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# Photochemical reactions of $T_1$ benzopyranthione in 3-methylpentane

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ABSTRACT: Photochemical properties of the lowest triplet state of 4*H*-1-benzopyran-4-thione (BPT) in 3-methylpentane were studied in the thione concentration range $10^{-7} - 10^{-3}$ M. The quantum yield of the photochemical decomposition of BPT was found to be highly concentration dependent. For low BPT concentrations ($<10^{-6}$ M) a reaction with the solvent is responsible for the consumption of the thione. In the concentration range $1 \times 10^{-6}$–$8 \times 10^{-5}$ M the main process is the reaction of thiyl radicals, formed in the primary reaction of hydrogen abstraction from a solvent molecule, with BPT molecules in the ground state. For thione concentrations $>10^{-4}$ M, the BPT triplet decays almost entirely in a self-quenching process. HPLC analysis showed that five different photoproducts, including an oligomer, are formed. Knowledge of earlier studied photophysical properties of BPT in 3-methylpentane and perfluoroalkanes permitted a quantitative explanation of the mechanism of photochemical reactions of $^3$(BPT). The studies indicate, for BPT concentrations $<10^{-4}$ M, a dominant role of the interaction of $^3$(BPT) with the solvent and the subsequent caged radical recombination in deactivation of BPT in the $T_1$ state. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: $T_1$ benzopyranthione; 3-methylpentane; photochemical reactions

## INTRODUCTION

Although the photochemical properties of thioketones have been the subject of studies for many years, much less is known about them than about their oxygen analogues.[1–5] Relatively much attention has been devoted to photocycloaddition and photooxidation reactions and photoreduction and dimerization of thioketones.[3–5] The use of highly unreactive perfluoroalkanes as solvents[6] made it possible to investigate the photochemical properties of aromatic thiones in the absence of the solute–solvent interactions which can otherwise dominate the decay of thione triplets.[3,7] A number of studies have shown that self-quenching (concentration quenching) plays a very important (usually dominant) role in the deactivation of the lowest triplet state of thioketones.[3,8,9] This process, believed for a long time to be only physical in nature, has been shown to participate in the photochemical decomposition of thiones in perfluoroalkanes as solvents.[7]

The aim of this study was to investigate the photochemical properties of 4*H*-1-benzopyran-4-thione (BPT) in 3-methylpentane (3-MP) in the concentration range $10^{-7}$–$10^{-3}$ M. This is the first attempt to study the photochemistry of this thione in an active solvent in a concentration range wide enough to allow the investigation of all processes responsible for its photochemical decomposition. The photochemical properties of this thione in perfluoroalkanes and its photophysical properties in perfluoroalkanes and 3-MP have been described previously.[3,6,7,9] The photophysical and photochemical data given there allowed the determination of the role of self-quenching processes and $^3$(BPT) reaction with the solvent and also the subsequent reaction of radicals formed probably in the latter reaction with BPT molecules in their ground state. It should be pointed out that photochemical studies of thioketones are particularly difficult owing to their high photoreactivity towards solvent impurities and oxygen, the need to use very low thione concentrations to prevent BPT triplet deactivation from being dominated by the self-quenching process, possible thermal instability of photoproducts and the tendency of the photoproducts to undergo further photoreactions leading to the formation of polymers.[3–5,10–12]

## RESULTS AND DISCUSSION

The $S_1$ state of BPT was initially populated by absorption of laser radiation ($\lambda_{exc} = 515$ nm, $\varepsilon = 8$ l mol$^{-1}$ cm$^{-1}$). The lifetime of the lowest excited singlet state of

