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## Relaxation of the Second Excited Singlet States of Aromatic Thiones: The Role of Specific Solute-Solvent Interactions

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**Abstract:** Second excited singlet state ( $S_2$ ) fluorescence quantum yields and lifetimes of six aromatic thiones have been measured in solution at room temperature. Intramolecular  $S_2 \rightarrow S_1$  internal conversion dominates  $S_2$  decay in inert perfluoroalkane solvents, but intermolecular photochemical and photophysical processes dominate in more strongly interacting solvents. Stern-Volmer quenching is observed when perfluoroalkane solutions of 2,2,3,3-tetramethylindanthione, a model thione, are spiked with addends at concentrations up to ca. 0.3 M. Measurements of the rate constants for the bimolecular quenching of  $S_2$  fluorescence by 26 different addends reveal that the thione  $S_2$  state is highly reactive and that the initial intermolecular interaction path divides into physical and chemical branches, the branching ratio being a function of the nature of the quencher.

Electronic energy transfer is one of the most extensively studied processes in photochemistry and photophysics. When a donor (D) and an acceptor (A) are chosen so that  $E_D > E_A$ , energy transfer can occur by either resonance (Forster) or exchange (Dexter) mechanisms.<sup>1,2</sup> However, even when  $E_D < E_A$ , efficient quenching of the excited donor is possible. In such cases, the appearance of changes in the absorption spectrum of the donor upon addition of acceptor may signal the formation of a ground-state complex. On the other hand, if the absorption spectrum of D is independent of A, but the emission spectrum of  $D^*$  reveals a structureless band to the red of the  $D^*$  monomer emission, which grows with increasing concentration of A, exciplex formation is indicated.

Unequivocal interpretation is more difficult when efficient quenching of  $D^*$  by acceptors having  $E_D < E_A$  is not accompanied by changes in either the absorption or the emission spectra. In such cases the formation of dark exciplexes has been proposed.<sup>3-6</sup> The most significant recent advances in the study of such exciplexes have been achieved through the use of time-resolved absorption spectroscopy which permits the dynamics of their formation and decay and some of their spectral properties to be investigated. The contributions of Mataga et al.<sup>8,9</sup> to understanding the nature and the dynamics of charge transfer and hydrogen-bonding complexes are most notable.

Solvent is thought to play important roles in stabilizing excited charge-transfer complexes and perhaps in determining the nature and rates of specific donor-acceptor interactions of excited species. We have recently reported<sup>10,11</sup> that both the lifetimes and the fluorescence quantum yields of the second singlet states of several rigid aromatic thiones vary dramatically with the choice of solvent. Following the lead of Parker and Joyce,<sup>12</sup> we have employed perfluoroalkanes as solvents in order to measure the parameters

of thione  $S_2$  decay in the absence of the stronger "chemical interactions" which appear to characterize excited thiones in more common solvents.<sup>10</sup> By spiking perfluoroalkane solutions with various addends, we have also shown<sup>11</sup> that molecules such as 3-methylpentane and benzene efficiently quench thione  $S_2$  fluorescence despite the facts that the singlet electronic energies of these quenchers are higher than those of the thiones, the quantum yields of overall photochemical consumption of thione are very small, and no evidence of either ground- or excited-state complexes is found.

In the present work, we have attempted to determine more precisely the nature of the mechanism whereby the second excited

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**Table I.** Parameters Characterizing the Decay of the Second Excited Singlet States of Several Aromatic Thiones

thione	$E_{S_2}^{a,b}$ kcal mol <sup>-1</sup>	$\tau_{S_2}^{a,b}$ ps	$\phi_f^b$	$\tau_{S_2}^{PF}/\tau_{S_2}^{3MP}$	$\phi_f^{PF}/\phi_f^{3MP}$	$k_{q,3MP} \times 10^{-9},^a$ M <sup>-1</sup> s <sup>-1</sup>	$k_{q,C_6H_6} \times 10^{-9},^b$ M <sup>-1</sup> s <sup>-1</sup>
1	83.0	880	0.14	11.4	10.8	6.8 ± 0.5	10.6 ± 0.9
2	72.8	210	0.023	8.8	10.0	11.0 ± 0.8	22.0 ± 3.0
3	68.3	175	0.014	4.6	4.7	9.7 ± 0.7	11.2 ± 0.9
4	68.1	410	0.017	8.2	8.5	8.3 ± 0.8	
5	66.4	101	3.8 × 10 <sup>-3</sup>	3.7	3.2	7.0 ± 2.0	
6	62.2	64	2.3 × 10 <sup>-3</sup>	2.1	2.3	c	c

<sup>a</sup> Perfluoro-*n*-hexane solvent. <sup>b</sup> Perfluoromethylcyclohexane solvent. <sup>c</sup> Efficient quenching observed but  $k_q$  not determined due to very short  $\tau_{S_2}$ .

singlet states of aromatic thiones are quenched with unexpectedly high efficiency by common aliphatic and aromatic molecules.

### Experimental Section

**Materials.** 2,2,3,3-Tetramethylindanthione (1), 4*H*-1-benzopyran-4-thione (2), xanthione (3), 10,10-dimethylanthrathione (4), and thioxanthione (6) were all prepared by reaction of the corresponding ketone with P<sub>2</sub>S<sub>5</sub> (P<sub>4</sub>S<sub>10</sub>) following the methods of Arndt and Lorenz.<sup>13</sup> 2,6-Dimethyl-4*H*-1-benzothiopyran-4-thione (5) was prepared according to the procedure of Pederson et al.<sup>14</sup> Perfluoroalkane solvents (Aldrich, P.C.R. and K. and K.) were purified by long-term irradiation of the oxygenated material in a quartz cell with a low-pressure mercury arc rich in 253.7-nm radiation, followed by fractional distillation. The resulting materials contained <0.2 mol % impurities observable by flame ionization gas chromatography. Other materials used as quenchers were purified by standard methods and contained little or no fluorescent impurities.

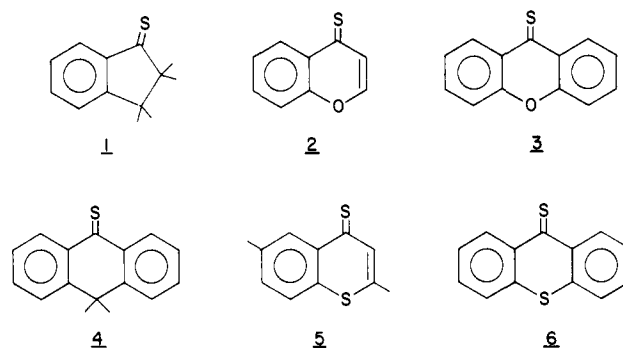
**Apparatus and Techniques.** Absorption spectra were taken on a Cary 118 spectrophotometer, and steady-state emission spectra were taken on a modified fluorometer of our own construction which has been previously described.<sup>15</sup> All measurements were made at room temperature, 22 ± 2 °C.

