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Photophysics and Intramolecular Photochemistry of Adamantanethione, Thiocamphor, and Thiofenchone Excited to Their Second Excited Singlet States: Evidence for Subpicosecond Photoprocesses

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Abstract: The absorption, emission, and excitation spectra of adamantanethione (I), perdeuterioadamantanethione, thiofenchone (II), and thiocamphor (III) have been measured in a variety of solvents including inert perfluoroalkanes. Weak $S_2 \rightarrow S_0$ fluorescence has been observed for the first time in these compounds, and its quantum yields have been measured. Quantum yields of phosphorescence resulting from $S_2 \leftarrow S_0$ excitation and the quantum yields of net thione consumption in dilute solutions where photodimerization is unimportant have also been measured. The S_2 states have lifetimes which are <1 ps and, therefore, contrary to previous reports, are not the immediate precursors responsible for the intermolecular photochemical reactions of these compounds. Evidence is presented that an intermediate, X, derived from S_2 is involved, and that the most probable decay path is $S_2 \rightsquigarrow X \rightsquigarrow T_2 \rightleftarrows T_1 \rightsquigarrow S_0$. Rydberg states lie higher in energy than S_2 and are not involved. In II and III, intramolecular photochemical reaction to give the previously observed homothioenol product occurs via X.

Efficient chemical reaction,[1] energy transfer,[2] and emission[3] from highly excited electronic states (S_n or T_n, $n > 1$) of polyatomic molecules in fluid solution are of inherent interest because they are atypical. Although such processes were once described as violating Kasha's and Vavilov's rules[1,4] or as unusual exceptions to photochemical norms, modern radiationless transition theory[5] now provides a framework for understanding why such processes can and do occur.

Radiative, nonradiative physical, and nonradiative chemical relaxation processes all occur in parallel in any electronic excited state. Whenever physical radiationless relaxation processes such as internal conversion are unusually slow, the other parallel processes can compete more effectively. For highly excited electronic states, slow intramolecular radiationless decay most often occurs when these states are bound and are separated from lower adjacent states by relatively large energy gaps.[6] In such cases small Franck–Condon factors (and perhaps small electronic matrix elements) for the coupled states produce relatively slow radiationless decays, as described by the energy gap law.[6] Competing, allowed radiative decay results in "anomalous" fluorescence (e.g., $S_2 \rightarrow S_0 + h\nu_f$), whereas fast chemical transformations are observed as "wavelength-dependent photochemistry".

The thiocarbonyls are prominent among those polyatomic molecules which exhibit both anomalous fluorescence and wavelength-dependent photochemical reactions in liquid solutions.[3,7-9] In these molecules the second excited single state, of π,π^* character, can be as much as 20 000 cm^{-1} higher in energy than S_1 or T_2. The slow rate of intramolecular S_2 radiationless decay which results can be exposed by using perfluoroalkane solvents[10,11] in order to minimze the rate of intermolecular, solvent-assisted electronic relaxation.

Both aromatic and alicyclic thiones have been studied extensively. The former are apparently "well-behaved" in the sense that their S_2 radiationless decay rates quantitatively follow the predictions of the energy gap law.[12] However, the bridged alicyclic thiones (Figure 1), such as adamantanethione (I), thiofenchone (II), and thiocamphor (III), remain somewhat puzzling. These molecules have very large S_2–S_1 energy gaps and exhibit intermolecular photochemical reactions which are wavelength dependent,[13-19] implying that their S_2 states are relatively long-lived. Indeed, I has been used as a model to study the intermolecular photochemical reactions of molecules in their S_2, $^1(\pi,\pi^*)$, states.[13,16-19] In this system the existence of a transient intermediate having a lifetime of ca. 200 ps,[20] assigned to S_2, has been deduced using competitive quenching experiments. However, fluorescence from the S_2 states of these molecules has never been observed,[21] despite the fact that their $S_2 \rightarrow S_0$ transitions are fully allowed. The latter observation implies that the S_2 states of these molecules have subpicosecond lifetimes and that they themselves cannot be the intermediates which are responsible for the observed intermolecular photochemical reactions.[21]

We have undertaken an extensive study of the photophysics and intramolecular photochemistry of I, II, and III in order to help solve this puzzle.

Experimental Section

Materials. Compounds I, II, and III were prepared by reaction of the corresponding ketone (Aldrich) with P_4S_{10} in pyridine, following the method of Greidanus.[22] Perdeuteriated I was prepared by similar

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Table I. Parameters Describing the S_2–S_0 Transitions of Thiones I, II, and III

parameter	I PFDMCH[d]	I c-C_6H_{12}	I CH_3CN	II PFCMCH	III PFDMCH
$\bar{\nu}_{0,0}^{abs}$ ($\times 10^{-3}$ cm^{-1})[a]	38	37	36	38	37
ϵ_{max} ($\times 10^{-3}$ M^{-1} cm^{-1})	11.5	12.5	11.1	9.8	11.2
$\bar{\nu}_{max}^{abs}$ ($\times 10^{-3}$ cm^{-1})	42.0	41.3	40.3	41.8	41.5
$\bar{\nu}_{max}^{em}$ ($\times 10^{-3}$ cm^{-1})	28	29	27	29	29
Stokes shift ($\times 10^{-3}$ cm^{-1})[b]	14	12	14	13	13
$\bar{\nu}_{1/2}^{em}$ ($\times 10^{-3}$ cm^{-1})	12	9	5	7	9
$\bar{\nu}_{1/2}^{abs}$ ($\times 10^{-3}$ cm^{-1})[c]	6.0	6.3	6.2	5.7	6.0

[a] Transition origins from onset of $S_2 \leftarrow S_0$ absorption. [b] Difference between absorption and emission maxima. [c] The major contribution to the error in this measurement is due to overlap with the $S_3 \rightarrow S_0$ band. [d] PFDMCH = perfluoro-1,3-dimethylcyclohexane.