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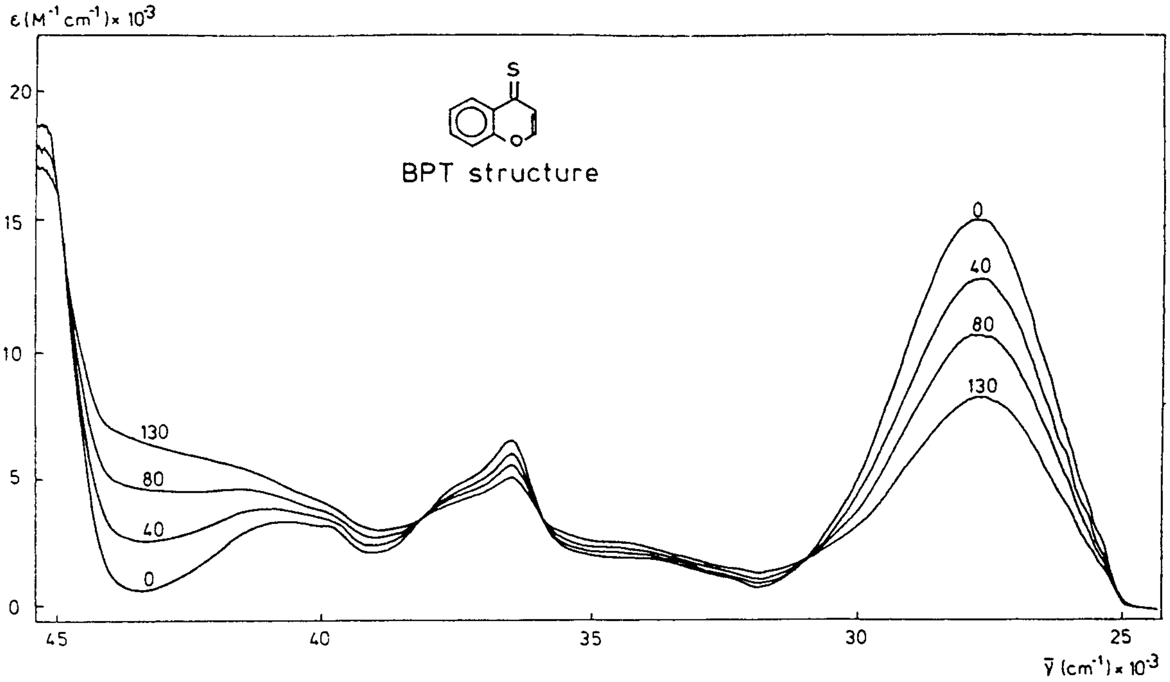


**Figure 1.** Spectral changes in the UV–visible absorption spectra of BPT in 3-MP ([BPT] = 1 × $10^{-3}$ M) upon irradiation at 515 nm. The numbers on the curves are the irradiation time in minutes

thioketones is very short (*ca* $10^{-12}$ s) because of the very efficient and fast intersystem crossing $S_1 \rightarrow T_1$.[13,14] This is the reason why the $T_1$ state is entirely responsible for the photochemical decomposition of BPT under excitation to $S_1$. Absorption changes during irradiation of BPT are shown in Fig. 1.

Figure 2 shows the concentration dependence of quantum yield of photochemical decomposition ($\phi_D$) for BPT in 3-MP and perfluoroalkanes. $^3$(BPT) in 3-MP can decay in both intramolecular and intermolecular processes connected with interactions with the solvent and through the self-quenching process. That is why the overall photochemical decomposition of BPT can be represented as a sum of three components:

$$\phi_D = C_{intra}\phi_{intra} + C_{inter}\phi_{inter} + C_{sq}\phi_{sq}$$

where $C_{intra}$ is the contribution of intramolecular processes, $C_{inter}$ is the contribution of the intermolecular processes other than self-quenching, $C_{sq}$ is the contribu-