Quantum yields of fluorescence were measured by using the relative method previously described<sup>11</sup> and making appropriate solution refractive index corrections.<sup>16</sup> Quinine sulfate in 0.1 N H<sub>2</sub>SO<sub>4</sub> ( $\phi_f = 0.52^{16,17}$ ) and 9,10-diphenylanthracene in cyclohexane or 3-methylpentane ( $\phi_f = 0.93^{16a,18}$ ) were used as standards. Quantum yields were measured with a precision of ±3% and an estimated accuracy of ±10%. Quantum yields of overall photochemical consumption of thione were estimated from the decrease in absorbance upon irradiation, monitored at the maximum of the first strong thione absorption band in the UV-blue. Absorbed light intensities were determined by Reinecke salt actinometry.<sup>19</sup>

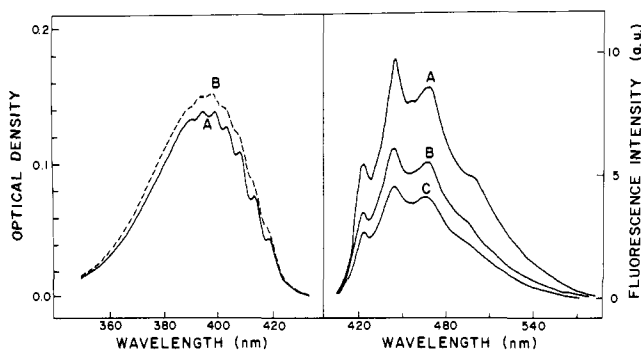
Subnanosecond fluorescence lifetimes were measured with a Spectra-Physics synchronously pumped, cavity-dumped, frequency-doubled dye laser system previously described.<sup>20</sup> Magic angle excitation/detection was employed in order to avoid distortions of the fluorescence decay due to rotational depolarization.<sup>21</sup> Time-correlated single photon counting detection was used to accumulate instrument response and sample fluorescence decay curves, and a reverse start-stop timing configuration was employed in order to accommodate the 4-MHz cavity dumping frequency. The pulse-shape-mimic technique<sup>20</sup> was used for instrument response function-sample fluorescence deconvolution, and the distribution of weighted residuals, shape of the autocorrelation function, and reduced  $\chi^2$  value were used as measures of the goodness-of-fit between the computed and observed decays. Lifetimes were measured with a typical precision of ±10 ps in these experiments.

### Results

Photostable aromatic thiones having a wide range of S<sub>2</sub> energies and S<sub>2</sub>-S<sub>1</sub> energy gaps were chosen for study (Figure 1). Their



**Figure 1.**



**Figure 2.** Absorption and emission spectra of xanthione in perfluoromethylcyclohexane at 293 K. Absorption spectrum: [xanthione] = 1 × 10<sup>-5</sup> M; (A) in pure perfluoromethylcyclohexane; (B) with 0.50 M benzene added. Emission spectrum: [xanthione] = 1 × 10<sup>-5</sup> M; (A) in pure perfluoromethylcyclohexane; (B) with 0.15 M benzene added; (C) with 0.27 M benzene added.

second excited state lifetimes,  $\tau_{S_2}$ , S<sub>2</sub> → S<sub>0</sub> fluorescence quantum yields,  $\phi_f$ , S<sub>2</sub> electronic energies,  $E_{S_2}$ , and S<sub>2</sub>-S<sub>1</sub> electronic energy gaps,  $\Delta E(S_2-S_1)$ , all taken in perfluoroalkane solvents, are summarized in Table I. Both  $\tau_{S_2}$  and  $\phi_f$  are substantially greater in perfluoroalkanes than in other solvents. Although the largest differences in  $\tau_{S_2}$  and  $\phi_f$  which result from substituting a perfluoroalkane solvent for 3-methylpentane are obtained for 1 (with the highest  $E_{S_2}$ ), and the smallest differences are obtained for 6 (with the lowest  $E_{S_2}$ ), no general correlation between the magnitude of the solvent effect and  $E_{S_2}$  was observed over the six thiones examined. The fact that, for all six thiones, both  $\tau_{S_2}$  and  $\phi_f$  change by the same relative amounts when the solvent is changed (cf. Table I) should be taken as a measure of the good internal consistency of the measurements.

Absorption, emission, and emission excitation spectra of 1, 3, and other aromatic thiones in both hydrocarbon and perfluoro-carbon solvents have been published previously.<sup>10,11,22,23</sup> In agreement with these reports, the spectra of all six thiones examined in the present study exhibit vibrational structures which are best resolved in perfluoroalkane solvents. In addition, nearly coincident S<sub>2</sub>-S<sub>0</sub> emission and absorption origin bands are found

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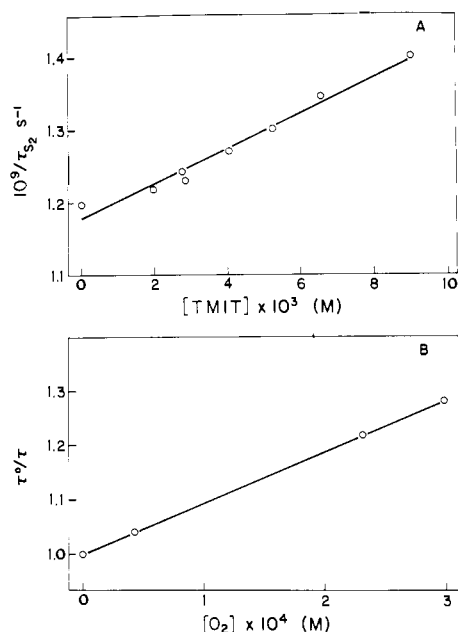
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**Figure 3.** (A) Stern-Volmer plot for the self-quenching of the second excited singlet state of TMIT (**1**) in undegassed perfluoro-*n*-hexane at 293 K. (B) Stern-Volmer plot of the oxygen quenching of the second excited state of TMIT (**1**) at 293 K. [TMIT] =  $1 \times 10^{-5}$  M.

for the thiones in perfluoroalkanes, whereas the maxima of these bands are separated by  $>200 \text{ cm}^{-1}$  in 3-methylpentane and by what is estimated to be considerably larger amounts in benzene or ethanol.

