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The photophysics of thioflavone in solution

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Abstract

The absorption, emission and emission excitation spectra, $S_2 \rightarrow S_0$ fluorescence and $T_1 \rightarrow S_0$ phosphorescence quantum yields and S_2 and T_1 excited state lifetimes of thioflavone (TF) were measured in perfluoro-1,3-dimethylcyclohexane (PFDMCH) and 3-methylpentane (3-MP) at room temperature. The results were analysed to provide a quantitative description of the decay processes of excited TF, with emphasis on the effect of the phenyl rotor on the radiationless decay rates. In the inert perfluoroalkane solvent, both S_2 and T_1 relax intramolecularly via an $S_2 \rightarrow S_1 \rightarrow T_1 \rightarrow S_0$ path. $S_2 \rightarrow S_0$ fluorescence and $T_1 \rightarrow S_0$ phosphorescence also account for a small fraction of the excited state decay events, but no thermally activated delayed fluorescence, $S_1 \rightarrow S_0 + h\nu_{df}$, is observed. In 3-MP, the decay mechanism is dominated by intermolecular interactions between excited TF and the solvent. The rates of intramolecular radiationless decay are larger in TF than in rigid thiones having the same electronic energy gaps owing to the influence of the torsional motion of the phenyl group. By comparison of the observed rate constants for intramolecular radiationless decay of excited TF with those of a hypothetical rigid thione having the same electronic energy spacings, contributions to the radiationless decay rates of S_2 and T_1 due to torsional motion of the phenyl group were quantified. The second-order rate constants for quenching of triplet thione by molecular oxygen and by ground state thione were also measured. Excitation of TF to singlet excited states higher in energy than S_2 results in decay to S_1 and T_1 which partially bypasses S_2.

Keywords: Internal rotation; Non-radiative transitions; Photophysics; Thioflavone

1. Introduction

Compounds containing the thiocarbonyl group are of spectroscopic, photophysical and photochemical interest because, like azulene and other non-alternant aromatic hydrocarbons, they provide a window on the behaviour of excited states higher in the electronic manifold than S_1 and T_1 [1]. Like azulene and its derivatives [2], thiones have large S_2–S_1 energy gaps, which result in Franck–Condon inhibition of their rates of S_2 radiationless relaxation [3]. The S_2 states are therefore relatively long lived and, because the $S_2 \rightarrow S_0$ transition is electric dipole allowed, intense $S_2 \rightarrow S_0$ fluorescence is often observed. Fluorescence spectroscopy has thus been employed in thiocarbonyls, not only to examine the photophysics and photochemistry of S_2 itself, but also to measure the temporal evolution of the S_1 state in $S_0 \rightarrow S_1 \rightarrow S_2$ pump-probe experiments [4] and the dynamics of $2T_1 \rightarrow S_2$ and $2S_1 \rightarrow S_2$ annihilation processes [5].

For thiones in solution, measurement of both the lifetime of the S_2 state and the quantum yield of $S_2 \rightarrow S_0$ fluorescence allows the rate constants for excited state decay to be determined as a function of the excitation wavelength, temperature, solvent polarity, quencher concentration and other parameters [6]. Carrying out such measurements in inert perfluoroalkane solvents [7] containing low concentrations of thiones enables specific intermolecular contributions to the decay of S_2 to be eliminated and intramolecular processes to be unmasked. Adding quenchers to dilute perfluoroalkane solutions of thiones results in excited state interactions which can often be treated in a standard Stern–Volmer fashion to obtain second-order quenching constants [6]. However, the quenching of short-lived S_2 states can only be described adequately by using an extension of diffusion kinetics to account for the "transient effect" [8]. The nature of the interaction between the S_2 states of aromatic thiones and quenchers containing C–H bonds is of ongoing interest; reversible hydrogen abstraction leading primarily to relaxation from S_2 to S_1/T_1 appears to be involved [9,10].

The aromatic thiones offer additional advantages for studying the photophysics of polyatomic molecules in solution because excitation to states S_n $(n \geq 2)$ produces not only fluorescence from S_2 [11], but also phosphorescence from

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T_1 [12,13] and, at sufficiently high temperatures, thermally activated delayed fluorescence from S_1 [14]. Thus the pathways of relaxation from S_2 to the ground state can be elucidated by measuring the quantum efficiencies of luminescence and the lifetimes of three different excited states [15].

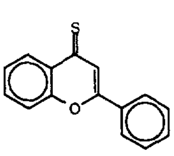
The following summarizes the photophysical behaviour of a typical rigid aromatic thione in inert perfluoroalkane solvent at room temperature.

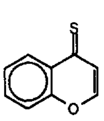
1. S_2 decays mainly by radiationless relaxation to S_1. Radiative decay and vibrational, energy-dependent radiationless decay directly to the ground state are interesting minor processes.
2. S_1 is very short lived (picosecond timescale) and decays promptly to T_1 with near unit efficiency.
3. T_1, of approximately microsecond duration, decays by a combination of phosphorescence, intersystem crossing to the ground state and back-intersystem crossing to S_1.

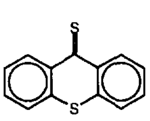
The proportions of the last two processes depend on the temperature and the S_1–T_1 and T_1–S_0 energy spacings. Recent reviews have provided a comprehensive picture of the photophysics and photochemistry of thiones in solution and may be consulted for further information [1,16].

Despite continuing interest in the photoprocesses of thiocarbonyls, the role played by internal rotations in determining the rates of relaxation of the excited states has received very little attention. It is clear from previous studies of thiobenzophenone and its derivatives [12,17,18] that the excited states of thiones having free aryl rotors exhibit somewhat faster rates of radiationless relaxation than their rigid counterparts with similar electronic energy spacings. However, unlike other non-rigid polyatomic organic molecules, little quantitative information is available for the thiones.

Thiobenzophenone itself is difficult to study because it dimerizes and oxidizes rather easily. We have therefore chosen to examine thioflavone (flavene-4-thione or 2-phenylchromene-4-thione, TF), which has a single rotatable phenyl group β to the thiocarbonyl moiety, because it is stable and can be compared nicely with 4H-1-benzopyran-4-thione (BPT) for which photophysical data are already available [5,6,11–15].


TF


BPT


TXT

2. Experimental section

The equipment and methods used to obtain the luminescence quantum yields and excited state lifetimes have been described in detail elsewhere [11,15,19]. Only a brief summary will be provided here.