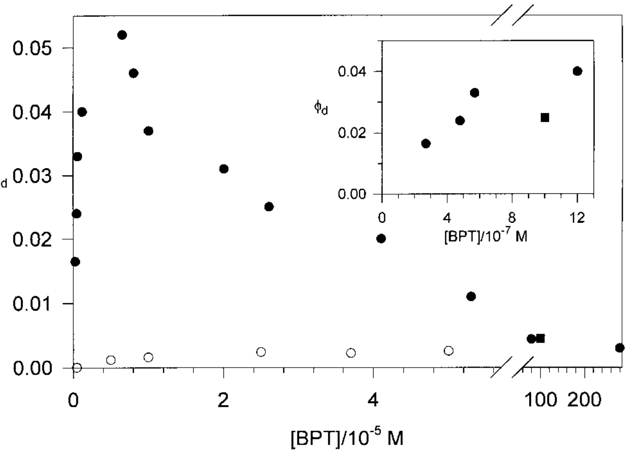


**Figure 2.** Concentration dependence of the quantum yield of photochemical decay of BPT in 3-MP (full circles, original results; squares, from Ref. 18) and perfluoro-1,3-dimethylcyclohexane (open circles, from Refs 7 and 9); $\lambda_{exc}$ = 515 nm

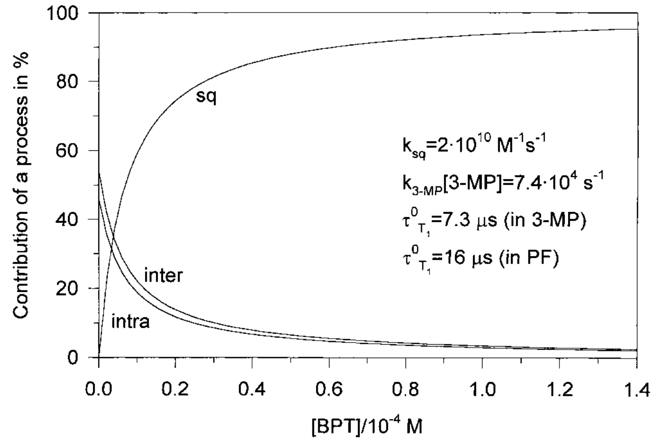
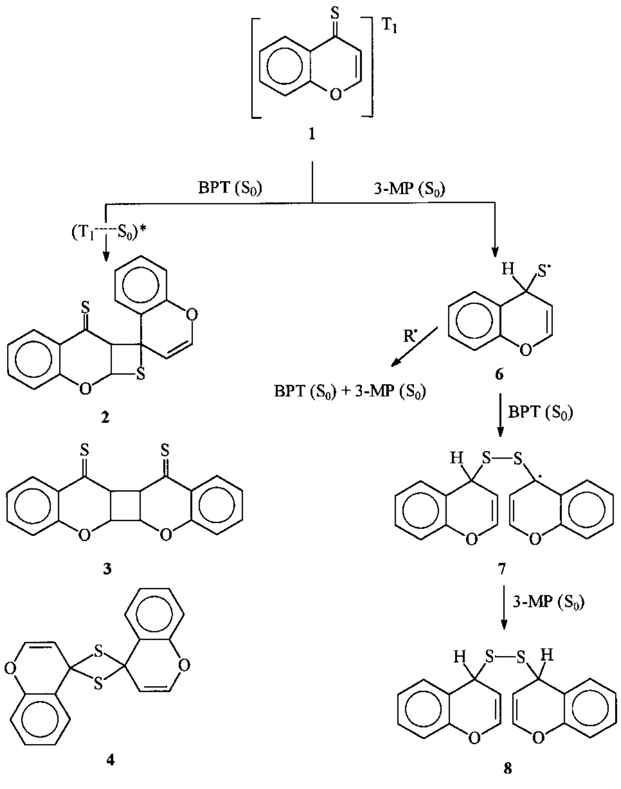