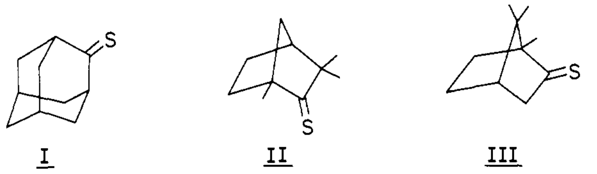

Figure 1. I, adamantanethione (tricyclo[3.3.1.1^{3,7}]decane-2-thione); II, thiofenchone (1,3,3-trimethylbicyclo[2.2.1]heptane-2-thione); III, thiocamphor (1,7,7-trimethylbicyclo[2.2.]heptane-2-thione).

treatment of the perdeuteriated ketone which, in turn, was prepared by repeated D/H exchange using the method of Nguyen and Stenhagen.[23] The product contained >98% D by MS analysis. The crude thiones were purified by column chromatography (silica/hexane) followed by vacuum sublimation. Samples were prepared from stock solutions which were stored at −20 °C in the dark under N_2 and which, under these conditions, showed no significant loss of thione for up to 1 week.

Because the quantum yields of $S_2 \rightarrow S_0$ fluorescence are very small, special care was taken to ensure that solvents contained negligible amounts of fluorescent impurities. Glass-distilled methanol and *n*-hexane (BDH Omnisolve) were used without further purification for a final cleaning of all glassware. Cyclohexane (Aldrich), acetonitrile (BDH Ominisolve), and perfluoroalkanes (PRC Research Chemicals) were purified by passage through a 14 × 1 cm column, the bottom half of which contained baked 40–200 mesh silica, and the top half of which contained the same material impregnated with 10% (w/w) $AgNO_3$. The eluent was fractionally distilled twice. The perfluoroalkane solvents were found, by proton NMR, to contain ca. 99.8 atom % fluorine. Some samples of "perfluoro-1,3-dimethylcyclohexane" were found to consist of the labeled compound and its other two positional isomers in approximately equimolar quantities. However, this did not affect their use as "inert", nonfluorescent solvents. All solvents were checked for negligible emission by exciting them at 250 nm in a spectrofluorometer.

Apparatus and Techniques. Absorption spectra and solution concentrations were measured with a Cary 118 spectrophotometer using a constant 0.3-mm slit width to provide band-passes of 5.0 nm at 500 nm and 0.5 nm at 250 mm. Cells of 10-cm length were used to record the weak, visible absorption spectra of the thiones in perfluoroalkanes owing to their low solubilities in these solvents. Corrected emission and emission excitation spectra were recorded as previously described,[24] using a Spex Fluorolog 222 spectrofluorometer equipped with a single photon counting detection system, a rhodamine B quantum counter, and a "Datamate" computer. Spectral band-passes of 7.0 nm were used to record emission spectra, and cutoff filters were placed in front of the emission monochromator when UV excitation was used so that second-order diffraction of the exciting light would not be detected as scatter in the emission.

Fluorescence quantum yields were measured as previously described,[25] using quinine sulfate in 0.1 N H_2SO_4 ($\phi_f = 0.52$)[26] as a reference, and taking care to correct for solvent refractive index effects.[27] Test and reference solutions of the same optical density (od < 0.2) were employed for all quantum yield measurements. The band-pass used to measure the optical densities in quantum yield measurements was identical with that used for fluoresence excitation.

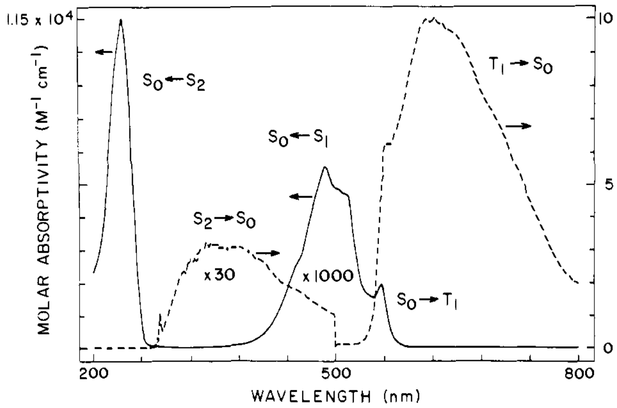

Figure 2. Absorption (—) and emission (- - -) spectra of I in perfluoroalkane solvents.

All samples were degassed and measured in quartz cells equipped with Teflon high-vacuum stopcocks and seal-off O-rings. Particular care was required to prevent contamination of the sample with fluorescent impurities during degassing. Degassing was effected by repeated (ca. 15 cycles) equilibration of solutions with a large volume of air-free solvent vapor at room temperature. (For details see ref 28.) In early experiments failure to deoxygenate samples or purify solvents adequately resulted in the appearance of emission from the corresponding ketone, which is excited to S_1 in the same spectral region of $S_2 \leftarrow S_0$ in the thione. The distinct spectral and temporal characteristics of fluorescence from the ketones[29,30] are readily recognizable, and samples showing such emission were discarded.

The relative rates of photodecomposition of adamantanethione in various solvents were obtained by observing the decrease in the thione UV absorption as a function of time of illumination in its $S_2 \leftarrow S_0$ absorption system. For this purpose the 450-W high-pressure xenon arc lamp and excitation monochromator ($\Delta\lambda$ = 9 nm) from the Spex spectrofluorometer were used as an excitation source.

Several unsuccessful attempts were made to measure the fluorescence lifetimes of the S_2 states directly, using both our frequency-doubled, synchronously pumped argon ion/dye laser excitation system which is capable of ca. 10-ps resolution,[31] and a frequency-quadrupled Nd:YAG laser excitation system capable of ca. 20-ps resolution at the Canadian Center for Picosecond Spectroscopy, Concordia University, Montreal. In neither case could the emission be temporally resolved, implying that the S_2 fluorescence lifetimes of these compounds are less than 10–20 ps.