Absorption spectra were measured with Cary 118 and Carl Zeiss Jena M40 UV–visible spectrophotometers. Emission and excitation spectra and emission quantum yields were measured using a Spex Fluorolog 222 spectrofluorometer equipped with a Datamate data analysis system and on an upgraded Perkin–Elmer MPF-3 instrument. Excitation spectra were corrected using a rhodamine B quantum counter and emission spectra were corrected using manufacturer's data for the relative sensitivity of the thermoelectrically cooled RCA 31034A photomultiplier detector as a function of wavelength.

Quantum yields of emission ϕ were measured using the relative method described previously [19]. 9,10-Diphenylanthracene in cyclohexane ($\phi_f = 0.93$ [20]) was employed as reference, and the measured emission intensities were corrected for differences in the refractive indices of the sample and the standard.

Excited state lifetimes τ were measured using a Spectra-Physics mode-locked, synchronously pumped, cavity-dumped argon ion–dye laser system described previously [21,22]. Excitation in the UV was accomplished by frequency doubling the fundamental output of the dye laser using a KDP crystal. The time-correlated, single-photon counting detection system employed a Hamamatsu microchannel plate photomultiplier detector and fast amplifier with an instrument response function of 33 ps full width at half-maximum (FWHM). Magic angle detection was employed to avoid artefacts associated with the rotational diffusion of the sample. Iterative reconvolution of the instrument response function with trial single-exponential functions, followed by comparison with the measured decay, was used to extract the picosecond S_2 decay time of the sample. The distribution of weighted residuals and the reduced χ^2 value were employed as criteria for the goodness-of-fit. Triplet decays of microsecond duration were obtained straightforwardly without deconvolution.

To obtain photophysical data for triplet thiones at infinite dilution (i.e. at thione concentrations at which concentration quenching is negligible), emission quantum yields and lifetimes were taken at a number of relatively low concentrations ($(1–9) \times 10^{-6}$ M). The data were then cast in Stern–Volmer form, and the plots of $1/\phi_p$ or $1/\tau$ vs. thione concentration were extrapolated to infinite dilution to obtain ϕ_p^0 and τ^0 [11,12].

TF was prepared by reaction of flavone (Aldrich) with P_2S_5 (P_4S_{10}) or Lawesson's reagent following the methods of Pedersen et al. [23] or Scheermer et al. [24]. The crude material was purified by preparative thin layer chromatography (TLC) and by fractional recrystallization from ethanol–benzene. Perfluoro-1,3-dimethylcyclohexane (PFDMCH) and 3-methylpentane (3-MP) solvents were purified by fractional distillation and/or column chromatography and contained no impurities which contributed significantly to the emission when illuminated at the excitation wavelengths used for the samples.

The data of Murov et al. [25] were used to obtain the oxygen concentrations of air-saturated solutions employed in oxygen quenching experiments.

3. Results

The absorption spectrum of TF in 3-MP is shown in Fig. 1. Like other aromatic thiones [1], TF exhibits absorption bands throughout the visible and UV regions. A weak band in the visible ($\epsilon_{max} = 37\ M^{-1}\ cm^{-1}$ at 600 nm) is attributable to the electric-dipole-forbidden $S_1 \leftarrow S_0$ ($n \rightarrow \pi^*$) transition, overlapped by its companion spin-forbidden $T_1 \leftarrow S_0$ transition. As with BPT [5], the feature of lowest energy in this region is assigned to the $T_1 \leftarrow S_0$ origin, whereas the feature next highest in energy is assigned to the $S_1 \leftarrow S_0$ origin. Three strong transitions are observed in the UV; the lowest energy feature may be assigned to the electric-dipole-allowed $S_2 \leftarrow S_0$ ($\pi \rightarrow \pi^*$) transition on the delocalized thiocarbonyl π system. Unlike the spectra of rigid aromatic thiones [6], these absorption bands are almost completely devoid of vibrational structure, and are significantly broader, as measured by their full widths at half-height ($\Delta \nu^{1/2}$).

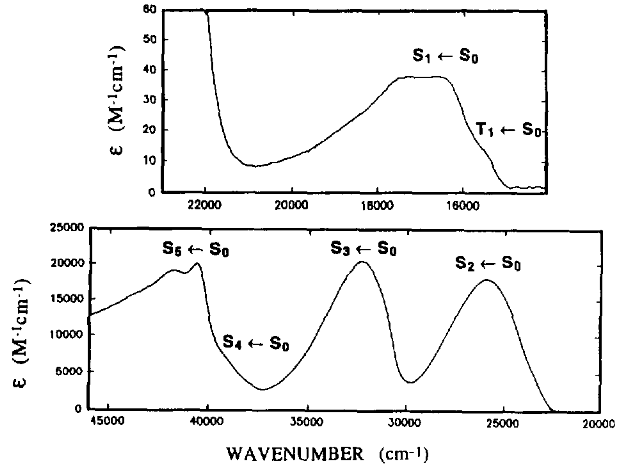


Fig. 1. Absorption spectrum of 6.07×10^{-4} M TF in 3-MP at room temperature.

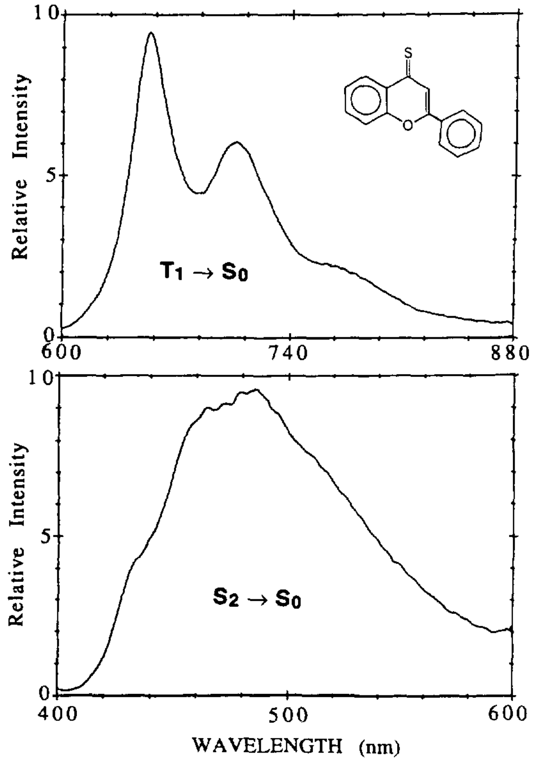


Fig. 2. Emission spectra of TF in solution at room temperature. Top panel: $T_1 \rightarrow S_0$ phosphorescence excited at 380 nm in 3-MP. Bottom panel: $S_2 \rightarrow S_0$ fluorescence excited at 380 nm in PFDMCH.

