 ps in 3-methylpentane [7]), even when their molecules possess C–H bonds of energy lower than the energies of C–H or O–H bonds in methanol, we can conclude that there must be another intermolecular pathway of deactivation of the S_2 state in methanol. The quenching of the second excited state of thioketones by molecules lacking abstractable hydrogen atoms like benzene has been attributed to the formation of a complex between S_2-thione and solvent [7]. Recently some evidence for the formation of such a complex (exciplex) in the xanthione–benzene system, from transient absorption experiments on the picosecond time scale, has been reported [58]. Although the nature of molecular interactions between molecules of BPT or its derivatives in the S_2 state and methanol in a possible complex would be different from that in the above-mentioned exciplex, an analogous quenching mechanism may also be operating in the system described in this paper. The conclusion about the importance of this mechanism is supported by the isotopic effect upon deuteration of hydroxyl group in methanol molecules. In view of our findings, the interaction with the hydroxyl group as well as the reversible

hydrogen abstraction from the methyl group accounts for the fast decay of the S_2 state of BPT and its derivatives in methanol. The lifetimes of the S_2 state obtained for the three tocketones in methanol can be compared with that obtained for xanthione in the same solvent (13 ps) [21]. The latter is much longer than that obtained for BPT and its two derivatives, which can be explained by the lower energy of the S_2 state of xanthione and thus its lower reactivity toward the solvent.

Due to effective spin–orbit coupling, radiative life-times for thione triplets are relatively short and the phosphorescence of thiones in solution at room temperature can be readily observed [8–12]. The phosphorescence spectra of BPT and BPTC$_{10}$ (for the other alkyl derivative of BPT, the shape of the spectrum is practically identical) are given in Fig. 4a. The shape of the phosphorescence spectra of thioketones depends on the configuration of the states from which phosphorescence originates. In non-polar solvents (e.g., PF, alkanes) the lowest triplet state (T_1) of aromatic thicketones has the (n,π^*) configuration, while the second triplet (T_2) state is characterized by the (π,π^*) configuration. In highly polar solvents (acetonitrile, water), an inversion of the two triplet states occurs [22, 59]. The difference in the configuration of the lowest triplet state for thiones dissolved in solvents of various polarity manifests itself in the shape of the phosphorescence spectrum as shown in Fig. 4b. The shapes of the phosphorescence spectra of the three thiones studied indicate the contribution of both triplet states in emission, which means that both states are of similar energy. However, it should be noted that all phosphorescence decays were perfectly monoexponetial despite involvement of the two states in the emission. Likewise for xanthione [59], it can be explained in terms of strong vibronic coupling and thermal equilibrium between these states.

The two lowest triplet states are efficiently populated upon excitation to the S_1 and higher singlet states including S_2 [54]. Since the quantum yields of photochemical decay of BPT and its derivatives on excitation to the S_2 state are very low (*vide supra*), like those of phosphorescence, we can conclude that the deactivation of the two lowest triplet states is mainly radiationless.

The triplet lifetimes obtained from the analysis of the phosphorescence decays are concentration dependent (Fig. 5), which can be ascribed to the occurrence of self-quenching [12,23,28–31]. The concentration dependence of $1/\tau_{ph}$ observed can be described by the Stern–Volmer equation:

$$\frac{1}{\tau_{ph}} = k_0 + k_{sq} \text{ [thione]}$$

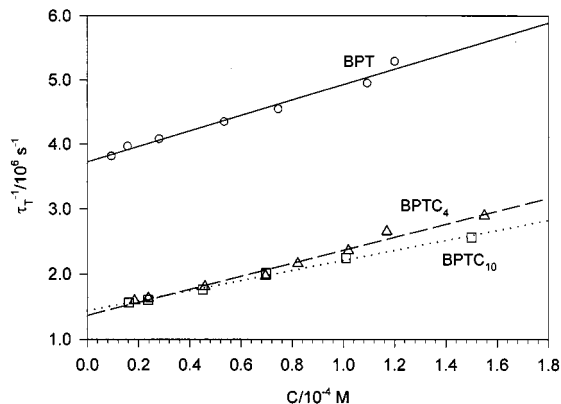where k_0 denotes the phosphorescence decay rate constant