Results

The absorption and emission spectra of adamantanethione (I) in perfluoro-1,3-dimethylcyclohexane (Figure 2) are typical of the three bridged alicyclic thiones. Weak absorptions in the visible are assignable to symmetry-forbidden transitions to S_1 and T_1, both of which are of (n,π^*) character.[7] The strong, structureless absorption with an onset near 280 nm and a maximum near 240 nm is due to the electric dipole allowed $S_2 \leftarrow S_0$ transition ($^1A_1$–$^1A_1$

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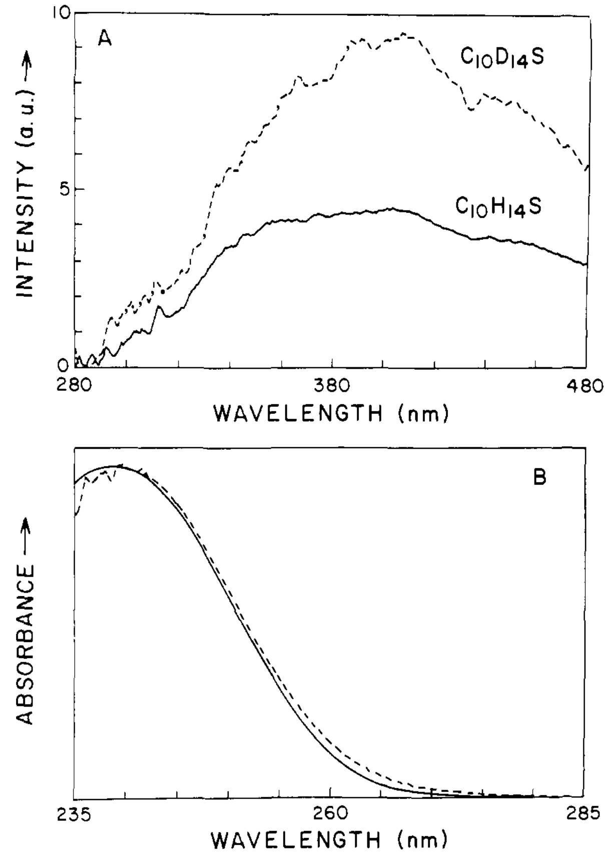

Figure 3. (A) $S_2 \rightarrow S_0$ fluorescence spectra of I (—) and perdeuteriated I (---) in perfluoro-1,3-dimethylcyclohexane. (B) $S_2 \leftrightarrow S_0$ absorption (—) and emission excitation (---) spectra of perdeuteriated I in perfluoro-1,3-dimethylcyclohexane. The spectra are normalized to their maxima for comparison.

in C_{2v}) which is associated with a $\pi \rightarrow \pi^*$ one-electron promotion isolated on the thiocarbonyl group.[13-19] Not distinguishable in this spectrum, but readily observable in the gas phase, are three Rydberg transitions, the lowest energy of which occurs just to the blue of the $S_2 \leftarrow S_0$ maximum.[32]

Excitation in the $S_2 \leftarrow S_0$ absorption system produces two distinctly different emissions (cf. Figure 2) in all three thiones. A strong emission band with a maximum in the red is assignable to phosphorescence. This emission consists of both "normal" phosphorescence, $T_1 \rightarrow S_0$, and thermally activated phosphorescence from $T_2 \rightarrow S_0$.[28] An extremely weak, broad emission with an onset near 280 nm and a maximum 100 nm to the red can be assigned to $S_2 \rightarrow S_0$ fluorescence. This portion of the spectrum was obtained by the numerical addition of ca. 30 digitized spectra obtained by slow scans of the emission wavelength using several different samples. For this reason and because the phosphorescence intensity is a function of concentration, only an approximate scaling of the two sections of the emission spectrum is given in Figure 2. Important data obtained from these spectra are summarized in Table I.

Figure 3A shows expanded, corrected $S_2 \rightarrow S_0$ emission spectra of solutions containing the same concentration of adamantanethione and perdeuterioadamantanethione in perfluoro-1,3-dimethylcyclohexane. In these spectra the relative intensities of the emissions from the two compounds are correctly scaled. The general shapes of the two spectra are similar, but the perdeuteriated compound exhibits an integrated intensity which is about twice that of the perhydro compound. That these weak emissions are indeed due to S_2 of the thione and not some impurity is shown in Figure 3B. Here the corrected emission excitation and absorption spectra of perdeuterioadamantanethione in the 235–280-nm region are compared. Given the considerable noise in the corrected excitation spectrum, the two should be considered identical.

Table II. Quantum Yields of $S_2 \rightarrow S_0$ Fluorescence and $T_n \rightarrow S_0$ Phosphorescence Following Excitation to S_2

thione	solvent[a]	$\phi_f(S_2) \times 10^{5\,b}$	$\phi_p^0(S_2)^c$
I	PFDMCH	17	0.023
	PFH	17	0.025
	c-C_6H_{12}	9.0	0.011
	CH_3CN	5.0	
II	PFDMCH	3.4	0.056
III	PFDMCH	6.5	0.024

[a] PFDMCH = perfluoro-1,3-dimethylcyclohexane; PFH = perfluoro-*n*-hexane. [b] Estimated errors are ±20%. [c] Estimated errors are ±10%.

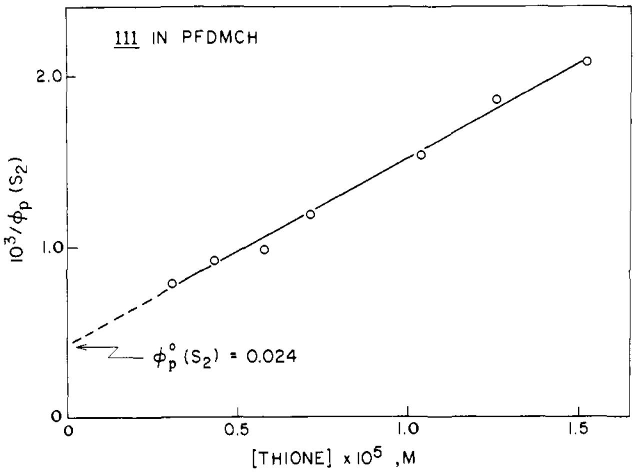

Figure 4. Stern–Volmer plot of $1/\phi_p^0(S_2)$ vs thione concentration for III in perfluoro-1,3-dimethylcyclohexane at 22 °C.