**Figure 3.** Contributions of intramolecular processes (intra), interactions with the solvent (inter) and self-quenching (sq) in deactivation of $^3$(BPT) as functions of BPT concentration. The following photophysical parameters for BPT triplets in 3-MP are also given: $k_{sq}$, the self-quenching rate constant; $k_{3\text{-MP}}$[3-MP], the rate of the process of interaction with the solvent; and $\tau^0_{T_1}$, the triplet lifetimes extrapolated to infinite dilution in 3-MP and PF (perfluoro-1,3-dimethylcyclohexane)

tion of self-quenching and $\phi_{intra}$, $\phi_{inter}$ and $\phi_{sq}$ are the photochemical decomposition quantum yields for each of the processes determined assuming that each particular process would be the only one. To give a quantitative description of a photochemical decomposition of BPT in 3-MP, the earlier measured photophysical parameters were used, including the triplet lifetimes and the self-quenching rate constant.[3,7,9] These values permitted the exact determination of the contributions of the above-mentioned processes in the deactivation of $^3$(BPT) (Fig. 3). As we have shown for several thioketones, their photochemical decomposition in chemically inert perfluoroalkanes occurs only in intramolecular and self-quenching process[3,7]. For $[\mathrm{BPT}] < 10^{-6}$ M, the self-quenching is negligible and only intramolecular processes are responsible for the decay of BPT in perfluoroalkanes. The value of $\phi_\mathrm{D}$ measured under these conditions is not higher than $4.4 \times 10^{-4}$, which can be considered as the upper limit of $\phi_\mathrm{intra}$.[7]

The value of $\phi_\mathrm{D}$ measured in 3-MP for the lowest BPT concentration ($[\mathrm{BPT}] = 2.7 \times 10^{-7}$ M) is 0.0165. It is significantly higher (*ca* 40 times) than $\phi_\mathrm{intra}$. Since the contribution of self-quenching for this BPT concentration can be neglected, such a high value of $\phi_\mathrm{D}$ can be attributed only to the occurrence of processes in which the solvent plays an active role, namely it acts as a hydrogen atom donor in the reaction of hydrogen atom abstraction by BPT triplets. An analogous reaction has been proposed by Brühlmann and Huber[10] for xanthione in methylcyclohexane. The product of this primary process is a caged radical pair. Two structures of radicals formed from a BPT molecule in this reaction are possible. In the thiyl radical the lone electron is localized on the sulfur atom (indicated as **1** in Scheme 1) and in the thioketyl radical the electron is localized on the carbon atom of the thiokarbonyl group. The radicals can recombine in a solvent cage reproducing substrate molecules in the ground state or form stable photoproducts, the sulfide and/or thiol (not shown in Scheme 1). Analogous products were observed by Kito and Ohno[15] for the reaction of thiobenzophenone with tetrahydrofuran. The UV–visible absorption spectrum of the products could be obtained on the basis of the changes in the absorption spectrum of the irradiated solution, but HPLC analysis was not possible owing to the extremely low concentration ($<10^{-6}$ M) of BPT that had to be used in this case.