The effect on the absorption and emission spectra of adding successively greater amounts of benzene to perfluoroalkane solutions of **3**, representative of the thiones studied, is shown in Figure 2. At constant thione concentration, the absorbed intensity increases slightly, and the vibrational structure becomes less well resolved as the concentration of benzene increases, but the overall spectral shape remains the same.<sup>24</sup> The emission intensity decreases considerably with increasing benzene concentration, however, as a consequence of electronic quenching of the excited thione (vide infra). No new features are observed to the red of the structured emission in either perfluoroalkane-benzene mixtures or in pure benzene.<sup>25</sup> However, the origin band (along with the entire spectral envelope) appears to be shifted considerably toward the red in pure benzene. Similarly, no evidence of a ground-state complex is found in the absorption spectra for concentrations of benzene in perfluoromethylcyclohexane up to 0.68 M. Similar spectral results were obtained for other thione-addend combinations examined in this work.

The fluorescence spectra, quantum yields, and  $S_2$  lifetimes are all independent of exciting wavelength within the  $S_2 \leftarrow S_0$  absorption system. In particular, no evidence of emission from vibrationally unrelaxed thione, similar to that seen<sup>26</sup> in several other aromatics in solution, was observed for excitation in energies well above the electronic origin. Moreover, in molecules such as **1** in which the  $S_3 \leftarrow S_0$  absorption overlaps that due to  $S_2 \leftarrow S_0$ , excitation into  $S_3$  produced no significant differences in these quantities, presumably as a consequence of rapid  $S_3 \rightarrow S_2$  decay. Corrected excitation spectra closely mimic the absorption spectra of the thiones in the  $S_{3,2} \leftarrow S_0$  absorption regions.

Second excited singlet state lifetimes of the thiones in pure, deoxygenated perfluoroalkane solvents have been reported previously.<sup>10,11</sup> As was the case with the former experiments, thione fluorescence decays measured in perfluoroalkanes spiked with

**Table II.** Effects of Substituting C-F for C-H in Several Quenchers of the Second Excited Singlet State of **1** in Perfluoromethylcyclohexane

quencher	$k_q \times 10^{-9}, \text{ M}^{-1} \text{ s}^{-1}$	$k_q^{\text{C-H}}/k_q^{\text{C-F}}, \text{ M}^{-1} \text{ s}^{-1}$
$\text{C}_6\text{H}_6$	$10.6 \pm 0.6$	$0.88 \pm 0.12$
$\text{C}_6\text{F}_6$	$12.0 \pm 0.9$	
pyridine	$11.5 \pm 0.5$	$1.22 \pm 0.17$
perfluoropyridine	$9.4 \pm 0.8$	
acetonitrile	$11.2 \pm 0.9$	$2.7 \pm 0.6$
perfluorooctanonitrile	$4.2 \pm 0.6$	
cyclohexane	$7.6 \pm 0.6$	$8.9 \pm 1.4$
perfluorocyclopentene	$0.85 \pm 0.07$	
tetrahydrofuran	$11.4 \pm 0.5$	$\sim 570$
perfluoro-2-butyltetrahydrofuran	$\sim 0.02$	
3-methylpentane	$4.6 \pm 0.5$	$>460$
perfluoro- <i>n</i> -hexane	$<0.01$	
1 <i>H</i> -perfluoro- <i>n</i> -heptane	$1.8 \pm 0.3$	
cyclohexane	$7.0 \pm 0.5$	$>700$
perfluoromethylcyclohexane	$<0.01$	

**Table III.** Rate Constants for the Quenching of the Second Excited Singlet State of **1** in Perfluoromethylcyclohexane

quencher	$k_q \times 10^{-9}, \text{ M}^{-1} \text{ s}^{-1}$
Effects of Unsaturation	
cyclohexane	$7.0 \pm 0.5$
cyclohexene	$7.6 \pm 0.6$
1,3-cyclohexadiene	$8.8 \pm 0.7$
benzene	$10.6 \pm 0.6$
Effects of Other Quenchers	
$\text{CCl}_4$	$7.4 \pm 0.6$
$\text{CS}_2$	$11.6 \pm 0.9$
thiacyclohexane	$9.4 \pm 0.6$
ethylenediamine	$7.5 \pm 0.8$

numerous quenchers at concentrations within their solubility limits all could be described very well by single exponential functions. Observation of either dispersed emission at any wavelength in the emission spectrum or spectrally undispersed emission yielded the same  $\tau_{S_2}$  within an experimental error of ca.  $\pm 10$  ps.

The results of both steady-state fluorescence quenching measurements using a conventional spectrofluorometer<sup>15</sup> and dynamic fluorescence quenching experiments may be interpreted in terms of a simple competitive Stern-Volmer mechanism. Both steady-state and dynamic techniques yielded similar results, but the dynamic measurements were of higher precision and were less susceptible to errors due to transient diffusion effects. Bimolecular quenching constants were therefore determined exclusively from dynamic measurements in most cases.

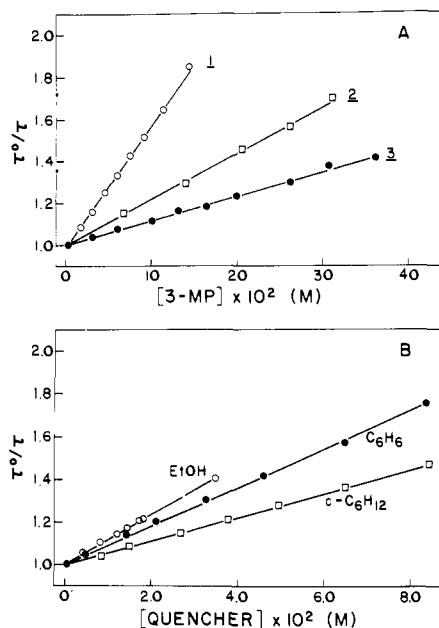
Both bimolecular self-quenching and quenching by  $\text{O}_2$  were found to be exceedingly efficient. Stern-Volmer plots for the quenching of the second excited singlet state of **1** by its ground state and by  $\text{O}_2$  are shown in Figure 3. Rate constants  $k_{q,\text{self}} = (2.4 \pm 0.2) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{q,\text{O}_2} = (1.16 \pm 0.09) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  are obtained. In all other quenching studies the use of thione concentrations  $<10^{-5}$  M eliminated self-quenching as a significant competitive decay process. Interestingly, both the solubility of  $\text{O}_2$  in perfluorocarbons and  $k_{q,\text{O}_2}$  are sufficiently large that  $\text{O}_2$  quenching of  $S_2$  thione is not negligible in air-saturated solutions at room temperature even though  $\tau_{S_2}$  is subnanosecond. If necessary, degassing was used to eliminate oxygen quenching.