Fig. 5. Plots of $1/\tau_T$ vs BPT, BPTC$_4$, and BPTC$_{10}$ concentration in methanol.

extrapolated to infinite dilution and k_{sq} is the self-quenching rate constant. All the values of k_{sq} are high, close to the rate constants of diffusion-controlled processes (Table III). They show a clear dependence on the presence and the length of the alkyl substituent in a thione molecule. This dependence can be explained as related to two possible factors. First, the addition of the alkyl chain to a thione molecule must result in a chain length-dependent decrease in the diffusion coefficient without increasing the effective radius of the molecule, since the alkyl chain is practically inactive in the self-quenching process. Second, an alkyl chain may constitute a steric hindrance, making the reactive centers in the thioketone molecule less accessible for another molecule of the same kind. Extensive studies on self-quenching have shown that this process involves two thiocarbonyl groups, one of an excited molecule and the other of a molecule in the ground state, the n-orbital of the latter acting as a donor toward the sulfur atom of the former [30,60]. This process is practically reversible since the formation of a photochemical product due to this process (1,3-dithiane) is inefficient

Table III. Triplet Decay Parameters of BPT, BPTC$_4$, and BPTC$_{10}$

Thioketone	Solvent	ϕ^0_{ph} $(10^{-3})^a$	τ^0_T (μs)	k_{sq} $(10^{10}\ M^{-1}\ s^{-1})$
BPT	PF-1,3-DMCH^{b,c}	76	16	0.69
	3-MP^{b,d}	32	7.3	2.0
	Methanol	0.84	0.27	1.2
BPTC$_4$	Methanol	2.7	0.73	1.0
BPTC$_{10}$	Methanol	2.7	0.70	0.77

^{a} On excitation to the S_2 state.
^{b} Taken from Ref. 12.
^{c} Perfluoro-1,3-dimethylcyclohexane.
^{d} 3-Methylpentane.

[24]. A decyl chain is long enough to shield, in some of its conformations, a thiocarbonyl group, decreasing the efficiency of the self-quenching process. Moreover, there is some indirect but convincing evidence from studies on photochemistry of the triplet state of BPT and its derivatives [24] that there may be two other possible channels of concentration quenching in these molecules, namely, interaction of the thiocarbonyl group of a thione molecule with the double bond of another one and interaction of the double bonds of two thione molecules. In the case of unsubstituted BPT all three channels of self-quenching lead, at low quantum yields, to the formation of photochemical products, which have been analyzed chromatographically (HPLC). However, in the case of the derivatives with an alkyl group at position 2, owing to the steric hindrance, the only product formed as a result of self-quenching is the corresponding 1,3-dithiane, which indicates that the other two channels of self-quenching do not play a significant role in deactivation of their triplets. This may also explain the observed differences between k_{sq} for the three thiones.

The kinetics of the triplet deactivation was investigated by monitoring the decay of relatively weak phosphorescence ($\phi_{ph} \leq 2.4 \cdot 10^{-3}$), and it was concluded that to achieve a sufficient accuracy of the measurements, it was necessary to apply an energy of exciting pulses as high as 1–5 mJ (for some selected samples the measurements were carried out at a lower energy to establish whether or not the triplet lifetime depends on the pulse energy). Taking into account presumably high quantum yields of triplet formation (for similar systems it was always higher than 0.5 [54]), there is another possible bimolecular process of triplet deactivation, namely, triplet–triplet annihilation. This process can occur according to two possible mechanisms [61]:

$$\text{triplet} + \text{triplet} \rightarrow S_2 + S_0 \qquad (1)$$

$$\text{triplet} + \text{triplet} \rightarrow \text{triplet} + S_0 \qquad (2)$$
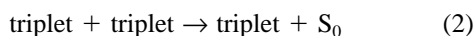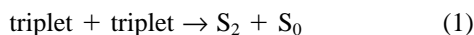
If mechanism (1) had a significant part in triplet deactivation, it would lead to a noticeable shortening of the triplet lifetime with increasing pulse energy. Since this is not the case, we can conclude that mechanism (1) does not play an important role in the deactivation of the triplet state of the thioketones. This is in agreement with the findings of Nickel and co-workers [62], who established that the quantum yield of the formation of S_2 through triplet–triplet annihilation of BPT in perfluoro-1,3-dimethylcyclohexane was as low as 0.03. Because we cannot expect that either the effective radius or the diffusion coefficient of a thione molecule in the triplet state is markedly different from these parameters in the ground