Table 1
Spectroscopic properties of TF and BPT in the T_1, S_1 and S_2 states

Data[a]	TF		BPT[b]	
	PFDMCH	3-MP	PFDMCH	3-MP
S_2 state				
$E^{0-0}_{abs}(S_2–S_0)$	~23500	23250	25540	25200
$E^{0-0}_{em}(S_2–S_0)$	23040	22520	25420	–
ϵ_{max} ($M^{-1}\ cm^{-1}$)	–	18700	15100	16060
$\Delta \bar{\nu}^{1/2}_{abs}$ (cm^{-1})	4100	4100	3630	3600
$\Delta \bar{\nu}^{1/2}_{em}$ (cm^{-1})	4320	4485	4590	–
$\Delta E^{0-0}_{abs}(S_2–S_1)$	6900	6580	8700	8400
S_1 state				
$E^{0-0}_{abs}(S_1–S_0)$	–	16640	16800	16780
$\Delta \bar{\nu}^{1/2}_{abs}$ (cm^{-1})	–	3230	–	2830
ϵ_{max} ($M^{-1}\ cm^{-1}$)	–	37	11.9	–
T_1 state				
$E^{0-0}_{abs}(T_1–S_0)$	–	15430	16030	16030
ϵ_{max} ($M^{-1}\ cm^{-1}$)	–	10.0	10.4	10.1
$\Delta \bar{\nu}_{0-0}$(abs–em) (cm^{-1})	–	115	100	130
$\Delta E^{0-0}_{abs}(S_1–T_1)$	–	1210	690	–

[a] All energies are in cm^{-1}.
[b] The data for BPT are from Refs. [11] and [12].

Excitation at $\lambda_{max} = 380$ nm in the $S_2 \leftarrow S_0$ band results in emission; the spectrum is shown in Fig. 2. (Similar spectra are observed on excitation at any of the strong bands in the UV region.) Two band systems are evident: $T_1 \rightarrow S_0$ phosphorescence in the red and near-IR and $S_2 \rightarrow S_0$ fluorescence in the mid-visible. The phosphorescence spectrum is typical of aromatic thiones in solution at room temperature [12,13]. Three distinct features may be seen, that of highest energy being the origin band. The difference in energy between the $T_1 \leftrightarrow S_0$ origin bands in absorption and emission is 115 cm^{-1} in 3-MP, which is typical of these compounds [12]. The $S_2 \rightarrow S_0$ fluorescence spectrum retains vestiges of some vibrational structure, and is slightly narrower than the corresponding spectrum of BPT in perfluoroalkane solvent. No thermally activated delayed $S_1 \rightarrow S_0$ fluorescence is evident in the emission spectrum of TF at room temperature.

The spectroscopic characteristics of TF in PFDMCH and 3-MP are summarized in Table 1. The data for BPT are also presented in Table 1 for comparison. The energies of the S_2, S_1 and T_1 states are the wavenumbers of the origin bands in the electronic transitions. Only the location of the $S_2 \leftarrow S_0$ origin is uncertain owing to the unstructured nature of the absorption spectrum. The substantially larger S_1–T_1 spacing and the substantially smaller S_2–S_1 spacing in TF compared with BPT should be noted.

Fig. 3 presents the emission excitation spectra obtained when the $S_2 \rightarrow S_0$ fluorescence (top panel) and $T_1 \rightarrow S_0$ phos-

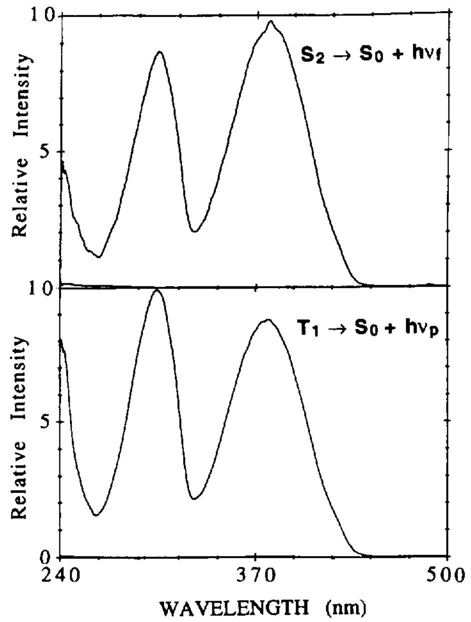


Fig. 3. Emission excitation spectra of TF in PFDMCH at room temperature. Top panel: $S_2 \rightarrow S_0$ fluorescence excitation spectrum monitored at 520 nm. Bottom panel: $T_1 \rightarrow S_0$ phosphorescence excitation spectrum monitored at 650 nm.

phorescence (bottom panel) of TF are monitored at 520 nm and 650 nm respectively and the excitation wavelength is scanned through the strong absorption bands in the blue and near-UV. These spectra are similar in shape to the absorption spectra, but are of different relative intensities. More intense fluorescence is obtained by exciting in the $S_2 \leftarrow S_0$ system than in the $S_3 \leftarrow S_0$ and $S_4 \leftarrow S_0$ systems to higher energies, whereas more intense phosphorescence is obtained by exciting in the $S_3 \leftarrow S_0$ and $S_4 \leftarrow S_0$ systems than in $S_2 \leftarrow S_0$.

The quantum yields of $S_2 \rightarrow S_0$ fluorescence ϕ_f and the S_2 lifetimes $\tau(S_2)$, obtained by excitation of TF in its $S_2 \leftarrow S_0$ absorption band, in both 3-MP and PFDMCH are presented in Table 2. The concentration of TF employed in these experiments was $(1.3–9.1) \times 10^{-6}$ M, too low for concentration quenching to play a significant role. However, 3-MP quenches the S_2 state to a significant extent, as shown by the difference in both ϕ_f and $\tau(S_2)$ in this solvent compared with PFDMCH which is inert. It should be noted that the ratio of the quantum yields in the two solvents (ϕ(PFDMCH) : ϕ(3-MP) = 4.67 : 1) is the same as the ratio of the lifetimes (4.56 : 1), indicating that 3-MP acts to increase the non-radiative decay rate of the excited thione. Data for BPT are also presented in Table 2 for comparison.

