Photodimerization of Thianaphthene 1,1-Dioxide. Mechanism

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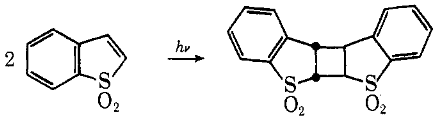
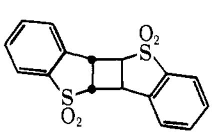
Abstract: The photodimerization of thianaphthene 1,1-dioxide (**1a**) proceeds *via* an attack by its triplet excited state on the ground-state molecule with a quantum yield (Φ_{DIM}) of 0.18. The quantum yield for the attack of the triplet excited state on the ground state ($\Phi_c + \Phi_{c'}$) is 1.0. This was determined by comparing the quantum yield of the unsensitized dimerization (Φ_{DIM} = 0.18) with that of the benzophenone-sensitized dimerization. A chemical method for determining the intersystem crossing efficiency to the triplet excited state has been devised for compounds with low-energy triplets ($E_T \geqslant$ 58 kcal/mol). A solvent effect on the ratio of head-to-head anti to head-to-tail anti dimer is attributed to a preferential solvation of the more polar transition state leading to the head-to-head dimer.

In a previous paper[2] we reported the isolation and structure elucidation of the head-to-head anti **2** and the head-to-tail anti **3** photodimers obtained upon irradiation of thianaphthene 1,1 dioxide (**1a**) with light of wavelength greater than 300 nm. The photodimerization of compounds with general structure **1b–d** has been reported and is observed to proceed only in the presence of triplet sensitizers.[3–5] In contrast, sulfone **1a** undergoes photodimerization by direct irradiation.[2] To date, there have been no additional studies on the mechanism of the photodimerization of compounds with structure **1**. In this paper we have described the mechanistic properties of the photodimerization of thianaphthene 1,1-dioxide (**1a**) from data obtained from sensitization, quantum yield, and solvent studies.



1a **2**



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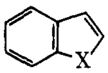

1a, X = SO_2
b, X = CH_2
c, X = $C(CH_3)_2$
d, X = O

Results

Multiplicity of Excited State. In order to investigate the multiplicity of the excited state of thianaphthene 1,1-dioxide (**1a**) responsible for photodimerization, attempts were made to inhibit the dimerization with a triplet quencher, *trans*-α-methylstilbene (**4**). This quencher has a triplet energy level at about 50 kcal/mol[6] and does not absorb at the irradiating wavelength of 313 nm (λ max for *trans*-α-methylstilbene is 276 nm). When thianaphthene 1,1-dioxide (**1a**) (0.05 *M*) was irradiated in the presence of **4** (0.05 *M*), the production of photodimers was negligible. The simultaneous irradiation of the same concentration of **1a** without quencher resulted in a 70% production of photodimers. Also, some isomerization of the quencher, sensitized by the triplet excited state of **1a**, was observed (Table II). Therefore, the triplet excited state of **1a** was quenched.

Thianaphthene 1,1-dioxide (**1a**) was irradiated at 366 nm in the presence of a variety of triplet sensitizers (Table I). At this wavelength **1a** does not absorb any light; in all cases, greater than 98% of the light is absorbed by the sensitizers. Benzene solutions of **1a** (0.024 *M*) and sensitizer (0.024 *M*) were irradiated for 24 hr. Dimer production for each sensitized reaction is summarized in Table I. The ratio of HH and HT photodimers did not vary significantly with the triplet energy of the sensitizer.

Table I. Sensitized Photodimerization of Thianaphthene 1,1-Dioxide

Triplet sensitizer	Triplet energy, kcal/mol (119)	Intersystem crossing efficiency (Φ_{isc})	Dimer yield, %	HH/HT
Benzophenone	69	1.0	82	2.7
Chrysene	57	0.67	65	2.8
Benzil	54	0.92	85	2.7
Fluoren-9-one	53	0.93	47	2.7
Pyrene	49		0	
No sensitizer			0	

Experiments of the type described above have been used to support a mechanism proceeding wholly *via* the triplet excited state.[7] In the case of the photodimerization of thianaphthene 1,1-dioxide (**1a**), the fact that *trans*-α-methylstilbene quenches the production of both HH and HT photodimers and that these dimers

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(1) NRCC Bursary holder, 1968–1970.