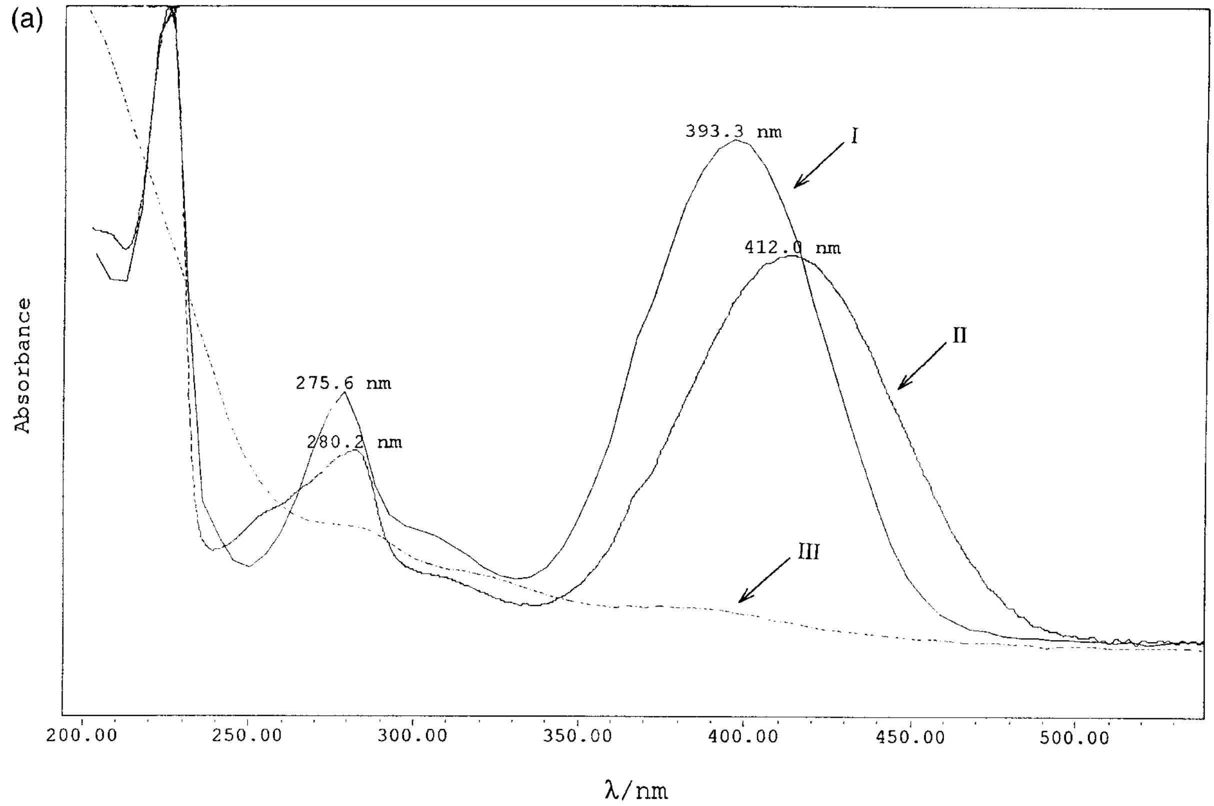
It should be noted that radical recombination is a very efficient process since the above-described interaction with the solvent is responsible for a deactivation of BPT triplets by 54% and the value of $\phi_\mathrm{D}$ is much lower ($\phi_\mathrm{D} = 0.0165$) than the yield of the primary process. We can conclude that in fact the majority of the radicals formed recombine and the efficiency of the recombination is as high as 97%. This is in agreement with earlier work by de Mayo and co-workers,[16,17] who reported that the process of recombination of radicals formed by thione molecules in the triplet state occurred with an efficiency of *ca* 90%.



BPT = benzopyranthione, 3-MP = 3-methylpentane, R• = 3-methyl radical

**Scheme 1.**

For high concentrations of BPT ($>10^{-4}$ M) the mechanism of its photochemical decomposition is relatively simple because then the self-quenching process is mainly responsible for deactivation of $^3$(BPT) (Fig. 3).[18] Self-quenching was for a long time considered to be an entirely physical process.[3–5,8,10] However, we have shown that in perfluoroalkanes, for BPT concentrations $>10^{-4}$ M, this is the only process leading to the photochemical decomposition of BPT, with a quantum yield of $3.6 \times 10^{-3}$.[3,7] A very similar and almost constant value of $\phi_\mathrm{D}$ was obtained in 3-MP for BPT concentrations $>10^{-4}$ M.[3,18] Also, the changes in the absorption spectra of irradiated solutions in these two solvents were very similar. These observations suggest that in both cases the same process, namely self-quenching, is responsible for photochemical consumption of BPT. The use of HPLC showed that under these conditions three products are formed. Taking into account the fact that they are formed as the result of self-quenching, we can expect that they all are dimers of various structure. Their UV–visible spectra obtained by means of HPLC are presented in Fig. 4(a). In two of them there is a long-wavelength band similar to the $S_0 \rightarrow S_2$ band characteristic of BPT. This indicates the presence of a thiocarbonyl group in the molecules of these two