The quantum yields of $S_2 \rightarrow S_0$ fluorescence and of total phosphorescence resulting from $S_2 \leftarrow S_0$ excitation of II and III in perfluoro-1,3-dimethylcyclohexane and of I in perfluoro-1,3-dimethylcyclohexane, perfluoro-*n*-pentane, cyclohexane, and acetonitrile are given in Table II. Values of $\phi_p^0(S_2)$ were obtained by extrapolation of $\phi_p(S_2)$ data taken at finite thione concentration to infinite dilution, using Stern–Volmer plots of the type shown in Figure 4. These data, therefore, are the unquenched phosphorescence quantum yields obtained on excitation to S_2. The $S_2 \rightarrow S_0$ fluorescence quantum yields reported in Table II are averages of several replicate determinations, but because the values are so small, they are subject to an estimated error of ca. ±20%. Note that the values of both $\phi_f(S_2)$ and $\phi_p^0(S_2)$ for I are identical, within experimental error, in the two perfluoroalkane solvents and are lower in acetonitrile and cyclohexane than in the more weakly interacting perfluoroalkanes. Note also that for I the ratio of $\phi_f(S_2)$ in perfluoroalkane to $\phi_f(S_2)$ in cyclohexane ($17 \times 10^{-5}/9 \times 10^{-5} = 1.9$) is the same as the ratio of the values of $\phi_p^0(S_2)$ in the same two solvents ($0.023/0.011 = 2.1$) within experimental error.

In order to determine the pathway by which phosphorescence is produced following initial excitation to S_2, the ratios of the phosphorescence quantum yields resulting from $S_2 \leftarrow S_0$ excitation to those resulting from $S_1 \leftarrow S_0$ excitation, $\phi_p(S_2)/\phi_p(S_1)$, were determined using the following expression:

$$\frac{\phi_p(S_2)}{\phi_p(S_1)} = \frac{A_p(S_2)}{A_p(S_1)} \frac{\epsilon(S_1)}{\epsilon(S_2)} \frac{I_0(S_1)}{I_0(S_2)} C \qquad (1)$$

Here A_p refers to the integrated area under the phosphorescence emission spectrum, ϵ is the molar extinction coefficient at the wavelength of excitation, I_0 is the corrected incident intensity at the excitation wavelength, C is a small correction factor to account for the greater rate of photochemical consumption of thione on excitation to S_2 compared to S_1, and the quantities in parentheses indicate excitation to either S_2 or S_1. The ratios of $\phi_p(S_2)/\phi_p(S_1)$ were independent of thione concentration in all solvents, and

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Table III. Quantum Yields of Net Consumption of Thione Following $S_2 \leftarrow S_0$ Excitation and Relative Quantum Yields of Phosphorescence Following $S_2 \leftarrow S_0$ Compared with $S_1 \leftarrow S_0$ Excitation

thione	solvent	$\phi^0_p(S_2)/\phi^0_p(S_1)^a$	$\phi^0_{-T}(S_2)$
I	PFDMCH	1.1	0.04
	PFH	1.1	0.04
	c-C_6H_{12}	0.9	0.11^b
	CH_3CN	0.9	
II	PFDMCH	0.8	
III	PFDMCH	0.8	0.18^c

^{a}Estimated absolute errors are ±0.2. ^{b}Reference 19. ^{c}Reference 18.

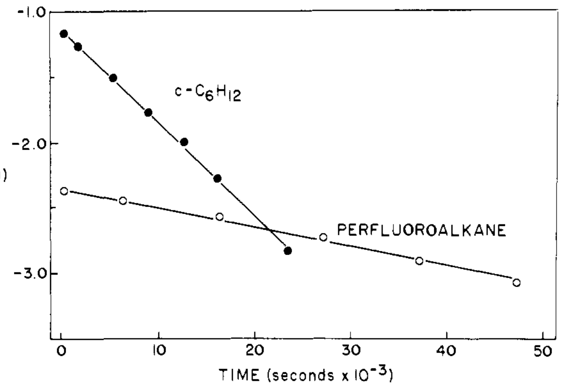

Figure 5. Natural logarithm of the optical density (taken at λ_{max} of the thione $S_2 \leftarrow S_0$ absorption) vs time of illumination for 1 in perfluoro-*n*-hexane (○) and cyclohexane (●).

absolute values of $\phi^0_p(S_1)$ could therefore be determined from $\phi^0_p(S_1) = \phi^0_p(S_2)\phi_p(S_1)/\phi_p(S_2)$. We assume that the same ratio applies at infinite dilution, and for this reason the values in Table III are given as $\phi^0_p(S_2)/\phi^0_p(S_1)$. Owing to the difficulty in measuring $I_0(S_1)/I_0(S_2)$ accurately, the absolute values of $\phi^0_p(S_2)/\phi^0_p(S_1)$ are known to no better than ±0.2. The relative values of these ratios are much better known, however, so the fact that $\phi^0_p(S_2)/\phi^0_p(S_1)$ is larger for I than for II or III in the same solvent is significant.

The rate of photochemical consumption of I was also measured in various solvents under conditions of very low thione concentration ($<10^{-5}$ M), so that dimerization would not be a significant thione loss process. At these low thione concentrations,

$$-\mathrm{d}\ln[\mathrm{T}]/\mathrm{d}t \propto \phi^0_{-\mathrm{T}} I_0 \epsilon \qquad (2)$$

where [T] is the concentration of thione, ϕ^0_{-T} is the quantum yield of thione disappearance, and I_0 and ϵ are the incident intensity and molar extinction coefficient at the excitation wavelength employed. Plots of the natural logarithm of the optical density (OD $\propto$ [T]) versus time of illumination for I in perfluoro-*n*-hexane and cyclohexane are shown in Figure 4, and confirm the validity of eq 2. The ratio of the slopes of the two lines, together with the ratios of ϵ and I_0 appropriate to the two systems, yields the ratio of the quantum yield of consumption of I in perfluoro-*n*-hexane to that in cyclohexane. Using a value of $\phi^0_{-T} = 0.115$ for the absolute quantum yield of consumption of I in cyclohexane at infinite dilution, previously determined by Law and de Mayo,[19] we calculate $\phi^0_{-T} = 0.04$ for I in perfluoro-*n*-hexane. The complete set of values of $\phi^0_{-T}(S_2)$ for the consumption of thione on excitation to S_2 at infinite dilution in various solvents is given in Table III. Note that the largest values of $\phi^0_{-T}(S_2)$ are associated with the smallest values of $\phi^0_p(S_2)/\phi^0_p(S_1)$. In agreement with previous results,[15,18] excitation of any of I, II or III to S_1 in any solvent resulted in a negligible rate of consumption of thione under conditions comparable to those when S_2 was excited.