The photophysical properties of triplet TF are presented in Table 3. The data in this table were obtained by exciting TF in its strong $S_2 \leftarrow S_0$ absorption band in degassed 3-MP and PFDMCH at room temperature. Phosphorescence quantum yields $\phi_p(S_2)$ and triplet lifetimes $\tau(T_1)$ were obtained at several thione concentrations in the $(1–10) \times 10^{-6}$ M range. These data were then cast in Stern–Volmer form. The slope of the Stern–Volmer plot of $1/\tau(T_1)$ gives the second-order

Table 2
Photophysical data for the second excited singlet states of TF and BPT in PFDMCH and 3-MP at room temperature ($c = (1.3–9.1) \times 10^{-6}$ M)

Data	TF		BPT[a]	
	PFDMCH	3-MP	PFDMCH	3-MP
ϕ_f	$(2.8 \pm 0.3) \times 10^{-3}$	$(6 \pm 0.4) \times 10^{-4}$	2.3×10^{-2}	2.3×10^{-3}
$\tau(S_2)$ (ps)	41 ± 2	9 ± 1	210	24
$k_{f2,0}$ (s^{-1})	6.8×10^7	6.7×10^7	11×10^7	9.6×10^7
Σk_{nr} (s^{-1})	2.4×10^{10}	11×10^{10}	0.48×10^{10}	4.2×10^{10}
$k_{f2,0}^{S-B}$ (s^{-1})	–	6.7×10^7	11×10^7	–
ϕ_{S_2,S_1}	–	0.96	0.88	0.95

[a] The data for BPT are from Refs. [11] and [12].

Table 3
Photophysical properties of triplet TF and BPT in PFDMCH and 3-MP

Data	TF		BPT[b]	
	PFDMCH	3-MP	PFDMCH	3-MP
ϕ_p^{0} [a]	1.15×10^{-2}	0.75×10^{-2}	7.6×10^{-2}	3.2×10^{-2}
$\tau^0(T_1)$ (μs)	3.85	2.1	16.0	7.3
$k_{p1,0}$ (s^{-1})	3.1×10^3	3.7×10^3	8.1×10^3	7.4×10^3
Σk_{nr} (s^{-1})	2.7×10^5	4.9×10^5	0.54×10^5	1.3×10^5
$k_{Q,conc}$ ($M^{-1}\,s^{-1}$)	6.5×10^9	17×10^9	6.9×10^9	20×10^9
$k_{Q,ox}$ ($M^{-1}\,s^{-1}$)	4.5×10^9	4.4×10^9	–	–
E^{0-0} (kcal mol^{-1})	43.9	43.8	45.6	45.5

[a] For excitation to S_2.
[b] The data for BPT are from Refs. [11] and [12].

Table 4
Quenching of triplet TF by oxygen in PFDMCH and 3-MP

Data	PFDMCH		3-MP	
	Degassed	Air saturated	Degassed	Air saturated
τ_{T1} (μs)	3.32	0.045	1.98	0.07
$\phi_p(S_2)$	1.04×10^{-2}	1.64×10^{-4}	6.1×10^{-3}	3.34×10^{-4}
[TF] (M)	6×10^{-6}	1.46×10^{-5}	1.8×10^{-6}	4.36×10^{-5}

rate constant for concentration quenching of T_1 by ground state thione, whereas linear extrapolation to infinite dilution provides values of $\phi_p^0(S_2)$ and $\tau^0(T_1)$, which are unaffected by concentration quenching. These quantities were then used to obtain the intramolecular decay parameters of triplet TF. It should be noted that the solvent affects T_1 and S_2 in a qualitatively similar fashion; both quantum yields and lifetimes are higher in PFDMCH than in 3-MP (1.53 : 1 and 1.83 : 1 respectively). Again, data for BPT are given in Table 3 for comparison.

The rate constants for quenching of T_1 by molecular oxygen (k_{Qox}) were obtained by measuring $\phi_p(S_2)$ and $\tau(T_1)$ in degassed and air-saturated solutions at room temperature for two separate concentrations of thione; the data were assumed to follow a simple Stern–Volmer relationship. The data are given in Table 4.

4. Discussion

The purpose of this paper is to provide a quantitative description of the photophysics of TF and, in particular, to elucidate the contribution of the internal rotational motion of the phenyl group to the non-radiative relaxation of the excited molecule in its S_2 and T_1 states. This objective is accomplished by using the spectroscopic, emission quantum yield, excited state lifetime and quenching data presented above to calculate the radiative, non-radiative and quenching rate constants for each state. The results are then compared with those expected for a hypothetical rigid thione having the same structural and electronic characteristics as TF without its phenyl group. BPT and thioxanthione (TXT), which have been investigated previously in some detail, serve as useful reference compounds in making this comparison.

First, let us consider the most important processes by which S_2 can relax in degassed dilute perfluoroalkane solution, and the rate constants of these processes

$$S_2 \rightarrow S_0 + h\nu_f \quad k_{f2,0} \qquad (1)$$

$$S_2 \rightarrow S_1 \quad k_{ic2,1} \qquad (2)$$

$$S_2 \rightarrow S_0 \quad k_{ic2,0} \qquad (3)$$

The subscripts f and ic refer to fluorescence and internal conversion respectively and the numerals designate the identities of the coupled states. Here, it is assumed that photochemical decomposition does not contribute significantly to the decay of TF in perfluoroalkane solution, in agreement with the observed negligible rate of net consumption of the thione ($\phi < 10^{-2}$) in such solvents both here and in other systems [26]. It is also assumed that, in agreement with previous work on other thiones [15], direct intersystem crossing from S_2 to the triplet manifold does not compete with internal conversion within the singlet manifold. (Including intersystem crossing would not affect the subsequent steps in the relaxation sequence, since S_1 decays promptly to T_1 with near unit efficiency [15,27].) Concentration quenching can be disregarded in solutions which are as dilute as those investigated here.