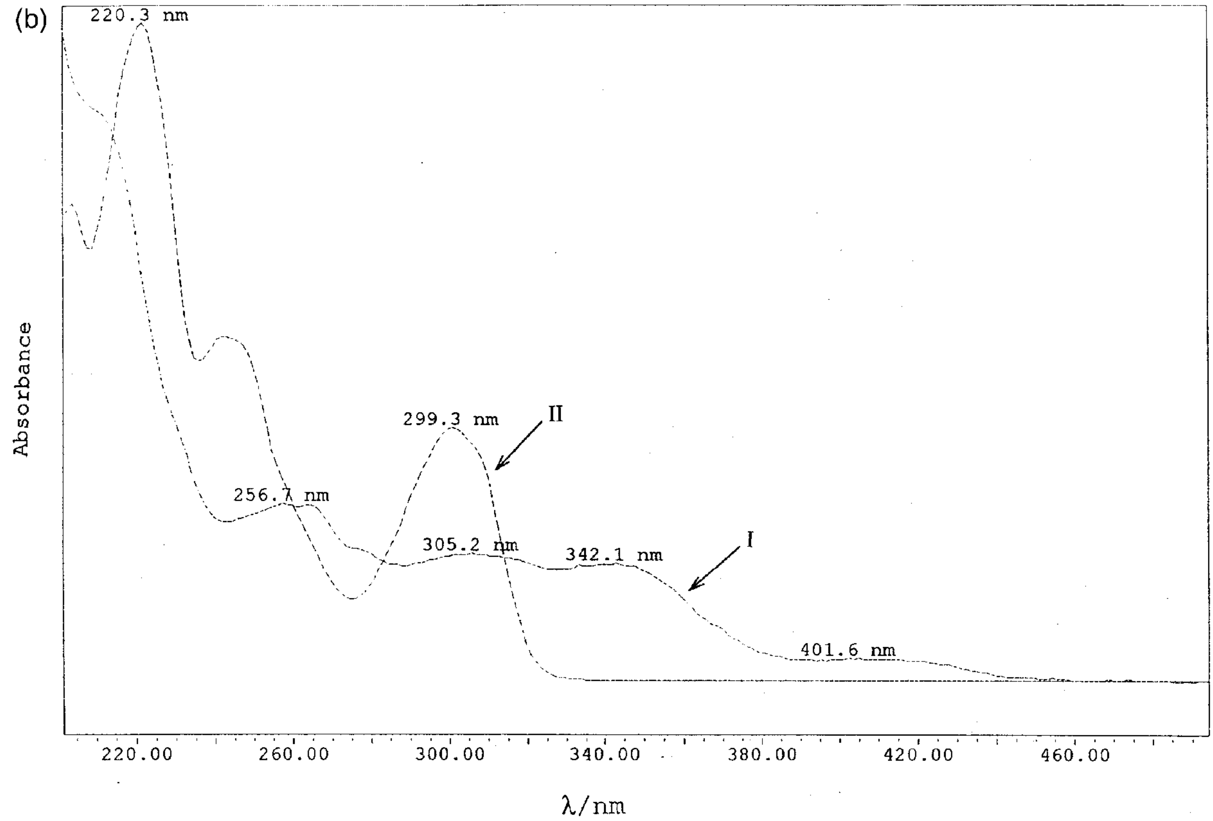


**Figure 4.** UV–visible absorption spectra of products of photochemical decay of $^{3}$(BPT) in 3-MP. (a) Dimers with thiocarbonyl groups (I) and (II) and 1,3-dithiane (III); (b) disulfide (I) and chromone (II)