Figure 4 shows a typical set of Stern-Volmer plots for the quenching of the second excited singlet state fluorescence of **1**, **2**, and **3** by 3-methylpentane and of that of **1** by ethanol, benzene, and cyclohexane. In all cases linear plots are obtained for concentrations of quencher in perfluoroalkanes up to ca. 0.3 M. Many of the quenchers studied were only moderately soluble in perfluoroalkanes, preventing measurements from being extended to higher concentrations.

(24) **1**, in which four methyl rotors contribute to spectral congestion, exhibits insufficiently well-resolved spectra to permit the origin band to be distinguished clearly even in perfluoroalkanes.

(25) Concentrations of thione are sufficiently low that inner filtering of exciplex emission, if present, by the weak  $n \rightarrow \pi^*$  absorption of the thione would be negligible.

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**Figure 4.** (A) Stern-Volmer plots for the quenching of the second excited singlet states of **1** ( $0.5 \times 10^{-5}$  M in perfluoro-*n*-hexane), **2** ( $2.0 \times 10^{-5}$  M in perfluoro-*n*-hexane), and **3** ( $1.0 \times 10^{-5}$  M in perfluoromethylcyclohexane) by 3-methylpentane at 293 K. (B) Stern-Volmer plots for the quenching of the second excited singlet state of **1** ( $0.5$ – $2.0 \times 10^{-5}$  M) by ethanol (in perfluoro-*n*-hexane), benzene, and cyclohexane (both in perfluoromethylcyclohexane) at 293 K.

**Table IV.** H/D Isotope Effect on the Quenching of the Second Excited Singlet State of **1**

quencher	cyclohexane <sup>a</sup>	benzene <sup>a</sup>	ethanol <sup>b</sup>	acetonitrile <sup>b</sup>
$k_q \times 10^{-9}$ , $M^{-1} s^{-1}$	$7.0 \pm 0.5$	$10.6 \pm 0.6$	$16.5 \pm 0.9$	$16.6 \pm 0.9$
$k_q^H/k_q^D$	$1.49 \pm 0.21$	$1.03 \pm 0.12$	$1.23 \pm 0.17$	$1.00 \pm 0.18$

<sup>a</sup> Perfluoromethylcyclohexane solvent. <sup>b</sup> Perfluoro-*n*-hexane solvent.

The rate constants for the quenching of the second excited singlet state of **1** by addends having a variety of structures and physical properties are summarized in Tables II and III. In all cases each value of  $k_q$  was obtained from the slope of the Stern-Volmer plot divided by the measured lifetime of the excited thione in pure perfluoroalkane solution. Errors quoted represent one standard deviation in the least-squares fit to the data ([quencher] < 0.3 M) and are generally on the order of  $\pm 10\%$ . Measurements of the rate constants for quenching of excited **1** by benzene, ethanol, cyclohexane, acetonitrile, and their perdeuterated analogues allowed the H/D isotope effect for the quenching process to be calculated for these four molecules. These results are given in Table IV.

The quantum yields of overall photochemical consumption of thione,  $\phi_d$ , varied widely with solution composition but, importantly, were estimated to be no greater than  $10^{-4}$  in deoxygenated perfluoroalkane solutions in which the thione concentration was small enough to permit bimolecular self-quenching to be neglected (<  $10^{-5}$  M). In solvents possessing abstractable hydrogen atoms,  $\phi_d$  was much larger; the value of 0.018 for xanthione (concentration <  $5 \times 10^{-5}$  M) excited to  $S_2$  in neat deoxygenated 3-methylpentane is typical of  $\phi_d$  in the saturated hydrocarbons. For **1** in neat 3-MP or cyclohexane,  $\phi_d$  is <  $10^{-2}$  and is <  $10^{-3}$  in neat benzene. Furthermore, changes in absorbance during or after illumination of solutions of thiones in mixed perfluoroalkane-addend solvents were negligible. Thus, although  $\tau_{S_2}$  in perfluoroalkanes are substantially longer than in other solvents (so that  $\phi_d$  might be proportionately larger), it may be safely assumed that net photochemical consumption of thione is the end result of only a very small fraction of excited thione decay events in deoxygenated perfluoroalkane solutions spiked with these addends. (The values of  $\phi_d$  were, however, not measured routinely so that

it is not possible to state unequivocally that photochemical consumption of thione was negligible in all the solutions examined.)

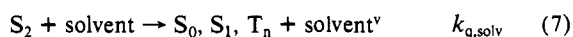
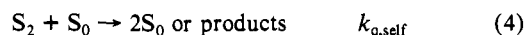
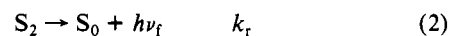
Four different perfluoroalkanes, perfluoro-*n*-hexane, perfluoromethylcyclohexane, perfluoro-1,3-dimethylcyclohexane, and perfluorodecalin, were employed in the above studies. The cyclic perfluoroalkanes are known<sup>27</sup> to have significantly higher electron affinities than the linear perfluoroalkanes and can perturb the absorption spectra of hydrocarbons through what is thought to be a contact charge-transfer process.<sup>28</sup> Their viscosities, polarities, refractive indexes, and dielectric constants differ significantly. Nevertheless, the spectra and the values of  $\phi_f$  and  $\tau_{S_2}$  for **1** and **3** were identical within experimental error in all four perfluoroalkane solvents, and no deviations from linearity of Stern-Volmer plots were observed in any of the mixed hydrocarbon-perfluoroalkane solvents (for hydrocarbon concentrations < 0.3 M). In particular, the values of  $\tau_{S_2}$  for each thione exhibited differences of less than 10 ps among the four pure perfluoroalkanes employed.

## Discussion

The aromatic thiones exhibit several electronic transitions in the near-UV-visible region. Weak singlet and triplet  $n \rightarrow \pi^*$  electron promotions occur in the visible, the oscillator strength of the triplet absorption often being only ca. a factor of 10 smaller than that of the singlet.<sup>29</sup> The first strong absorption in the near-UV blue has been assigned to an electric dipole allowed  $\pi \rightarrow \pi^*$  transition ( $^1A_1 \leftarrow ^1A_1$ , based on  $C_{2v}$  local symmetry about the thiocarbonyl moiety) on the basis of its oscillator strength, polarization,<sup>22</sup> and correlation with theory.<sup>22,30</sup> In thiofluorenone,<sup>30</sup> a weaker  $^1B_2 \leftarrow ^1A_1$  transition, located between the  $^1A_1 \leftarrow ^1A_1$  and  $^1,3A_2 \leftarrow ^1A_1$  systems, has been reported, but no evidence of such a transition has been found in any of the thiones examined in the present work. There can be little doubt that the emitting species observed in these experiments are the second excited singlet states ( $^1(\pi, \pi^*)$ ,  $^1A_1$ ) of the thiones in all cases.