Previous studies of many other thiones have shown that perfluoroalkane solvents act as inert heat baths which cause efficient vibrational thermalization of the excited solute, but not electronic quenching [7]. However, interaction with the solvent dominates the relaxation of excited thiones in hydrocarbons and most other solvents [5]. Comparing the values of ϕ_f and $\tau(S_2)$ in PFDMCH with those in 3-MP (Table 1) provides clear evidence that TF behaves in a similar fashion. Therefore, in 3-MP, interaction with the solvent, which results in net quenching of S_2, must also be considered. This interaction is treated here as a second-order kinetic process (pseudo-first-order process in 3-MP solvent) without specifying the products, i.e.

$$S_2 + Q \rightarrow X \quad k_Q(S_2) \qquad (4)$$

where X may be a photochemical product or the thione in any of its lower excited electronic states.

In dilute perfluoroalkane solution, we may assume [5] that the pseudo-first-order rate constant for TF quenching by the solvent ($k'_Q(S_2)$) is much smaller than $(k_{f2,0}+k_{ic2,1}+k_{ic2,0}) = 1/\tau(S_2)$. Then $k_{f2,0} = \phi_f/\tau(S_2)$ and $\Sigma k_{nr} = (k_{ic2,1}+k_{ic2,0}) = (1-\phi_f)/\tau(S_2)$, which permits $k_{f2,0}$ and Σk_{nr} to be obtained from measurements of ϕ_f and $\tau(S_2)$. The values of $k_{f2,0}$ and Σk_{nr} for TF in PFDMCH are given in Table 2. In 3-MP, an additional term must be added to the sum of the non-radiative decay constants: $\Sigma k_{nr} = (k_{ic2,1}+k_{ic2,0}+k'_Q(S_2))$. The final term in this sum accounts for the greatly increased rate of decay of TF in 3-MP. Because photochemical consumption of TF is also negligible in 3-MP, an estimate of $k'_Q(S_2)$ for this process can be obtained by assuming that $(k_{ic2,1}+k_{ic2,0})$ is the same in both PFDMCH and 3-MP. On this basis, we obtain $k'_Q(S_2) = 8\times10^{10}\ s^{-1}$ for the S_2 state of TF in 3-MP.

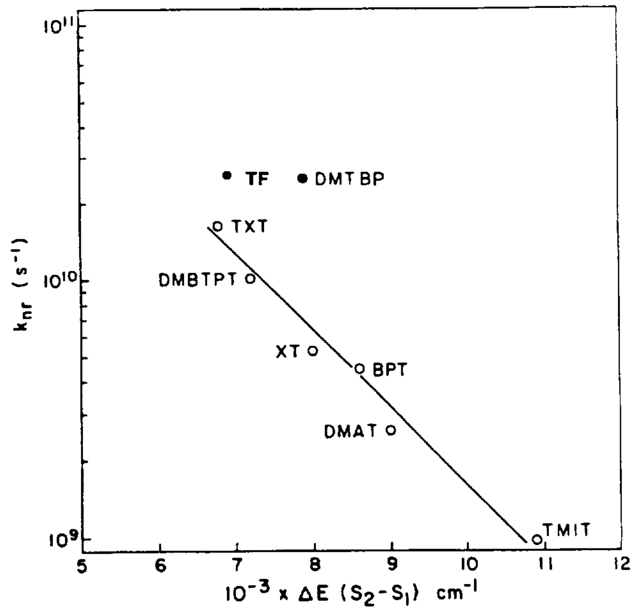


Fig. 4. Semilogarithmic plot of Σk_{nr} vs. S_2–S_1 energy gap for aromatic thiones in perfluoroalkane solvents at room temperature. The full line is the correlation obtained for the rigid thiones. The points for TF and DMTBP are shown by filled circles. (After Ref. [11].)

An estimate of $k_{f2,0}$ can also be obtained from the integrated absorption intensity of the $S_2 \leftarrow S_0$ transition, using the Strickler–Berg formalism [28]. In 3-MP, a value of $k_{f2,0} = 6.7 \times 10^7$ s^{-1} is found, in perfect agreement with the experimentally determined value obtained via $k_{f2,0} = \phi_f / \tau(S_2)$.

We may also determine the fraction of molecules in S_2 that reach S_1 by radiationless decay by measuring the relative quantum yields of $T_1 \rightarrow S_0$ phosphorescence produced on $S_2 \leftarrow S_0$ compared with $S_1 \leftarrow S_0$ excitation, assuming that prompt $S_1 \rightarrow T_1$ intersystem crossing occurs with near unit efficiency, as described in detail in Ref. [15]. The quantum yield of $S_2 \rightarrow S_1$ internal conversion obtained for TF in 3-MP is 0.96, which compares with values of 0.95 and 0.88 for BPT in 3-MP and PFDMCH respectively [15]. Thus the presence of a phenyl rotor in TF increases the rate at which $S_2 \rightarrow S_1$ internal conversion occurs, but does not change the pathway of relaxation. Therefore, within experimental error, $\Sigma k_{nr} = k_{ic2,1}$ for TF in PFDMCH.

This observation makes it possible to quantify the effect of rotational motion of the phenyl group on the rate of S_2 relaxation in TF. In perfluoroalkane solution, rigid aromatic thiones exhibit non-radiative $S_2 \rightarrow S_1$ internal conversion rates which are well described by the energy gap law of radiationless transition theory [3,11]. Thus their rates of radiationless relaxation are directly proportional to the Franck–Condon factors for S_2–S_1 coupling, which in turn are inversely proportional to $\exp\{E(S_2) - E(S_1)\}$ when $k_{ic2,1}$ is sufficiently large [29]. Thus $\log(k_{ic2,1})$ decreases linearly with increasing $E(S_2) - E(S_1)$ as shown in Fig. 4. It should be noted that the value of $k_{ic2,1}$ for TF is significantly larger than that predicted on the basis of the energy gap law correlation for rigid thiones. *p,p′*-Dimethoxythiobenzophenone (DMTBP), which has two rotatable aryl groups attached to the thiocarbonyl moiety, behaves similarly, but has a proportionately larger value of $k_{ic2,1}$ compared with rigid thiones having the same energy gap [11].

Substituting an aromatic thione with a pendant aryl group has two important effects on the non-radiative decay rate of S_2. First, the aryl group extends the conjugation of the π electron system, decreasing the S_2–S_1 electronic energy spacing and increasing the non-radiative decay rate. Second, the phenyl group increases the density of states coupling S_1 and S_2 owing to the relatively close spacing of internal torsional and rotational levels in a molecule containing an internal rotor. This is also expected to increase the rate of non-radiative decay of S_2. Because both effects occur together when BPT is substituted at the 2-position with a phenyl group to obtain TF, it is not appropriate to compare BPT and TF directly. Instead, we compare the observed value of $k_{ic2,1}$ of TF with that of a hypothetical rigid thione having the same $E(S_2) - E(S_1)$ value and assume that the difference between the two is due entirely to the incremental promoting effect of phenyl rotation. The rigid thione which has an energy gap closest to that of TF is TXT [11].