Discussion

Of the three thiones studied, only I has perfect C_{2v} symmetry. Nevertheless II and III exhibit local C_{2v} symmetry about the C–CS–C framework, and thus the electronic transitions in all three molecules may usefully be described in terms of the symmetry of the C_{2v} point group. The two lowest energy electronic transitions observed in the absorption spectra (Figure 2), $S_1(^1A_2) \leftarrow S_0(^1A_1)$ and $T_1(^3A_2) \leftarrow S_0(^1A_1)$, are both electric dipole forbidden and are weak. The $T_1 \leftarrow S_0$ absorption is also electron spin forbidden, but is observed as a result of relatively strong spin–orbit coupling in the thiones.[33] The lowest energy allowed transition, $S_2(^1A_1) \leftarrow S_0(^1A_1)$, populates the second excited singlet state which is of primarily $^1(\pi,\pi^*)$ character. Because this transition is localized on the thiocarbonyl group in these alicyclic thiones, the C–S bond order will be approximately 1 in the S_2 state, compared with 2 in the ground state. A substantial elongation of the C–S bond is therefore anticipated as a consequence of $S_2 \leftarrow S_0$ excitation. This distortion/displacement is reflected in the S_2–S_0 absorption and emission spectra, which are broad and exhibit very large Stokes' shifts and relatively low intensities in the origin region (cf. Table I). Several tetratomic thiocarbonyls exhibit similar spectral features,[7] and these molecules are known to undergo C–S bond elongation of up to 0.5 Å on $S_2 \leftarrow S_0$ excitation.[34]

The states with the next highest energies are the $^1B_2[^1(n,4s)]$, $^1A_1[^1(n,4p_y)]$, $^1B_2[^1(n,4p_z)]$, and $^1A_2[^1(n,4p_x)]$ Rydberg states. One-photon, electric dipole-allowed transitions from the ground state have been observed[32] to all but the last of these ($^1A_2 \leftarrow {}^1A_1$ is symmetry forbidden). These observations and confirmatory SCF–MO–CI calculations[35] place the lowest of the singlet Rydberg states, $^1B_2[^1(n,4s)]$, at energies which lie ca. 8000 cm^{-1} above the $S_2(^1A_1)$ states. Because Rydberg triplet states are seldom found more than 5000 cm^{-1} below their corresponding singlets of the same orbital symmetry,[36] it therefore appears unlikely that any of the Rydberg states participate directly in the decay processes which follow excitation to S_2.

In all three thiones the T_2 ($^3A_1$) state, which has the same orbital symmetry as S_2, is located some 18–19 000 cm^{-1} below S_2, near the S_1 and T_1 states. The magnitude of the S_2–T_2 gap may be understood by considering the large electron correlation effects of two unpaired electrons confined on the C–S moiety in π and π^* orbitals with substantial spatial overlap.[37] There is strong evidence in some aromatic thiones that T_1 and T_2 are separated by no more than ca. 2500 cm^{-1} in nonpolar media,[38,39] and that their order may be inverted in polar solvents.[40] In solutions of I and III thermally activated phosphorescence from T_2 has been observed, locating T_2 no more than ca. 500 cm^{-1} higher than T_1 in the nonpolar solvents used in the present study.[28] This places T_2 lower in energy than S_1 in I and III. The same is likely in II, although the activation energy for its thermally activated phosphorescence has not yet been measured. Therefore, there are probably no intervening bound electronic states between S_2 and S_1 in all three of the parent thiones.

The preferred intramolecular radiationless decay process for S_2 should therefore be $S_2 \rightsquigarrow S_1$, internal conversion, if the weak coupling case prevails[6] as it does for the aromatic thiones.[12] However, the very large S_2–S_1 energy gaps in all three molecules ($\Delta E > 18\,000$ cm^{-1}) suggest that if $S_2 \rightsquigarrow S_1$ internal conversion does occur, it should be relatively slow. Nonradiative decay of the S_2 states of rigid, photostable aromatic thiones follows the energy gap law quantitatively (linear ln k_{nr} versus $\Delta E(S_2$–$S_1)$).[12] If the three thiones used in the present study were to conform even crudely to the same model, values of $k_{nr} < 10^8$ s^{-1} would be expected. This is clearly not the case ($k_{nr} > 10^{12}$ s^{-1}; vide infra), so we are led to seek an alternate S_2 decay mechanism.

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Table IV. Calculated S_2 Lifetimes, Radiative Rate Constants, and Nonradiative Rate Constants

thione[a]	$\phi_f(S_2) \times 10^5$	k_r^{calc} (s^{-1})	$\tau(S_2)^{calc}$ (ps)	k_{nr}^{calc} (s^{-1})
I	17	6×10^8	0.3	3×10^{12}
II	3.4	7×10^8	0.05	2×10^{13}
III	6.5	6×10^8	0.1	1×10^{13}

[a] All in perfluoroalkane solvents.

The rate constants for the radiative and nonradiative intramolecular decay of the S_2 states can be calculated from the quantum yields of $S_2 \rightarrow S_0$ fluorescence and the lifetimes of the S_2 states using $k_r = \phi_f/\tau$ and $k_{nr} = (1 - \phi_f)/\tau$. In a previous communication[21] we reported that we were unable to detect fluorescence from the S_2 state of I in several solvents. A crude estimate of the sensitivity of the spectrofluorometer used in these measurements thus yielded a lower limit for its quantum yield of fluorescence and an upper limit for its S_2 lifetime. Since then improvements in both experimental technique and instrumental sensitivity have permitted us to measure the $S_2 \rightarrow S_0$ fluorescence quantum yields directly. However, the S_2 lifetimes are still too short ($<10^{-11}$ s) to be measured by the emission decay techniques which we have employed. Nevertheless, reasonable estimates of k_r can be obtained from measurements of the integrated molar extinction, $\int \epsilon(\bar{\nu})\,d\bar{\nu}$, for the $S_2 \leftarrow S_0$ transition using the method of Strickler and Berg.[41] The S_2 lifetimes and nonradiative decay constants can then be calculated indirectly. The results of these calculations are given in Table IV.