The changes in electron density on  $^1A_1 \leftarrow ^1A_1$  excitation of **3** and thiofluorenone have been probed by CNDO/CI calculations.<sup>22,30</sup> In both thiones, large amounts of electron density are transferred from the S of the thiocarbonyl group to the adjacent carbon atom and small amounts of other ring carbons. The  $^1A_1 \leftarrow ^1A_1$  transition before assumes some characteristics of an intramolecular charge-transfer band, and the thione in the  $^1(\pi, \pi^*)$  state might be expected to exhibit intermolecular interactions consonant with an electron deficiency (relative to the ground state) on the S atom. Such a picture would appear to be largely consistent with the known photochemistry of the  $S_2$  states of several aromatic, aralkyl, and alicyclic thiones<sup>31</sup> which are ubiquitous H atom abstractors and which add to olefins and nitriles.

The following is the minimum number of reactions required to describe the kinetics (but not the mechanism) of the  $S_2 \leftarrow S_0$  excitation and decay of aromatic thiones in inert perfluoroalkane solutions containing potential quenchers.



Here  $T_n$  represents any triplet state of the thione lower in energy

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(29) Steer, R. P. *Rev. Chem. Intermed.* **1981**, *4*, 1.

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than  $S_2$ , Q represents an added quencher (excluding solvent), and the remaining notation is obvious. Note that the nonradiative relaxation of  $S_2$  has been separated arbitrarily (for the present) into an "intramolecular" path, (3), the first-order rate constant for which is  $k_{nr}$ , and an "intermolecularly solvent-assisted" path, (7), the products of which could be any of  $S_0$ ,  $S_1$ , or  $T_n$  plus vibrationally "hot" solvent. The pseudo-first-order rate constant for the latter is  $k_{q,solv}[\text{solvent}]$ . Intramolecular photochemical processes have been ignored on the basis that  $\phi_d$  is very small in pure deoxygenated perfluoroalkane solvents in all cases. No step in which photochemical reaction with  $O_2$  takes place is included because  $\phi_d$  is also small when  $O_2$  is present.

Application of the usual steady-state approximation yields  $k_t = \phi_f/\tau_{S_2}$  and  $k_{nr} + k_{q,seif}[S_0] + k_{q,O_2}[O_2] + k_q[Q] + k_{q,solv}[\text{solvent}] = (1 - \phi_f)/\tau_{S_2}$ . When  $O_2$  or self-quenching rate constants are measured experimentally, the conditions  $[Q] = 0$  and  $[\text{solvent}] = \text{constant}$  are realized, so that Stern-Volmer plots of either  $I_f^\circ/I_f$  or  $\tau_{S_2}^\circ/\tau_{S_2}$  vs.  $[O_2]$  and  $\tau_{S_2}^\circ/\tau_{S_2}$  vs.  $[S_0]$  yield straight lines of slope  $k_{q,O_2}\tau_{S_2}^\circ$  and  $k_{q,seif}\tau_{S_2}^\circ$ , respectively. Independent measurements of  $\tau_{S_2}^\circ$  in the absence of  $O_2$  or extrapolated to  $[S_0] = 0$  can then be used to calculate  $k_{q,O_2}$  and  $k_{q,seif}$ . Both rate constants are very large ( $>10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ), indicating that both oxygen quenching and self quenching approach the diffusion-controlled limit. In degassed solutions in which  $[S_0] < 10^{-5} \text{ M}$ , conditions usually employed for measuring  $k_q$  of added quenchers in perfluoroalkane solutions,  $(1 - \phi_f)/\tau_{S_2} = k_{nr} + k_{q,solv}[\text{solvent}] + k_q[Q]$ . When  $[Q] \ll [\text{solvent}]$  so that the former can be varied while the latter remains approximately constant,<sup>32</sup> plots of either  $I_f^\circ/I_f$  or  $\tau_{S_2}^\circ/\tau_{S_2}$  vs.  $[Q]$  will be linear (if the kinetic description is adequate) with slope  $\tau_{S_2}^\circ k_q$ ; again values of  $k_q$  (as reported in Tables II-IV) can be extracted if  $\tau_{S_2}^\circ$  is measured.

The quantity  $k_{nr}$  is the rate constant for the intramolecular radiationless decay of  $S_2$  which would be observed if the thione were dissolved in a heat bath which acts as an efficient thermalizing medium but which causes negligible perturbations of the rates of nonradiative electronic transitions in the excited molecule.<sup>33</sup> On the other hand,  $k_{q,solv}[\text{solvent}]$  represents, kinetically, the pseudo-first-order rate constant of the intermolecular process(es) whereby specific solvent-excited solute interaction enhances the rate of radiationless decay. The available evidence suggests that  $k_{q,solv}[\text{solvent}] \ll k_{nr}$  in perfluoroalkane solvents; i.e., perfluoroalkanes act as effective vibrational relaxers on the subnanosecond time scale of relevance here (no evidence of vibrationally unrelaxed emission), but they are sufficiently inert that they do not cause significant enhancement in the rate of electronic relaxation. In support of this suggestion, we note that, qualitatively, the thione spectra are better resolved in perfluoroalkanes than in other solvents, all other factors being the same. Vibrational structure becomes significantly more poorly resolved as the concentration of addend is increased in mixed perfluoroalkane-addend solvents (cf. Figure 2), indicating that specific solute-addend interactions are greater even when the addends are "inert" substances such as alkanes. In addition, the same photophysical decay parameters were obtained in all four pure, deoxygenated perfluoroalkane solvents employed, despite significant differences in their densities, viscosities,<sup>34</sup> electron affinities,<sup>27</sup> and solvatochromic  $\pi^*$  values.<sup>35</sup> Quantitatively, the radiationless decay rates of the second excited singlet states of rigid aromatic thiones in perfluoroalkanes conform to the predictions of the energy gap law of Englman and Jortner,<sup>36</sup> assuming that  $S_2 \xrightarrow{\text{vib}} S_1$  internal conversion is the major non-radiative decay path.<sup>10</sup> Of importance to the present argument, the average  $S_2 - S_1$  interstate coupling energy is found<sup>10</sup> to be ca.  $190 \text{ cm}^{-1}$ , whereas the intermolecular solute-solvent perturbation