Using this approach, $k_{ic2,1}$ can be expressed as a sum of two terms: $k_{ic2,1} = k^0_{ic2,1} + k'_{ic2,1}$, in which $k^0_{ic2,1}$ is the rate constant for a hypothetical rigid thione having $E(S_2) - E(S_1) = 6900$ cm^{-1} (that of TF), and $k'_{ic2,1}$ is the rate constant representing the incremental effect of having a rotatable phenyl group in the molecule. A value of $k^0_{ic2,1} = 1.3 \times 10^{10}$ s^{-1} is obtained from the data for rigid thiones used to construct Fig. 4 [11], which then gives $k'_{ic2,1} = 1.1 \times 10^{10}$ s^{-1}. These data are summarized in Table 5. On this basis, we conclude that rotation of the phenyl group in the S_2 state of TF approximately doubles the rate of S_2–S_1 internal conversion.

The photophysical parameters for DMTBP have been measured previously [11]. Making the same assumptions as for TF, we calculate values of $k^0_{ic2,1} = 5.9 \times 10^9$ s^{-1} and $k'_{ic2,1} = 2.3 \times 10^{10}$ s^{-1}, i.e. having two aryl rotors attached to the thiocarbonyl chromophore results in an approximately fourfold increase in the rate of radiationless decay of S_2. As expected, the effect is greater in DMTBP with two strongly coupled rotors than in TF which has only one. On the other hand, having methyl rotors present in an otherwise rigid aromatic thione, such as 2,2,3,3-tetramethylindanethione (TMIT) or 2,6-dimethyl-4H-benzothiopyran-4-thione (DMBTPT) [11], apparently makes no substantial difference to the decay rates, since the radiationless decay rates of these molecules follow the energy gap correlation for rigid thiones.

Excitation to S_2 thus results in a near-quantitative relaxation to T_1, i.e. by Eq. (2) followed by

$$S_1 \rightarrow T_1 \quad k_{isc1,1} \qquad (5)$$

in perfluoroalkane solvents or by Eq. (4) in 3-MP and other more strongly interacting media. Subsequently, T_1 is depopulated via the following set of intramolecular processes

Table 5
Rate constants for the non-radiative deactivation processes of the S_2 and T_1 states of TF and BPT in PFDMCH and 3-MP

Data	TF		BPT[b]	
	PFDMCH	3-MP	PFDMCH	3-MP
S_2 state				
$1/\tau=\Sigma k$ (s^{-1})	2.4×10^{10}	11×10^{10}	0.48×10^{10}	4.2×10^{10}
$k^0_{ic2,1}$ (s^{-1})	1.3×10^{10}	1.3×10^{10}	0.48×10^{10}	0.48×10^{10}
$k'_{ic2,1}$ (s^{-1})	1.1×10^{10}	1.1×10^{10}	–	–
k'_Q (s^{-1})[a]	–	8×10^{10}	–	3.7×10^{10}
$E(S_2)-E(S_1)$[b] (cm^{-1})	≥6500	≥6000	8300	–
T_1 state				
$1/\tau^0=\Sigma k$ (s^{-1})	2.6×10^5	4.8×10^5	0.63×10^5	1.37×10^5
$k^0_{isc1,0}$ (s^{-1})	0.85×10^5	0.88×10^5	0.58×10^5	0.58×10^5
$k'_{isc1,0}$ (s^{-1})	1.75×10^5	1.75×10^5	–	–
k'_Q (s^{-1})	–	2.2×10^5	–	0.79×10^5
$k_{Q,ox}$ ($M^{-1}\,s^{-1}$)	4.5×10^9	4.4×10^9	–	–
$E(T_1)-E(S_0)$[b] (cm^{-1})	15360	15315	15930	–

[a] Pseudo-first-order quenching constant (see text).

[b] For the vibrationless levels in the excited states.

$$T_1 \rightarrow S_0 + h\nu_p \quad k_{p1,0} \tag{6}$$

$$T_1 \rightarrow S_0 \quad k_{isc1,0} \tag{7}$$

$$T_1 \rightarrow S_1 \quad k_{bisc1,1} \tag{8}$$

where $k_{bisc1,1}$ is the rate constant for back-intersystem crossing. In fact, in liquid solution S_1 and T_1 are in thermal equilibrium so that Eqs. (5) and (8) may be represented by

$$S_1 \leftrightarrow T_1 \quad K_{eq1,1} \tag{9}$$

where $K_{eq1,1}=[T_1]/[S_1]=(k_{isc1,1}/k_{bisc1,1})\exp\{E(S_1)-E(T_1)\}$ [14]. The thermal repopulation of S_1 leads to two further decay processes

$$S_1 \rightarrow S_0 + h\nu_f \quad k_{f1,0} \tag{10}$$

$$S_1 \rightarrow S_0 \quad k_{ic1,0} \tag{11}$$

which account for the observation of thermally activated delayed fluorescence at room temperature in thiones having small $E(S_1)-E(T_1)$ values.

No thermally activated delayed fluorescence is observed for TF in either PFDMCH or 3-MP. We ascribe this to two factors. First, TF exhibits a rather large value of $E(S_1)-E(T_1)=1210\ cm^{-1}$ (cf. Table 1) which causes the population of vibrational states in T_1 equiergic with levels in S_1 to be significantly smaller than in other thiones, such as BPT with smaller S_1–T_1 energy gaps. Second, TF exhibits a rate of intersystem crossing to the ground state which is enhanced, compared with rigid thiones with the same T_1–S_0 energy gap, by the phenyl rotor (see above). We therefore assume that TF decays primarily by Eq. (7) rather than by a combination of this and back-intersystem crossing to S_1 followed by Eqs. (10) and (11).