The calculated S_2 lifetimes are all <1 ps, consonant with our inability to measure them directly by fluorescence decay methods. Although these lifetimes are estimates, the method by which they are obtained is known to be very reliable for the radiatively allowed transitions of structurally rigid polyatomic molecules.[41] Indeed, in the aromatic thiones where $\phi_f(S_2)$ and $\tau(S_2)$ can both be measured, values of k_r calculated directly from $k_r = \phi_f(S_2)/\tau(S_2)$ and indirectly using the method of Strickler and Berg agree extremely well.[12] It is therefore highly unlikely that the calculated lifetimes in Table IV are in error by more than an order of magnitude, and are most likely good to at least within a factor of 2. One concludes that the intermediate of ca. 200 ps lifetime,[20] whose existence was deduced by de Mayo et al. from competitive quenching experiments in cyclohexane solutions of I, *cannot* be the S_2 state. In fact, the lifetimes of the S_2 states of all three thiones are too short to permit them to enter directly into any bimolecular reaction with any component of the solution except the solvent itself. Thus, although these three thiones do undergo bimolecular reactions following $S_2 \leftarrow S_0$ excitation, *the reactive species involved are not the initially formed S_2 states as previously supposed.*

An analysis of the data in Tables II, III, and IV provides clues to the processes which are initiated when S_2 is excited. First, it should be noted that all experiments in which these data were generated employed solutions which were very dilute. This rules out any significant reaction between the S_2 state (or any species having a lifetime <0.1 μs derived from the S_2 state) and ground-state thione or any impurity present in low concentration. In particular, significant consumption of thione due to photodimerization can be eliminated.

The only possible intermolecular photochemical initiated by excitation of I, II, or III to S_2 is reaction with the solvent. The net insertion of excited thione into the C–H bonds of saturated alkanes is well-documented.[13-19] Such a process cannot occur in pure perfluoroalkane solvents, and the higher values of $\phi_f(S_2)$ and $\phi_p^0(S_2)$ for I in perfluoroalkanes compared with cyclohexane reflect this. Note also that the quantum yield of net consumption of thione at infinite dilution, $\phi^0_{-T}(S_2)$, is significantly larger in cyclohexane than in the perfluoroalkanes. The residual loss of thione on excitation to S_2 in perfluoroalkanes ($\phi^0_{-T}(S_2) = 0.04$) can be attributed to the irreversible intramolecular photodecomposition of the thione and perhaps to the intermolecular reaction of S_2 or an intermediate derived from it with residual "impurities" in the solvent. These solvents contain ca. 0.2 atom % H as a result of incomplete fluorination of the parent hydrocarbon, and the "impurities" in question are likely to be more reactive than the corresponding alkanes as a result of fluorine activation of the residual C–H bonds.

The following intramolecular processes subsequent to $S_2 \leftarrow S_0$ excitation should therefore be considered.

$$S_2 \rightarrow S_0 + h\nu_f \qquad (3)$$

$$S_2 \rightarrow S_1 \qquad (4)$$

$$S_2 \rightarrow X \qquad (5)$$

$$X \rightarrow S_1 \qquad (6)$$

$$X \rightarrow T_n \ (n = 1 \text{ or } 2) \qquad (7)$$

$$X \rightarrow \text{homothioenol} \qquad (8)$$

$$S_1 \rightarrow T_n \qquad (9)$$

$$T_n \rightarrow S_0 \qquad (10)$$

$$T_n \rightarrow S_0 + h\nu_p \qquad (11)$$

$$\text{homothioenol} \rightarrow \text{thione} \qquad (12)$$

Here X is an intermediate, of as yet unspecified nature, derived from the S_2 state. Higher Rydberg states are not considered, for reasons previously discussed. T_2 is in thermal equilibrium with T_1 and is only a few hundred cm^{-1} higher in energy. Its decay is therefore coupled to that of T_1, and for this reason the two triplets are considered together as T_n for purposes of this discussion. Nonradiative decay from S_2 directly to T_1, T_2, or S_0 are assumed, from radiationless transition theory,[5,6] to be much less efficient than (4) (which itself must be slow; vide supra), and such processes are not included.

There are two possible routes from S_2 to T_n; direct decay of $S_2 \rightarrow S_1 \rightarrow T_n$ (processes 4 + 9), and indirect decay via intermediate X (processes 5 + 7 or 5 + 6 + 9). Two lines of experimental evidence suggest that direct decay is the slower of the two by a large margin, owing to the inherently slow rate of process 4, $S_2 \rightsquigarrow S_1$. First, the S_2–S_1 energy gap is very large, ca. 18–19 000 cm^{-1}, in all three thiones. The energy gap law would suggest that if the weak coupling case prevails $S_2 \rightsquigarrow S_1$ should be relatively slow (k_{nr} should be $<10^8$ s^{-1}, based upon the observed behavior of the aromatic thiones;[12] vide supra). Second, for such a large energy gap a larger D/H isotope effect is to be expected[42] for the $S_2 \rightsquigarrow S_1$ process. For example, the triplet lifetimes of aromatic hydrocarbons having T_1–S_0 energy gaps of 18–20 000 cm^{-1} exhibit an increase in lifetime of a factor of ca. 8 on perdeuteriation,[43] much smaller than the factor of 2.1 observed here.

The major decay process for S_2 is therefore proposed to involve relaxation on the S_2 surface to an intermediate, X, which itself does not radiate, but could yield S_1, T_n, S_0, or net photochemical product. Of these, either $X \rightarrow S_1$ (process 6) or $X \rightarrow T_n$ (process 7) must dominate, as may be seen by considering the values of $\phi_p^0(S_2)/\phi_p^0(S_1)$ in Table III. Nearly the same phosphorescence quantum yield is obtained on excitation to either S_2 or S_1. Since $S_1 \rightsquigarrow T_1$ with efficiencies approaching 100% in most thiones in solution,[3,16,17,19] the quantum yield of T_n resulting from initial excitation must be close to 1. Because direct $S_2 \rightsquigarrow S_1$ internal conversion is ruled out and there are no bound states of the thione between S_2 and S_1, one of the two indirect routes of populating T_n must be very efficient. We cannot distinguish between the two, (5) + (7) or (5) + (6) + (9), on the basis of the present experiments. Note also (Table III) that $\phi_p^0(S_2)/\phi_p^0(S_1)$ is smallest when $\phi^0_{-T}(S_2)$ is largest, indicating that photochemical loss of thione, either directly from S_2 or indirectly from X, is the major process competing with the production of T_n.