state, the annihilation process occurring according to mechanism (2) has the same impact on the kinetics of triplet deactivation and its concentration dependence as self-quenching. Interestingly, mechanism (2) implies that two thione molecules are in close proximity, which is a necessary condition of self-quenching. This explains the fact that no significant dependence of the triplet lifetime on the pulse energy was observed.

The Stern–Volmer treatment of experimental phosphorescence data also provides the triplet lifetimes extrapolated to infinite dilution (τ_T^0). Not disturbed by the concentration-dependent processes (self-quenching and triplet anihilation), these values enable us to determine the role of intramolecular and solvent-induced deactivation processes. The values for BPT given in Table III illustrate the effects of replacement of an inert solvent (PF) by methanol on the deactivation rate of the triplet state. In infinite dilution, only intramolecular processes are responsible for deactivation of the triplet state of thioketones in deoxygenated PF solution [12]. In methanol there is an additional important channel of deactivation—interaction with the solvent. The occurrence of this channel results in much shorter triplet lifetimes and lower phosphorescence quantum yields (ϕ_{ph}^0) for methanol solutions of the thioketones (Table III). If we assume that the rate constant of intramolecular deactivation processes of BPT in PF and methanol are the same, we can calculate the contributions of the intramolecular, solvent-induced, and self-quenching processes using the triplet decay parameters obtained from lifetime measurements as functions of the thione concentration. The results of such calculations are shown in Fig. 6. Since the triplet lifetimes extrapolated to infinite dilution for all three thiones studied are relatively short, in methanol self-quenching is a
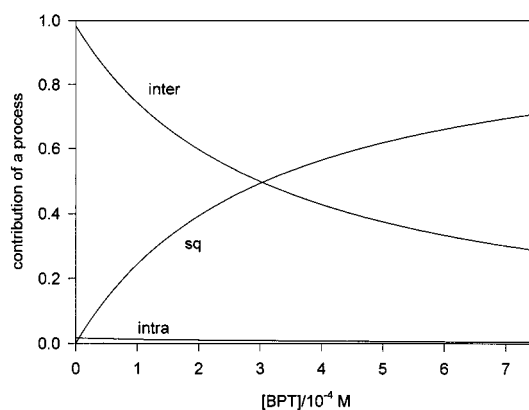

Fig. 6. Contributions of intramolecular processes (intra), interactions with the solvent (inter), and self-quenching (sq) in deactivation of ^{3}(BPT) as functions of BPT concentration.

much less important deactivation process than in PF or alkanes over a wide range of concentrations.