energy, crudely estimated from the differences in energies of the 0-0 bands in the emission and absorption spectra of rigid thiones, is  $<100 \text{ cm}^{-1}$  in perfluoroalkanes<sup>37</sup> but  $>200 \text{ cm}^{-1}$  in perhydroalkanes or more in polar solvents and benzene. Similar results were obtained by Lawson et al.<sup>38</sup> who reported that the displacement of vibronic bands of the  $S_1 \leftarrow S_0$  absorption and emission spectra of benzene caused by dissolving it in perfluoro-*n*-hexane was less than  $5 \text{ cm}^{-1}$  compared with the low-pressure vapor. Significantly, much better agreement between the predictions of the energy gap law<sup>36</sup> and experiment is found<sup>10</sup> for perfluoroalkane solutions (in which we would argue  $k_{nr} \gg k_{q,solv}[\text{perfluoroalkane}]$ ) than for alkane solutions (in which we would argue  $k_{nr} < k_{q,solv}[\text{alkane}]$ ). Knowing that the concentration of pure perfluoroalkanes is  $\sim 5 \text{ M}$ <sup>34</sup> and that  $(1 - \phi_f)/\tau_{S_2}$  for **1** is  $1 \times 10^9 \text{ s}^{-1}$ ,<sup>10</sup>  $k_{q,solv}$  is calculated to be  $<10^7 \text{ M}^{-1} \text{ s}^{-1}$  for perfluoroalkanes. Other independent evidence from quenching studies (vide infra) supports this estimate.

Assuming that excited solute-solvent interactions are sufficiently weak in perfluoroalkane solvents to permit observations of "intramolecular"  $S_2$  thione decay rates, spiking these solvents with low concentrations of addends may be expected to illuminate specific intermolecular excited thione-addend interactions. No new bands appear in the absorption spectra of thiones in hydrocarbon or alcohol solvents or in mixed perfluoroalkane-addend solvents, suggesting that strong ground-state association between the thiones and the various addends does not occur. New bands also do not appear in the emission spectra, and decays remain single exponential with constant  $\tau_{S_2}$  when observing either spectrally undispersed or dispersed emission, suggesting that radiative exciplexes are not formed. Nevertheless, the fact that remarkably efficient electronic quenching is observed might suggest that relatively strong interactions take place between the excited thiones and most of the addends examined.

**1** was chosen as a model compound for quenching studies because it has the longest  $S_2$  lifetime (880 ps in degassed perfluoroalkanes) of all the thiones examined, permitting accurate lifetimes to be measured at high quencher concentrations and minimizing transient diffusion effects.<sup>28</sup> Singlet-singlet energy transfer from any thione  $S_2$  (even **1** with the highest  $E_{S_2} = 83.0 \text{ kcal mol}^{-1}$ ) to any of the quenchers examined (Tables II-IV) would be highly endothermic, and therefore neither long-range dipole-dipole nor short-range exchange energy transfer could provide an efficient quenching path in these systems. Attempts to correlate the values of  $k_q$  with single parameters characteristic of the addends or the thiones were uniformly unsuccessful. No acceptable single parameter correlation with addend ionization potential, ground-state dipole moment, dielectric constant, or Dimroth polarity parameter<sup>39</sup> was found. Quenching by a single mechanism involving either the formation of a dark exciplex stabilized primarily by charge transfer or photoionization to a solvent trap<sup>40</sup> therefore seems unlikely. This suggestion is supported by the fact that  $k_q$ 's for the quenching of the second excited singlet states of **1-6** by a common quencher (either 3-methylpentane or benzene, Table I) are uniformly large and do not correlate with the  $E_{S_2}$ 's of the thiones.

The maximum  $S_2$  quenching rate will be controlled by diffusion, the rate constant for which can be estimated from the Stokes-Einstein-Smoluchowski equation<sup>28</sup> ( $k_{diff} = 8RT/(2000\eta)$ , in the slip limit). For perfluoro-*n*-hexane at 293 K ( $\eta = 0.71 \text{ cP}$ <sup>34</sup>),  $k_{diff} = 1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ; smaller values would be expected for the other perfluoroalkanes used which have higher viscosities. The Stokes-Einstein-Smoluchowski equation often underestimates  $k_{diff}$  by a factor of about 2 due to the failure of the Stokes-Einstein equation to properly predict the diffusion constant and the incorrect assumption in its derivation that the sum of the hydrodynamic radii of the excited solute and the quencher equal the

(31) de Mayo, P. *Acc. Chem. Res.* **1976**, *9*, 52 and references cited therein.

(32) In perfluoroalkane solvents,  $[Q]$  exceeds  $0.05[\text{solvent}]$  at  $[Q] = 0.25 \text{ M}$ .

(33) Such a medium is envisaged by Robinson and Frosch [*J. Chem. Phys.* **1962**, *37*, 1962; **1963**, *38*, 1187] in their pioneering work on radiationless transition theory and its subsequent modifications.<sup>36</sup>

(34) (a) Reed, T. M. In "Fluorine Chemistry"; Simons, J. H., Ed.; Academic Press: New York, 1964; Vol. 5, p 133 ff. (b) Green, S. W. *Chem. Ind.* **1969**, 63.

(35) Brady, J. E.; Carr, P. W. *Anal. Chem.* **1982**, *54*, 1751.

(36) Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145.

(37) Maciejewski, A., unpublished results.

(38) Lawson, C. W.; Hirayama, F.; Lipsky, S. *J. Chem. Phys.* **1969**, *51*, 1590.

(39) Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. *Ann. Chem.* **1963**, *661*, 1.

(40) Sadkowski, P. J.; Fleming, G. R. *Chem. Phys.* **1980**, *54*, 79.

Smoluchowski encounter radius.<sup>41</sup> Thus, for **1**, the measured self-quenching constant,  $2.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  in perfluoromethylcyclohexane at 295 K, is estimated to be approximately equal to  $k_{\text{diff}}$ . Quenching by "small molecules" exhibiting the largest  $k_q$  values, e.g.,  $\text{O}_2$ , acetonitrile,  $\text{CS}_2$ , ethanol, and benzene, would also appear to be very nearly diffusion limited.

The most striking feature of the entire collection of bimolecular quenching constants presented in Tables II–IV is that the excited thione quenching process is so ubiquitously efficient, considering the very wide range of quenchers examined. The largest  $k_q$ 's are approximately equal to  $k_{\text{diff}}$  (vide supra); the smallest occur for the most highly fluorinated saturated molecules such as (apart from the perfluoroalkanes themselves) perfluoro-*tert*-butylamine ( $k_q < 3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) and perfluoro-2-butyltetrahydrofuran. The fact that such a wide variety of quenchers exhibit  $k_q$ 's close to  $k_{\text{diff}}$  is also a source of difficulty in elucidating the excited thione–addend interaction mechanism. Even gross changes in the structures of the quenchers cannot be correlated with reactivity if the quenching process is always diffusion limited. One is therefore forced to focus attention on those quenchers having  $k_q < k_{\text{diff}}$ . Despite this difficulty, it is possible to discern a number of general and specific characteristics of the excited thione–addend interaction from the present data.