Two additional intermolecular processes must also be considered for these triplet thiones in liquid solution: concentration quenching by ground state thione and quenching by molecular oxygen

$$T_1 + S_0 \rightarrow 2S_0 \quad k_{Q,conc} \tag{12}$$

$$T_1 + O_2 \rightarrow S_0 + {}^1O_2 \quad k_{Q,ox} \tag{13}$$

Quenching by oxygen can be eliminated by thoroughly degassing the thione solutions, as performed in all experiments other than those designed to obtain the oxygen quenching rate constant. However, concentration quenching by ground state thione cannot be entirely eliminated, even in the most dilute solutions employed in these experiments. Hence it was necessary to measure the quantum yields of phosphorescence ϕ_p and triplet lifetimes $\tau(T_1)$ as a function of thione concentration, and then to extrapolate the data in Stern–Volmer form to infinite dilution to obtain ϕ^0_p and $\tau^0(T_1)$. These values are given in Table 3, and were employed to calculate the rate constants for radiative and non-radiative decay of the triplet using $k_{p1,0}=\phi^0_p/\tau^0(T_1)$ and $\Sigma k_{nr}=k_{isc1,0}=(1-\phi^0_p)/\tau^0(T_1)$, assuming a unit quantum yield of triplets. Thus $k_{p1,0}$ and $k_{isc1,0}$ may be obtained from the quantum yield and triplet lifetime measurements. The values of these rate constants are given in Tables 3 and 5 respectively.

We ascribe the smaller quantum yield of phosphorescence and the shorter triplet lifetime (larger triplet non-radiative decay rate) in 3-MP compared with PFDMCH to an additional, kinetic, pseudo-first-order interaction between the triplet thione and the hydrocarbon solvent, i.e. $\Sigma k_{nr}=k_{isc1,0}+k'_Q(T_1)$ in 3-MP, as is the case in other thione triplets [12,13]. Assuming that the value of $k_{isc1,0}$ is the same in both 3-MP and PFDMCH, we calculate $k'_Q(T_1)=2.2\times10^5\ s^{-1}$. Next, based on an analysis similar to that employed above for S_2, we compare the purely intramolecular non-radiative decay rate of triplet TF with that of a hypothetical rigid thione having the same T_1–S_0 energy gap. Since the radiationless decay rates of rigid thione triplets also follow an energy gap law as shown in Fig. 5 [12], the difference between the value of $k_{isc1,0}$ for TF and that calculated from the energy gap law for a rigid aromatic thione having $E(T_1)-E(S_0)=15\,360$

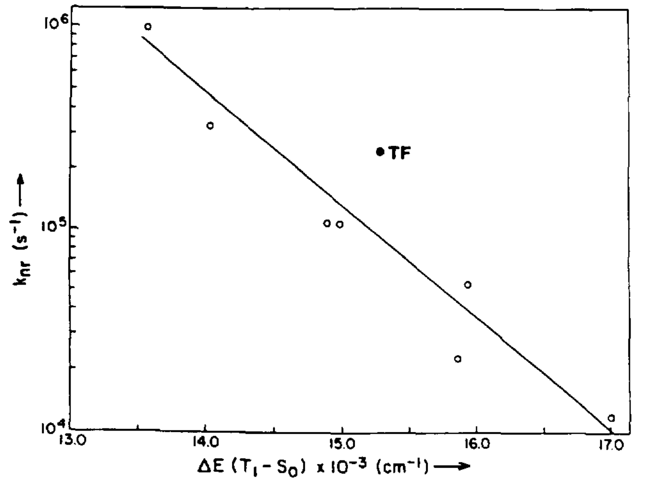


Fig. 5. Semilogarithmic plot of Σk_{nr} vs. T_1–S_0 energy gap for aromatic thiones in perfluoroalkane solvents at room temperature. The full line is the correlation obtained for the rigid thiones. The point for TF is shown by the filled circle. (After Ref. [12].)

cm^{-1} is taken to be the increment in the rate constant assigned to the promoting effect of the phenyl rotor. Thus $k_{isc1,0} = k^0_{isc1,0} + k'_{isc1,0}$ and the values of $k^0_{isc1,0}$ and $k'_{isc1,0}$ are 0.85×10^5 s^{-1} and 1.75×10^5 s^{-1} respectively. The complete set of rate constant data for triplet TF is summarized in Table 5, together with that for BPT for comparison.

Again the effect of the phenyl rotor on the rate of excited state decay is twofold. First, TF has a slightly smaller T_1–S_0 energy gap than BPT (cf. Table 1), and therefore a faster rate of radiationless decay owing to the effect of added delocalization in the former. However, the effect is smaller than that for the S_2–S_1 energy gap, since the S_2 state is of $^1(\pi,\pi^*)$ character and is lowered in energy by π delocalization to a greater extent than either S_1 or T_1, which are both of (n,π^*) character. Second, the phenyl rotor increases the non-radiative decay rate of triplet TF by about a factor of two compared with a rigid thione having the same T_1–S_0 energy gap due to the increase in the density of internal rotational states which are effective in coupling T_1 and S_0.

Finally, for triplet TF, we calculate values of the rate constants of the second-order processes (Eqs. (12) and (13)). Values of $k_{Q,conc} = 6.5 \times 10^9$ M^{-1} s^{-1} and 1.7×10^{10} M^{-1} s^{-1} are obtained for triplet TF in PFDMCH and 3-MP respectively by measuring the slopes of Stern–Volmer plots of the inverse lifetime vs. thione concentration data. Triplet quenching by oxygen proceeds with a rate constant of $k_{Q,ox} = 4.5 \times 10^9$ M^{-1} s^{-1} in PFDMCH at room temperature. This compares with a value of $k_{diff} = 1.9 \times 10^{10}$ M^{-1} s^{-1} under the same conditions, obtained via $k_{diff} = (4\pi N/1000)RD$ [30], where $R = r_{TF} + r_{ox}$ ($r_{TF} = 4$ Å, $r_{ox} = 1.7$ Å) and $D = D_{TF} + D_{ox}$ ($D_{TF} = 0.6 \times 10^{-5}$ cm^2 s^{-1} and $D_{ox} = 3.8 \times 10^{-5}$ cm^2 s^{-1} in PFDMCH) [31]. In this case $k_{Q,ox}/k_{diff} = 0.24$, suggesting that diffusion-limited quenching of triplet TF by oxygen occurs with a spin statistical factor of one-quarter. These data are summarized in Tables 3 and 5.