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It is tempting to try to deduce further information from the data in Table III, because it seems that the sum $\phi^0_{T}(S_2)$ + $\phi^0_p(S_2)/\phi^0_p(S_1)$ is ca. 1.0 for III in perfluoro-1,3-dimethylcyclohexane and for I in cyclohexane and is >1.0 for I in perfluoroalkanes. Unfortunately, although the trends in the relative values of $\phi^0_p(S_2)/\phi^0_p(S_1)$ and $\phi^0_{T}(S_2)$ are significant, the absolute values of $\phi^0_p(S_2)/\phi^0_p(S_1)$ are not sufficiently accurate to permit such conclusions to be drawn.

We now address the matter of the nature of the intermediate, X. It is derived from S_2, but is not any of T_1, T_2, or S_1. It does not emit with measurable intensity. It must live long enough to undergo intermolecular reactions[13-19] which are distinct from those resulting from excitation to S_1 or T_1, and therefore likely lies on a potential surface directly connected to the S_2 surface of the parent thione. If the reactive species deduced to be the scavengeable precursor in the intermolecular photochemical reactions of adamantanethione[16,19] is this intermediate, then it would have a lifetime of the order of 200 ps.

$S_2 \leftarrow S_0$ excitation of the bicyclic bridged thiones (II, III, and [2.2.2]bicyclothiooctanone[14,18]) leads in each case to intramolecular cyclization and the formation of cyclopropylthiols (the homothioenols). In the case of III, the quantum yield of homothioenol formation is 0.18. At infinite dilution in inert solvents homothioenol production constitutes the only net thione consumption process.[18] Elegant deuterium tracer studies[18] have unequivocally established that homothioenol formation results from transfer to the endo-H atom on the carbon β to the thiocarbonyl group. These atoms are located above or below the plane of the C–CS–C framework in the ground state, and are in the plane of the π and π* orbitals. Despite the availability of β, γ, or δ H atoms, only cyclopropylthiols and dihydrothiols are obtained when bridged bicyclic thiones having ethyl, propyl, and butyl side chains at the α and α′ positions are photolyzed.[18] A similar, homothioenol product is not observed in the UV photolysis[17,19] of the tricyclic thione, I. However, it should be noted that the homothioenols of II and III revert to the parent thione on heating,[14] so there is no guarantee that the homothioenol of I would necessarily be sufficiently stable at room temperature to be isolated.

In considering the S_2-initiated photochemistry of these compounds, we note that the C–S bond will be considerably elongated compared to the ground state, and the S atom may also be displaced from the plane of the three carbon atoms in the C–CS–C moiety. Because net homothioenol formation is one photochemical path available following $S_2 \leftarrow S_0$ excitation, the endo β-C–H bond must also elongate. The effects of simultaneously changing the sulfur to carbon and sulfur to hydrogen distances in various electronic states of a model thione (H_2CS) interacting with a model hydrocarbon (CH_4) have been considered theoretically by Bigot[44] and others.[45] Although only *intermolecular* hydrogen abstraction reactions of a small thione in its (n,π*) and π,π*) states have been considered, the model can be readily adapted to the intramolecular hydrogen abstraction case. Only the approach of hydrogen in the plane of symmetry of the π and π* orbitals (perpendicular to the C–CS–C plane in the ground state) need be considered.

Figure 6 shows the essential features of the result. The energies of some of the states which correlated with S_0, T_1, T_2, S_1, and S_2 of the parent thione are plotted as a function of the sulfur to β-carbon and sulfur to endo-β-hydrogen distances. Decreasing the sulfur to endo-β-hydrogen distance leads to a diradical, D, by hydrogen transfer or to a zwitterion, Z, by proton transfer. The ground state of the diradical can close, with suitable skeletal distortion, to form the observed homothioenol product. The S_2, $^1(\pi,\pi^*)$ state of the thione correlates, by two avoided crossings,[44] with the zwitterion in the limit of complete proton transfer in a species in which the sulfur to β-carbon distance remains constant. However, when both sulfur to β-carbon and sulfur to β-hydrogen distances decrease simultaneously, a minmum appears in this excited-state potential surface. This minimum is labeled X in Figure 6, and we assign this to the intermediate obtained on excitation to S_2 in these bridged bicyclic and tricyclic thiones.

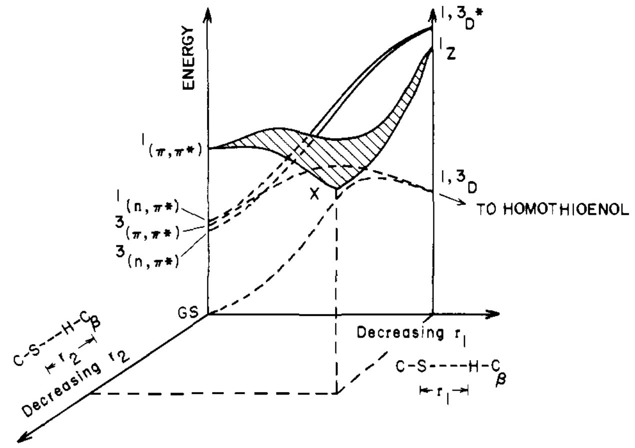

Figure 6. Partial potential energy surfaces for intramolecular S···C_β and S···H_β motion (see text). GS is the ground state, D is a diradical, D* is an electronically excited diradical, and Z is a zwitterion. X is the intermediate of lowest potential energy formed from the S_2 state on the same potential surface (hatched) (after Bigot, ref 44).

X is reached by transition from S_2 over a low barrier. This accounts for the short S_2 lifetime (a few C–H stretching vibrational periods) and the small deuterium isotope effect in I, which increases the lifetime of S_2 and $\phi_f(S_2)$ by a factor of 2.1. Fluorescence from X is not seen because emission in an observable portion of the spectrum (near UV–visible) will be highly Franck–Condon forbidden owing to the highly distorted/displaced nature of the intermediate relative to the ground state of the parent thione.