There are no data available concerning the triplet decay parameters for alkyl derivatives of BPT in PF. The possible additional intramolecular channel of deactivation of the decyl derivative triplets is interaction of the thiocarbonyl group with the alkyl chain. In the case of the butyl derivative this process is not possible and the rate of deactivation of its triplet state in PF should be similar to that of BPT in the same solvent. We can suppose that for BPTC$_{10}$ in PF the upper limit of the decay rate constant extrapolated to infinite dilution should not be much different from that for BPT in alkane (e.g., 3-methylpentane) solution, and may well be lower. Taking into account the results for other thioketones, we can infer that a slightly higher triplet energy for the alkyl derivative than for BPT itself cannot lead to a marked increase in reactivity of the thiocarbonyl group toward a C–H bond. Additionally, in methanol solution the reactivity of the triplet in hydrogen abstraction reaction may be lower than in PF or alkanes because of partial inversion of the (n,π^*) and (π,π^*) states. All these premises lead to the conclusion that intramolecular hydrogen abstraction in BPTC$_{10}$ is by no means an important channel of deactivation of its triplet in methanol. This is supported by the fact that for both alkyl derivatives, the triplet lifetimes extrapolated to infinite dilution are similar. Hence, we can infer that for all three thioketones the dominant pathway of deactivation of the triplet in infinite dilution is a solvent-induced intermolecular process. The longer τ_T^0 and the higher ϕ_{ph}^0 for BPTC$_4$ and BPTC$_{10}$ than for BPT suggest a lower reactivity of the triplets of the alkyl derivatives toward methanol, which is perhaps connected with a presumably higher electron density on the thiocarbonyl group due to the induction effect of an alkyl group. Not much is known about the mechanism of this process. It has been established that in solvents whose molecules have easily abstractable hydrogen atoms like ethanol, higher alcohols [15,34], and alkanes [12,15,23,24], this process is connected with hydrogen abstraction by a thione molecule from a solvent molecule. Often it is mainly reversible and the most important secondary process is recombination of the radicals formed in the primary process, resulting in the formation of the substrates in their ground states [12,23,24,33]. However, C–H as well as O–H bonds in methanol are too strong for the hydrogen atom abstraction to take place in this solvent [34]. Therefore in methanol there must be another process involving thione and solvent molecules, perhaps related to the formation of an exciplex resulting in triplet deactivation. Since the emission decay in the time range considered was always monoexponential, this exciplex, as well as a possible

excimer formed in the self-quenching process, would have to be dark. The lower, by ca. 20%, rates of repopulation of the ground state in the ground-state depletion experiments than the rates of phosphorescence decay measured for BPTC$_4$ at low thione concentrations indicate that some triplets do not decay directly to the ground state but through the formation of exciplex and/or excimer. However, this discrepancy vanishes at high thione concentrations and thus it should be ascribed to the formation of exciplex rather than excimer. This issue needs further investigation by means of transient absorption measurements.

CONCLUSION

The results of this investigation have shown a strong influence of an active solvent, methanol, on the spectral and photophysical properties of BPT and its two alkyl derivatives. Deactivation dynamics of the fluorescent S$_2$ state was studied by means of a picosecond time-correlated single-photon counting system, and that of the phosphorescent triplet states by a nanosecond laser flash photolysis setup. The studies proved that nonradiative deactivation of the fluorescent S$_2$ state and phosphorescent triplet states is accelerated by the interaction of these states with the solvent, which is revealed by a decrease in the emission quantum yields and shortening of the lifetimes of the emissions on the replacement of inert PF solvents by methanol. The solvent-induced deactivation processes are dominant pathways of the decay of the S$_2$ state as well as the triplet states, unless a concentration-dependent process of self-quenching becomes an important deactivation mechanism of the triplet state, which is the case at relatively high thione concentrations. The use of deuterated methanols permitted determination of the role of hydrogen atom abstraction and another mechanism perhaps involving the formation of an S$_2$-exciplex in deactivation of the S$_2$ state. The ground-state depletion experiments together with the results obtained from flash photolysis showed that the states emitting phosphorescence do not deactivate directly to the ground state but through the formation of the transient product, probably an exciplex. The substitution of the hydrogen atom in position 2 of a BPT molecule results in a decrease in the self-quenching rates constants for the triplet states, which is caused by a decrease in the diffusion coefficient of a molecule of the alkyl derivatives and shielding of the reactive centers of the thione molecules by alkyl groups.