The foregoing analyses indicate that internal rotation of the 2-phenyl group in TF has a significant enhancing effect on the rates of non-radiative decay of both the S_2 and T_1 states. We now address the question of the nature of the potential surfaces which govern this motion in the S_2, T_1 and S_0 states of TF and related compounds. For molecules other than those which have twisted intramolecular charge transfer (TICT) states [32] or torsional surface crossings, these potentials are of the form [33]

$$V(\phi) = 1/2\Sigma V_n(1 - \cos n\phi) \qquad (14)$$

where ϕ is the torsional angle and V_n is the barrier to n-fold rotation. The shapes of the bands in the electronic spectra of polyatomic molecules are determined by the relative shapes of the two radiatively coupled potential energy surfaces and the relative displacements of these surfaces along one or more internal coordinates. For aromatic molecules with a pendant phenyl group, ϕ is one such coordinate. Because all of the experiments in this study were conducted in liquid solution at room temperature, it is impossible to extract detailed information about the torsional potentials from the absorption, emission and excitation spectra. Nevertheless, these spectra provide important clues regarding the nature of the surfaces involved because, even in solution at room temperature, the location of the torsional maxima and minima of the upper surface relative to those of the ground state will at least in part determine the general shape, structure (if any) and width of the bands.

The locations of torsional minima and the barrier heights in molecules with pendant phenyl groups depend on a balance between the stabilization associated with extended π conjugation (maximized when $\phi = 0$) and the destabilization associated with steric repulsion (often involving ortho hydrogens). Thus although biphenyl [34] has a non-planar ground state and a planar S_1 state, tolane (diphenyl acetylene), in which steric repulsion is negligible, is planar in both S_0 and S_1 [35]. Increased conjugative stabilization causes the torsional barrier V_2 to be higher in the excited state in both molecules and this appears to be common to systems with rotatable phenyl groups in which the excited state is of (π,π^*) character [36].

Thus, for TF, we expect the ground state to have a non-planar equilibrium conformation and to tend more towards planarity in the S_2, S_1 and T_1 states. The barrier to internal rotation is expected to be largest in the S_2 state of (π,π^*) character, somewhat smaller in S_1 and T_1 of (n,π^*) character and smallest in the ground state. The spectra of TF in the non-polar solvents used in this study are consistent with these expectations. The bands in the absorption and emission spectra of TF (cf. Table 1) are wider than those of BPT and other rigid thiones, the $S_n \leftarrow S_0$ ($n \geq 2$) absorption systems of TF are completely structureless and the overlapping $S_1/T_1 \leftarrow S_0$ absorption, $S_2 \rightarrow S_0$ emission and $T_1 \rightarrow S_0$ emission systems all exhibit less structure than those of BPT in the same solvents. These data suggest that all of the bands in the electronic spectra of TF at room temperature arise from a large number of closely spaced thermally populated torsional levels. The near-gaussian shapes of the $S_2 \leftrightarrow S_0$ spectra compared with $S_1/T_1 \leftrightarrow S_0$ suggest that the largest geometry change occurs between S_2 and S_0, implying that, if the ground state is non-planar, then S_2 must be planar (or nearly so).

An interesting parallel can be drawn between the photophysical properties of the thiones under investigation here and those of the 2-substituted flavilium cations (benzopyrilium salts) which have similar structures [37]. Typical non-bridged 2-aryl-substituted benzopyrilium salts have electronic absorption spectra which also suggest that the radiative transitions occur from a distribution of non-planar conformations in the ground state to those in the excited state which relax to a more planar equilibrium geometry.

Finally, we note that the highly excited states of TF, S_n ($n>2$), exhibit a decay mechanism which is very unusual for photostable polyatomic molecules. A comparison of the relative intensities of the bands in the emission excitation spectra of TF (Fig. 3) reveals that excitation to S_n ($n>2$) results in a smaller quantum yield of $S_2 \rightarrow S_0$ fluorescence than does excitation to S_2 itself. On the other hand, the relative intensities of the phosphorescence excitation bands are the same as those of the absorption spectrum (Fig. 1). Thus all states S_n ($n \geq 2$) produce the same yield of triplets, but a significant fraction of S_n ($n>2$) decays to T_1 by a path which bypasses S_2. For example, from the relative intensities of the S_2 and S_3 bands in the fluorescence and phosphorescence excitation spectra, we estimate that approximately 28% of molecules in S_3 bypass S_2. TF therefore offers an interesting opportunity to examine the relaxation mechanism of these highly excited states.

5. Conclusions

The absorption, emission and emission excitation spectra, $S_2 \rightarrow S_0$ fluorescence and $T_1 \rightarrow S_0$ phosphorescence quantum yields and S_2 and T_1 excited state lifetimes of TF were measured in PFDMCH and 3-MP at room temperature. The results were analysed to provide a quantitative description of the decay processes of excited TF, with emphasis on the effect of the phenyl rotor on the radiationless decay rates.

In both 3-MP and inert perfluoroalkane solvents, TF exhibits spectroscopic, photochemical and photophysical characteristics which are qualitatively similar to those of other aromatic thiones in solution, but which are quantitatively different in important respects. In inert perfluoroalkane solvents, both S_2 and T_1 relax primarily via an intramolecular $S_2 \rightarrow S_1 \rightarrow T_1 \rightarrow S_0$ path, but radiationless decay to T_1 which bypasses S_2 is an unusual aspect of the decay of a significant proportion of TF excited to S_n ($n>2$). $S_2 \rightarrow S_0$ fluorescence and $T_1 \rightarrow S_0$ phosphorescence also account for a small fraction of the excited state decay events of TF, but no thermally activated delayed fluorescence is observed, consistent with its larger S_1–T_1 energy spacing. In 3-MP, the decay mechanism is dominated by intermolecular interactions between excited TF and the solvent.

The rates of intramolecular radiationless decay are larger in TF than in rigid thiones having the same electronic energy gaps owing to the influence of the torsional motion of the phenyl group. By comparing the observed rate constants for the intramolecular radiationless decay of excited TF with those of a hypothetical rigid thione having the same electronic energy spacings, contributions to the radiationless decay rates of S_2 and T_1 due to the torsional motion of the phenyl group were quantified. Phenyl torsion approximately doubles the rate of $S_2 \rightarrow S_1$ internal conversion and approximately triples the rate of $T_1 \rightarrow S_0$ intersystem crossing compared with a rigid thione having the same S_2–S_1 and T_1–S_0 energy gaps.

The second-order rate constants for quenching of triplet TF by molecular oxygen and by ground state thione were also measured. The oxygen quenching rate constant is one-quarter of the diffusion-limited value, whereas that of concentration quenching is near the diffusion-controlled limit.

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