The intermediate can relax either to a chemically distinct species (the diradical, D, which leads to homothioenol) or to a lower excited state of the thione: T_1, T_2, or S_1. Both processes involve motion over barriers, the relative heights of which will determine the relative efficiencies of the photochemical and the net photophysical pathways. Skeletal deformation will be easier in the bicyclic thiones, and the quantum yield of homothioenol production is relatively large as a result. In adamantanethione no homothioenol is observed, and the quantum yield of net photochemical consumption of thione is small. This may be a result of a higher barrier between X and the homothioenol surface, or may reflect the thermal instability of the homothioenol product in the adamantanethione system. In either case, the greater skeletal rigidity of the bridged tricyclic thione compared with the bicyclic thione is responsible.

Radiationless relaxation of X to T_1, T_2, or S_1 occurs with greatest efficiency. Of these three process, the correlations shown in Figure 6 suggest that X $\rightsquigarrow$ T_2 $^3(\pi,\pi^*)$ might be preferred. T_2 $^3(\pi,\pi^*)$ correlates by an avoided crossing[44] with the triplet diradical, ^3D, whereas S_1 and T_1 correlate with excited states of the diradical, $^{1,3}D^*$, which lie much higher in energy. Thus the T_2 surface is most likely to "intersect" that on which X lies in such a way as to produce a relatively low barrier between X and T_2. However, since T_1 and T_2 are in thermal equilibrium in the parent thione, T_1 is rapidly populated, and there should be little apparent difference in the $T_n \rightarrow S_0$ phosphorescence yields as a result of initial excitation to either S_2 or S_1. Curiously, Lawrence and de Mayo[13] originally postulated an $S_2 \rightsquigarrow T_n$ ($n \geq 1$) transition in I, but later rejected this on the basis of triplet sensitization experiments.[16] We note here that such experiments would not have excluded the existence of an intermediate such as X, and would not have distinguished between S_2 and X.

Finally, we ask if X has the chemical properties required by the intermediate which is the precursor in the intermolecular photochemistry of UV-excited adamantanethione. The lifetime, ca. 200 ps, is reasonable, and it could well be quenched efficiently by 1,1′-azoisobutane, the scavenger used by de Mayo et al.[16,19] in estimating the lifetime. Having excluded species in the triplet manifold as possible intermediates, de Mayo [16] notes that S_2 "...

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or some species derived from it ..." is responsible for the photochemistry. Although S_2 itself is now also excluded, X is produced as a result of motion of the system on the same potential surface as S_2, and therefore is expected to exhibit some of the same chemical characteristics. Finally, we note that X has some zwitterionic character, and zwitterions have been proposed as intermediates in the intermolecular S_2-excited photochemical reactions of some thioketenes.[46,47]

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Stereoselectivity of the Nucleophilic Addition of Organocopper Reagents to Chiral α,β-Unsaturated Carbonyl Compounds. Ab Initio Molecular Orbital Studies of Steric and Electronic Effects

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Abstract: Ab initio molecular orbital studies have been conducted on the conjugate addition of methylcopper to substituted enals. Transition structures have been located for the addition of methylcopper to (*E*)- and (*Z*)-2-butenal, and the effect of the methyl and hydroxyl substituents on the γ-carbon has been analyzed for both transition states. In the reaction with both (*E*)- and (*Z*)-2-pentenal, the most stable conformation in the transition state has the methyl group anti to the incoming nucleophile, with the *outside* position being preferred to the *inside* position. These conformational preferences are readily rationalized in terms of the relative steric encumbrance of the three positions. On the other hand, the conformational preference exhibited by the hydroxyl group is found to be dictated primarily by electronic factors. Thus, in the addition to both *E* and *Z* isomers of 4-hydroxy-2-butenal, the sterically unhindered anti position is the *least* favorable for the hydroxyl group. It is shown that electron-withdrawing groups in the anti position destabilize the transition state, whereas electron donors favor the anti position. From these calculations we have derived transition-state models that we have used to predict the diastereomeric excess of the addition to chiral 4-alkoxy α,β-unsaturated carbonyl compounds. *E* isomers prefer a conformation in which the alkyl and alkoxy group occupy the anti and inside positions, respectively, in the transition structure. In the *Z* isomers the favored conformation has the alkyl group outside the nucleophile and the alkoxy group inside; this conformation leads to formation of the other diastereoisomer. Good agreement with the observed stereoselectivity has been found in both cases. We have also performed model calculations that rationalize the stereoselectivity of the addition to *E* and *Z* isomers bearing an aryl group on the γ-carbon. These calculations suggest that the favored conformation in *E* isomers has the aryl and methyl groups in the anti and inside positions, respectively. In *Z* isomers, the aryl group lies *outside* and the methyl group *anti*, so that the same diastereomer is predicted to be the major product in both cases. This is also in agreement with recently reported experimental observations.

Several high-level theoretical studies of the addition of nucleophiles to carbonyl compounds have appeared in the recent literature. Many of these investigations deal with the stereochemical aspects of these reactions.[1] Theory is thus starting to catch up with a wealth of experimental evidence accumulated ever since Cram pioneered the field almost forty years ago.[2] Cram's rule and successive reinterpretations by Karabatsos,[3] Felkin,[4] and Anh[5] have become guidelines for the interpretation and prediction of the stereochemical course of the reaction. Recent evidence, both theoretical and experimental, provides strong support in favor of Felkin's and Anh's transition-state model (Figure 1).[6,7]

The closely related nucleophilic conjugate addition to chiral α,β-unsaturated carbonyl compounds, which is also widely employed in synthesis, has received relatively little attention from the theoretical point of view.[8,9] Addition to aldehydes or ketones on the one hand and conjugate addition to enals or enones on the other are obviously related. Thus, it is not surprising that the stereochemical course of conjugate additions to chiral substrates has often been empirically rationalized on the basis of "modified" Felkin–Anh models. The modification usually involves replacement of the C(R)=O group of Figure 1 with the conjugated C=C(R′)—C(R″)=O group, and the assumption that the substituents on C_γ are staggered[10] with respect to the forming C_β-nucleophile bond (Figure 2).

In spite of the similarities of the two reactions, it is difficult to speculate on the relative stabilities of various conformations for the transition states of conjugate addition reactions. This reaction is expected to have different steric requirements from

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