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REFERENCES

1. A. Maciejewski and R. P. Steer (1993) *Chem. Rev.* **93**, 67–98.
2. R. P. Steer and V. Ramamurthy (1988) *Acc. Chem. Res.* **21**, 380–386.
3. J. R. Huber and M. Mahaney (1975) *Chem. Phys. Lett.* **30**, 410–412.
4. M. Mahaney and J. R. Huber (1975) *Chem. Phys.* **9**, 371–378.
5. M. H. Hui, P. de Mayo, R. Suau, and W. R. Ware (1975) *Chem. Phys. Lett.* **31**, 257–263.
6. A. Maciejewski, A. Safarzadeh-Amiri, R. E. Verrall, and R. P. Steer (1984) *Chem. Phys.* **87**, 295–303.
7. A. Maciejewski, D. R. Demmer, D. R. James, A. Safarzadeh-Amiri, R. E. Verrall, and R. P. Steer (1985) *J. Am. Chem. Soc.* **107**, 2831–2837.
8. D. S. Blackwell, C. C. Liao, R. O. Loufty, P. de Mayo, and S. Paszyc (1972) *Mol. Photochem.* **4**, 171–188.
9. D. A. Capitanio, H. J. Pownall, and J. R. Huber (1974) *J. Photochem.* **3**, 225–236.
10. A. Safarzadeh-Amiri, R. E. Verrall, and R. P. Steer (1983) *Can. J. Chem.* **61**, 894–900.
11. M. Szymański, R. P. Steer, and A. Maciejewski (1987) *Chem. Phys. Lett.* **135**, 243–248.
12. A. Maciejewski, M. Szymański, and R. P. Steer (1988) *J. Phys. Chem.* **92**, 6939–6944.
13. P. de Mayo (1976) *Acc. Chem. Res.* **9**, 52–59.
14. N. J. Turro, V. Ramamurthy, W. Cherry, and W. Farneth (1978) *Chem. Rev.* **78**, 125–145.
15. V. Ramamurthy (1986) *Org. Photochem.* **7**, 231–338.
16. J. D. Coyle (1985) *Tetrahedron* **41**, 5393–5425.
17. A. Cox, D. R. Kemp, R. Lapouyade, P. de Mayo, J. Joussot-Dubien, and R. Bonneau, *Can. J. Chem.* **53**, 2386–2393.
18. A. Maciejewski and R. P. Steer (1983) *Chem. Phys. Lett.* **100**, 540–545.
19. A. Maciejewski and R. P. Steer (1983) *J. Am. Chem. Soc.* **105**, 6738–6740.
20. M. Mahaney and J. R. Huber (1984) *Chem. Phys. Lett.* **105**, 395–399.
21. C.-J. Ho, A. L. Motyka, and M. R. Topp (1989) *Chem. Phys. Lett.* **158**, 51–59.
22. M. Milewski, A. Maciejewski, and W. Augustyniak (1997) *Chem. Phys. Lett.* **272**, 225–231.
23. M. Szymański, A. Maciejewski, and R. P. Steer (1988) *Chem. Phys.* **124**, 143–154.
24. J. Kozlowski, A. Maciejewski, M. Milewski, and W. Urjasz (1999) *J. Phys. Org. Chem.* **12**, 47–58.
25. A. Maciejewski (1990) *J. Photochem. Photobiol. A* **51**, 87–131.
26. S. J. Formosinho (1976) *J. Chem. Soc. Faraday Trans. 2* **72**, 1332–1338.
27. A. Maciejewski (1988) *J. Photochem. Photobiol. A* **43**, 303–312.
28. A. H. Lawrence, P. de Mayo, R. Bonneau, and J. Joussot-Dubien (1973) *Mol. Photochem.* **5**, 361–365.
29. U. Brühlaman and J. R. Huber (1978) *Chem. Phys. Lett.* **54**, 606–610.
30. V. Ramesh, N. Ramnath, and V. Ramamurthy (1983) *J. Photochem. Photobiol. A* **23**, 141.
31. M. Sikorski, W. Augustyniak, I. V. Khmielinski, V. V. Korolev, and N. M. Bazhin (1993) *Chem. Phys. Lett.* **209**, 403–407.
32. A. H. Lawrence, C. C. Liao, P. de Mayo, and V. Ramamurthy (1976) *J. Am. Chem. Soc.* **98**, 2219–2226.
33. N. J. Turro and V. Ramamurthy (1977) *Mol. Photochem.* **8**, 239–253.