products.[3,7,9,19] The possible structures of the products are shown in Scheme 1 (structures **2** and **3**). The photoreaction leading to the formation of product **2** seems particularly likely since the formation of such a product can be considered as an example of a well known reaction of cycloaddition of a thiocarbonyl group to a carbon–carbon double bond.[3–5,20,21] It is interesting that these two products are not formed upon irradiation of BPT derivatives with an alkyl group (butyl or decyl) at the 2-position, owing to steric hindrance inhibiting the formation of these products. The products with thiocarbonyl groups can absorb incident light and, being photochemically reactive, they undergo secondary photochemical reactions including further polymerization. The photopolymerization can take place also when $^3$(BPT) reacts with product **2** or **3** in its ground state. Photopolymerization processes have been reported to occur also during the photolysis of other thioketones; however, the polymers formed have not been the subject of any studies so far. Formation of a precipitate was observed upon irradiation of a solution of BPT in 3-MP of relatively high concentration ($>10^{-4}$ M). Mass spectra of the isolated precipitate were recorded by positive and negative ion liquid secondary ion mass spectrometry). (LSIMS) The positive ion spectrum revealed an $[M+H]^+$ peak at *m/z* 811, whereas the negative ion spectrum indicated an $[M-H]^-$ peak at *m/z* 809, which proves that the molecular weight of the oligomer is 810, which corresponds to $5M_{\mathrm{BPT}}$. The *m/z* values show that BPT is indeed a monomer unit of the obtained oligomer. This conclusion was confirmed by the electron ionization (EI) mass spectrum with peaks at *m/z* 162 and 324, interpreted as corresponding to the monomer and dimer formed due to fragmentation of the oligomer. The UV–visible absorption spectrum of the oligomer dissolved in dimethyl sulfoxide shows a band with a maximum at the wavelength 378 nm. This indicates the presence of a thiocarbonyl group in the oligomer molecule.[7,9,19] The intensity of this band is lower, relative to those of the other absorption bands, than in the spectrum of the monomer, which is connected with the fact that only a small proportion of thiocarbonyl groups remain intact when the oligomer is formed. For BPT concentrations $>10^{-4}$ M, the oligomer is the main product of photochemical decomposition of BPT in 3-MP. The structures of products **2** and **3** seem to be particularly likely since they can yield the oligomer observed as a product in further photoreactions. The consumption of the primarily formed dimers makes it impossible to obtain them in quantities sufficient for more detailed spectral analysis.

The third product formed as a result of self-quenching is, as expected, 1,3-dithiane (shown in Scheme 1 as compound **4**). The molecules of this dimer do not contain a thiocarbonyl group and do not undergo thermal or photochemical decomposition. The UV–visible absorption spectrum of this product is shown in Fig. 4(a). Photochemical and thermal dimerization and formation of 1,3-dithiane have been reported for adamantanethione.[4,5,22] 1,3-Dithianes have been considered as the only products formed in the $T_1$ self-quenching process in perfluoroalkanes.[3,7] However, HPLC analysis of the products of photochemical decomposition of BPT in the concentration range where self-quenching is the dominant process in $^3$(BPT) decay proved that apart from 1,3-dithiane, two other primary products (**2** and **3**) of the photochemical decomposition of BPT are formed under such conditions.