The presence of either C–H bonds or unsaturation in the quencher is almost always sufficient to cause its value of  $k_q$  to lie within 1 order of magnitude of the diffusion-controlled limit. The data in Table II illustrates this in detail. Note that direct comparisons between molecules with precisely the same carbon skeleton are sometimes not possible due either to difficulties in obtaining pure perfluoro compounds or to limitations imposed by the low solubilities of some addends in perfluoroalkane solvents. Nevertheless, because perfluorinated alkyl groups are not expected to contribute significantly to the quenching ability of a molecule (vide infra), conclusions drawn from comparisons between quenchers such as tetrahydrofuran and perfluoro-2-butyltetrahydrofuran should be valid. Perfluorination of benzene and pyridine causes no significant change in  $k_q$ , demonstrating that the presence of copious  $\pi$ -electron density is almost exclusively responsible for quenching by these molecules. On the other hand, the importance of C–H bonds in imparting efficient  $\text{S}_2$  thione quenching properties to a molecule can be seen from a comparison of the values of  $k_q$  for 3-methylpentane, 1*H*-perfluoro-*n*-heptane and perfluoro-*n*-hexane. Even one C–H bond in an otherwise perfluorinated compound is sufficient to cause the molecule to be a relatively efficient quencher, whereas complete fluorination dramatically decreases its quenching ability. If each C–H bond in an alkane contributed equally to the quenching process, then all other factors aside, one would expect that  $k_q$  for 1*H*-perfluoro-*n*-heptane should be more than an order of magnitude smaller than that for 3-methylpentane. The fact that the  $k_q$ 's differ by a factor of ca. 3 probably indicates that the highly electronegative F atoms serve to enhance the quenching efficiency of the former by weakening its one C–H bond and thus making the H atom more labile.

It is not yet clear if similar effects cause the quenching ability of aliphatic molecules containing a heteroatom to be reduced due to inductively enhanced binding of their lone pair(s). It is obvious that perfluoro-2-butyltetrahydrofuran and perfluoro-*tert*-butylamine are much less efficient quenchers than tetrahydrofuran or ethylenediamine, respectively. Whether this is due exclusively to F for H replacement or to some combination of F/H replacement and inductive effects on the heteroatom lone pair cannot be assessed quantitatively from the present data. Further work is presently under way to elucidate this point.

Table III contains data which illustrate the effects of increasing unsaturation on the ability of a molecule to quench  $\text{S}_2$  thione fluorescence. Cyclohexene is only a marginally better quencher than cyclohexane, indicating that the presence of C–H not C=C bonds is the source of the majority of the quenching ability of the former. This observation is borne out by comparing cyclohexane

and perfluorocyclopentene;  $k_q$  of the former is ca. 9 times greater than that of the latter. Increasing the extent of unsaturation increases  $k_q$ . As has been shown in previous photochemical studies,<sup>42</sup> the nitrile group is not inert. Acetonitrile (or acetonitrile-*d*<sub>3</sub>) is a very efficient quencher, but perfluorooctanonitrile is also efficient, indicating that interaction with the  $\pi$ -electron density of the cyano group is responsible for a large fraction of the quenching.

Table IV gives measured H/D isotope effects for the quenching of excited **1** by four molecules. Inasmuch as  $E_a$  approaches zero as  $k_q$  approaches  $k_{\text{diff}}$ , one anticipates that  $k_q^{\text{H}}/k_q^{\text{D}}$  should be nearly unity for acetonitrile, ethanol, and benzene, as observed. The value of  $k_q^{\text{H}}/k_q^{\text{D}} = 1.23 \pm 0.17$  for ethanol may be significantly greater than unity (i.e., the ethanol quenching process has a positive isotope effect), and this is supported by the observation of an increase in  $\phi_f$  ( $\text{S}_2 \rightarrow \text{S}_0$ ) for xanthione on deuteration of either methanol or ethanol solvent.<sup>23</sup> However, in the present work, only  $k_q^{\text{H}}/k_q^{\text{D}} = 1.49 \pm 0.21$  for **1** in cyclohexane ( $k_q < k_{\text{diff}}$ ) is unquestionably significant. In light of the small value of  $E_a$  associated with quenching by cyclohexane, an H/D rate constant ratio of this magnitude is almost certainly indicative of a primary isotope effect and, therefore, the participation of C–H(D) bond<sup>43</sup> weakening along the initial part of the reaction coordinate which leads ultimately to electronic relaxation of the excited molecule. It is important to remember, however, that  $\phi_d < 10^{-2}$  for **1** in cyclohexane so that this initial elongation of the C–H(D) bond associated with the quenching process does not lead to *net* photochemical consumption of thione in the large majority of encounters.

None of the fluorescent thiones, **1**–**6**, has been the subject of a thorough  $\text{S}_2$  photochemical study, although **3** has been examined briefly.<sup>22</sup> The most thoroughly photochemically studied thiones, adamantanethione and thiobenzophenone,<sup>31</sup> do not emit measurable fluorescence. While the lack of detailed photochemical data for thiones whose  $\text{S}_2$  lifetimes can be determined directly by fluorometric methods is unfortunate, some insight into excited thione–quencher interactions may be gained from examining the known  $\text{S}_2$  photochemistry of other molecules containing the thiocarbonyl group. de Mayo and co-workers<sup>31</sup> have shown that thione  $\text{S}_2 \leftarrow \text{S}_0$  excitation in the presence of molecules containing C–H bonds leads to nonregiospecific insertion of the thione, either intermolecularly or intramolecularly, into C–H bonds without activation, observations which are entirely consistent with the present work. In the presence of olefins nonregiospecific, stereospecific addition is found, and there is kinetic evidence for the formation of complexes in some of these cycloadditions. Cycloaddition to nitriles has also been observed. Again the present evidence is in general accord with these findings.

The present results, however, shed a somewhat different light on the nature of the encounter between  $\text{S}_2$  thione and a potential quencher. First, the fraction of encounters leading to a chemically distinct end product is seen to be small in most cases; most encounters lead only to electronic relaxation of  $\text{S}_2$  without chemical reaction. The details of the mechanism(s) by which an encounter leads to product formation or physical quenching remain unknown, although various cases of hydrogen bonding–charge transfer<sup>8,9</sup> or other molecular interactions such as those described by Morokuma<sup>44,45</sup> can be envisaged. Whatever the nature of the interaction(s), the present results suggest that only a relatively slight intermolecular perturbation, perhaps with an energy of the order of a few hundred  $\text{cm}^{-1}$ , is required for the addend to "assist" strongly in the electronic relaxation of the excited thione and completely "swamp" the intramolecular decay process(es) which would prevail in an isolated molecule or in a pure perfluoroalkane solvent.