34. U. Brühlaman and J. R. Huber (1979) *J. Photochem.* **10**, 205–213.
35. L. W. Molenkamp, D. P. Weitekamp, and D. A. Wiersma (1983) *Chem. Phys. Lett.* **99**, 382–387.
36. D. Tittelbach-Helmrich and R. P. Steer (1996) *Chem. Phys. Lett.* **262**, 369–373.
37. A. Maciejewski, M. Szymański, and R.P. Steer (1986) *J. Phys. Chem.* **90**, 6314–6318.
38. M. Szymański, A. Maciejewski, and R. P. Steer (1991) *J. Photochem. Photobiol. A* **57**, 405–418.
39. M. Sikorski, I. V. Khmelinskii, W. Augustyniak, and F. Wilkonson (1996) *J. Chem. Soc. Faraday Trans.* **92**, 3487–3490.
40. V. Ramesh and V. Ramamurthy (1982). *J. Photochem.* **20**, 47–52.
41. A. Maciejewski, A. Jakubowska, E. Dutkiewicz, and W. Augustyniak (1996) *J. Colloid Interface Sci.* **177**, 528–541.
42. M. Milewski, M. Sikorski, A. Maciejewski, M. Mir, and F. Wilkinson (1997) *J. Chem. Soc. Faraday Trans.* **93**, 3029–3034.
43. M. Milewski, W. Augustyniak, and A. Maciejewski (1998) *J. Phys. Chem. A* **102**, 7427–7434.
44. M. A. Winnik (1977) *Acc. Chem. Res.* **10**, 173–179.
45. M. Milewski, W. Urjasz, A. Maciejewski, and W. Augustyniak (1998) *Polish J. Chem.* **72**, 2405–2417.
46. S. Meech and D. Phillips (1983) *J. Photochem.* **23**, 193–217.
47. J. B. Birks (1976) *J. Res. Natl. Bur. Stand.* **80A**, 389.
48. J. Karolczak, D. Komar, J. Kubicki, M. Szymański, T. Wróżowa, and A. Maciejewski (1999) *Bull. Pol. Acad. Sci.* **47**, 361–380.
49. J. Karolczak, J. Kubicki, D. Komar, T. Wróżowa, M. Szymański, B. Ciesielska, A. Cencek, and A. Maciejewski (in press).
50. M. Binkowski, M. Szymański, J. Baksalary, and A. Maciejewski (1996) *Opt. Appl.* **26**, 159–169.
51. K. J. Rosenberg (1962) *Acta Chem. Scand.* **16**, 2284–2292.
52. H. Eisenberger and B. Nickel (1996) *J. Chem. Soc. Faraday Trans.* **92**, 733–740.
53. M. Milewski, J. Kubicki, T. Wróżowa, A. Maciejewski, and W. Augustyniak (in press).
54. M. Szymański, A. Maciejewski, and R. P. Steer (1988) *J. Phys. Chem.* **92**, 2485–2489.
55. M. Milewski (1998) Ph.D. thesis (Faculty of Chemistry, A. Mickiewicz University, Poznań, Poland).
56. A. Maciejewski and R. P. Steer (1984) *J. Photochem.* **24**, 303–307.
57. A. Maciejewski (1989) *Chem. Phys. Lett.* **164**, 166–172; W. Augustyniak, J. Koput, A. Maciejewski, M. Sikorski, R. P. Steer, and M. Szymański (1993) *Polish J. Chem.* **67**, 1409–1423; A. Maciejewski. M. Sikorski, W. Augustyniak, and M. Fidecka (1996) *J. Photochem. Photobiol. A* **94**, 119–127.
58. M. Szymański, M. Balicki, M. Binkowski, J. Kubicki, A. Maciejewski, E. Pawlowska, and T. Wróżowa (1996) *A. Phys. Pol. A* **89**, 527–546.
59. A. Maciejewski, M. Szymański, and R. P. Steer (1988) *Chem. Phys. Lett.* **143**, 559–564.
60. R. Rajee and V. Ramamurthy (1979) *J. Photochem.* **11**, 135–138.
61. J. Saltiel, G. R. Marchand, W. K. Smothers, S. A. Stout, and J. L. Charlton (1981) *J. Am. Chem. Soc.* **103**, 7159–7164.
62. H. Eisenberger, B. Nickel, A. A. Ruth, and R. P. Steer (1996) *J. Chem. Soc. Faraday Trans.* **92**, 741–746.