The most remarkable feature of the concentration dependence of $\phi_{\mathrm{D}}$ is the rapid initial growth of $\phi_{\mathrm{D}}$ with increase in BPT concentration (Fig. 2). This can be explained neither by an increase in the contribution of self-quenching, since $\phi_{\mathrm{sq}}$ is low (see above), nor by a high quantum yield of the primary reaction with the solvent, because the contribution of the latter decreases with increasing BPT concentration. The only explanation for the increase in $\phi_{\mathrm{D}}$ can be an additional bimolecular process involving BPT molecules in the ground state and radicals formed in the reaction of hydrogen abstraction that would render the process of recombination of radicals less efficient. Such a process has been proposed by Brühlmann and Huber[10] for xanthione in methylcyclohexane. Also elsewhere aromatic thioketones have been reported to be very efficient radical scavengers.[23,24] In the first step of this process (Scheme 1), the thiyl radical, formed in the primary reaction with the solvent,[3,10,16] reacts with the BPT molecule in the $S_0$ state, forming a dimeric radical (structure **7**), which in the following step abstracts the second hydrogen atom from a 3-MP molecule, probably leading to disulfide formation (structure **8**). The UV–visible spectrum of this product is shown in Fig. 4(b). As the formation of the dimeric radicals is a competitive process with the thiyl radical recombination, it causes an increase in $\phi_{\mathrm{inter}}$ and the initial growth of the overall quantum yield of photochemical decomposition of BPT with increase in BPT concentration up to the value of 0.052 for $[\mathrm{BPT}] = 6.5 \times 10^{-6}$ M. We cannot rule out the possibility of formation of disulfide also in the reaction of two thiyl radicals following their escape from the solvent cage. In the range $1 \times 10^{-6}$ –$8 \times 10^{-5}$ M the process of disulfide formation dominates the photochemical decomposition of BPT. However, for increasing BPT concentration the increase in $C_{sq}$ at the expense of $C_{inter}$ is still more significant and when BPT concentration is further increased ($[\mathrm{BPT}] > 1 \times 10^{-5}$ M) a decrease in the experimental $\phi_{\mathrm{D}}$ is observed.

In the presence of oxygen an efficient (especially for low BPT concentrations) process of photooxidation takes place, as has been reported for some other thioketones.[3–5,25] This process can obscure other processes responsible for photochemical consumption of the thione in air equilibrated samples. The retention time and UV–visible spectrum [shown in Fig. 4(b)] of the main product obtained in the presence of oxygen perfectly match these properties of the chromone injected as a standard in various eluent compositions, which proves that a chromone is formed on irradiation of BPT in 3-MP in aerated solutions.

## EXPERIMENTAL

BPT was synthesized and purified by methods described elsewhere.[7,9] Chromone (Aldrich) was purified by column chromatography and crystallization. 3-MP (Aldrich) was purified by column chromatography and distillation. Deoxygenated (if not stated otherwise) samples were illuminated with 515 nm radiation from an argon laser (ILA-120, Zeiss). The intensity of the incident radiation was measured by means of a Reinecke salt actinometer. When an appropriately high conversion was achieved, the irradiated sample was analysed by HPLC using a diode-array detector (Waters 996). This technique permitted recording of the UV–visible absorption spectrum of each product. Since the quantum yield of the photochemical decomposition of BPT ($\phi_D$) was found to depend strongly on the thione concentration, $\phi_D$ was determined not only by extrapolation of the measured $\phi_D$ to zero percentage of thione consumed, but also using the differential method. Mass spectra were recorded on AMD 604 (LSIMS) and AMD 402 (EI) mass spectrometers. LSI mass spectra were recorded using *m*-nitrobenzyl alcohol as a matrix.

## CONCLUSION

The measurements of the quantum yield of photochemical decomposition of BPT in 3-MP over a wide range of concentration and HPLC analysis of irradiated samples together with reported earlier values of photophysical parameters of the BPT lowest triplet state enabled us to suggest a full and coherent mechanism for the photochemical decomposition of BPT. Despite the high ($>0.5$) yield of the primary reaction of hydrogen abstraction for low ($<10^{-6}$ M) BPT concentrations, the quantum yield of BPT decay is relatively low owing to the very efficient process of recombination of caged radicals. For high BPT concentrations ($>10^{-4}$ M), when self-quenching is the main process of deactivation of $^3$(BPT), not just one product (1,3-dithiane) is formed as has been assumed so far, but the formation of two more dimer products and an oligomer has been evidenced. An interesting and unexpected feature of the concentration dependence of the quantum yield of the photochemical decomposition of BPT is that the maximum value of $\phi_D$ (0.052) was found for BPT concentrations as low as $6.5 \times 10^{-6}$ M.

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