Parallelism between the present  $\text{S}_2$  quenching work and previous photochemical studies,<sup>31</sup> together with the above indication of a low perturbation energy requirement for the intermolecularly

(42) Blackwell, D. S.; de Mayo, P.; Suau, R. *Tetrahedron Lett.* **1974**, 91.

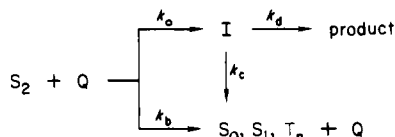
(43) Pryor, W. A.; Kneipp, K. G. *J. Am. Chem. Soc.* **1971**, 93, 5584.

(44) Morokuma, K. *Acc. Chem. Res.* **1977**, 10, 294.

(45) Morokuma, K.; Kitaura, K. In "Molecular Interactions"; Ratajczak, H., Orville-Thomas, W. J., Eds.; Wiley: New York, 1980; Vol. 1.

(41) For a recent discussion, see ref 28.

assisted electronic relaxation process, suggests that a bifurcation in the interaction path (leading to a chemically distinct intermediate in one branch and physical quenching in the other) may exist at relatively large  $S_2$ -quencher separations. The intermediate, I (vide infra), could be a free radical formed by H abstraction (initially trapped in a solvent cage with a second radical) or a dark excited complex. There is photochemical evidence<sup>31</sup> for both. A simple mechanism which incorporates these ideas follows:



If only one thione molecule is involved in the more detailed path, d, leading to chemical product, then the overall branching ratio,  $\phi_d/(1 - \phi_d) = k_{q,chem}/k_{q,phys}$ , would be equal to  $(k_a k_d)/(k_b k_c)$ . Complications requiring an expansion of this minimal set of reactions would occur if any step (e.g., step a) were reversible or if any of the products of electronic relaxation (e.g.,  $T_1$ ) were chemically reactive. No information concerning the magnitudes of the two separate branching ratios,  $k_a/k_b$  and  $k_d/k_c$ , can be inferred from the present data.<sup>46</sup> Path a followed by path c produces the same net effect as path b. The latter is included as a separate step because the magnitude of the  $S_2$ -Q interaction energy apparently required for assisting the radiationless relaxation of  $S_2$  is smaller than that normally needed to stabilize a chemically distinct intermediate such as an exciplex in solution. Thus, relaxation at relatively large intermolecular separation is envisaged.

The overall branching ratio varies with the nature of Q. Small values would appear to be characteristic of aromatics such as benzene and pyridine ( $\phi_d < 10^{-3}$ ), intermediate values ( $\phi_d \approx 10^{-2}$ ) for saturated aliphatics, and perhaps larger values for addends such as ethanol which have readily abstractable hydrogen atoms or for ground-state thione itself in which the quantum yield of dimerization approaches unity at high thione concentration in some systems.<sup>47</sup>

(46) Note that picosecond time-resolved absorption measurements might be used to measure the kinetics of I's formation and decay. Together with knowledge of the rate of product formation, such data could be used to determine  $k_a/k_b$  and  $k_d/k_c$  individually.

(47) Lawrence, A. H.; Liao, C. C.; de Mayo, P.; Ramamurthy, V. *J. Am. Chem. Soc.* 1976, 98, 3572.

Finally we suggest that the present observations, including the existence of an isotope effect in the overall thione quenching process (if slower than diffusion controlled), may necessitate a reinterpretation of the results of experiments in which mechanistic conclusions have been drawn primarily from the nature of the final products and the rates of their formation. Detailed photochemical studies of thiones 1, 2, and 3, whose second excited singlet states are radiative and for which rate constants for excited state quenching can be determined directly, are currently under way.

### Conclusions

Aromatic thiones excited to their second excited singlet,  $^1(\pi, \pi^*)$ , states are among the most reactive molecular species known in solution. Highly inert perfluoroalkane solvents are therefore needed to eliminate even relatively weak solute-solvent interactions which would otherwise mask the decay properties of the excited thiones themselves. In perfluoroalkane solution at room temperature, the  $S_2$  states of photostable, rigid aromatic thiones decay nonradiatively by  $S_2 \rightarrow S_1$  internal conversion according to the predictions of the energy gap law of Englman and Jortner.<sup>36</sup>

When perfluoroalkane solutions of thiones are spiked with addends, the nature of the specific  $S_2$  thione-addend interactions which lead to electronic quenching can be illuminated. Quenching occurs by both "photophysical" and "photochemical" means, although the fraction of encounters leading to chemically distinct end product is apparently small in most cases. The quenching process cannot be characterized by a single parameter mechanism, and the more general approach to understanding molecular interactions, such as the ECDD method developed by Morokuma,<sup>44,45</sup> may be required to interpret thione  $S_2$  quenching.

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**Registry No.** 1, 74768-62-0; 2, 6005-15-8; 3, 492-21-7; 4, 86399-30-6; 5, 86399-31-7; 6, 3591-73-9;  $C_6H_6$ , 71-43-2;  $C_6F_6$ , 392-56-3;  $CCl_4$ , 56-23-5;  $CS_2$ , 75-15-0; pyridine, 110-86-1; perfluoropyridine, 700-16-3; acetonitrile, 75-05-8; perfluorooctanonitrile, 647-12-1; cyclohexene, 110-83-8; perfluorocyclopentene, 559-40-0; tetrahydrofuran, 109-99-9; perfluoro-2-butyltetrahydrofuran, 335-36-4; 3-methylpentane, 96-14-0; perfluoro-*n*-hexane, 355-42-0; 1*H*-perfluoro-*n*-heptane, 375-83-7; cyclohexane, 110-82-7; perfluoromethylcyclohexane, 355-02-2; 1,3-cyclohexadiene, 592-57-4; thiacyclohexane, 1613-51-0; ethylenediamine, 107-15-3.

## The Origin of the Barriers to Thermally Allowed, Six-Electron, Pericyclic Reactions: The Effect of HOMO-HOMO Interactions on the Trimerization of Acetylene

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**Abstract:** The activation barrier to the trimerization of acetylene to form benzene is calculated to be 62 kcal/mol when both polarization functions (HF/3-21G) and electron correlation (MP3/3-21G) are taken into consideration. The electronic contribution to the barrier is dominated by closed-shell repulsions between filled  $\pi$  orbitals. The large favorable change in enthalpy attending this reaction can be attributed to the formation of three new  $\sigma$  bonds since no aromatic stabilization accompanies this six-electron pericyclic reaction at the transition state.

Frontier molecular orbital (FMO) theory has provided the organic chemist with a powerful tool for understanding chemo-

selectivity.<sup>1,2</sup> The use of quantum calculations in conjunction with FMO theory has been particularly successful in predicting