(2) D. N. Harpp and C. Heitner, *J. Org. Chem.*, **35**, 3256 (1970).

(3) G. O. Schenk, W. Hartmann, S.-P. Mannsfeld, W. Metzner, and C. H. Krauch, *Chem. Ber.*, **95**, 1642 (1962).

(4) J. J. McCullough, *Can. J. Chem.*, **46**, 43 (1968).

(5) C. H. Krauch, W. Metzner, and G. O. Schenk, *Chem. Ber.*, **99**, 1723 (1966).

(6) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

(7) J. L. Ruhlen and P. A. Leermakers, *ibid.*, **88**, 5671 (1966); **89**, 4944 (1967).

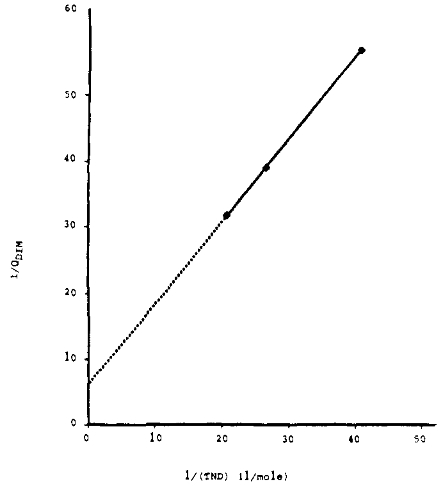

Figure 1. The photodimerization of thianaphthene 1,1-dioxide. The comparative insolubility of thianaphthene 1,1-dioxide precludes experimental points at concentrations greater than *ca.* 0.05 *M*.

are produced upon irradiation of several triplet sensitizers in the presence of the monomer **1a** is consistent with a triplet excited state as an intermediate.

Thianaphthene 1,1-Dioxide Triplet Energy. Attempts made to observe the phosphorescence from thianaphthene 1,1-dioxide (**1a**) in an ethanol glass at 77°K met with failure. Therefore, measurements of the triplet energy of thianaphthene 1,1-dioxide were made by two indirect methods. The first involved the use of several sensitizers of decreasing triplet energy. The results summarized in Table I indicate that E_{triplet} lies between 53 and 49 kcal/mol. The second method is more precise and involves the use of thianaphthene 1,1-dioxide as a sensitizer to establish a photostationary state of the α-methylstilbenes. The composition of the photostationary state of α-methylstilbene has been determined as a function of the triplet energy level of the sensitizer.[6]

Three tubes each containing a benzene solution of 0.05 *M* *trans*-α-methylstilbene and sensitizer (benzoquinone, pyrene, and thianaphthene 1,1-dioxide) were irradiated with light at wavelength 313 nm. The composition of the photostationary states produced by each sensitizer was determined by gas chromatography (see Experimental Section). The results are summarized in Table II and indicate a triplet energy for thianaphthene 1,1-dioxide of 50 ± 1 kcal/mol. This value is consistent with the results obtained in the sensitization experiment (Table I).

Table II. Photostationary State of α-Methylstilbene

Sensitizer	Triplet energy, kcal/mol	Cis/trans
Benzoquinone	50	0.88
Pyrene	48.5	2.38
Thianaphthene 1,1-dioxide	50	0.83 0.85

Quantum Yield of the Photodimerization of Thianaphthene 1,1-Dioxide (1a). Quantum yields of the photodimerization of compound **1a** were determined in benzene as a function of concentration (Table III). Each quantum yield was determined by parallel irradiation of four degassed samples with uranyl oxalate actinometer at 313 nm. Dimer yields were based upon the disappearance of **1a** as monitered by uv analysis assuming that for every mole of dimer found 2 mol of compound **1a** was consumed; $1/\Phi_{\text{DIM}} = 2\Phi_{\text{TND}}$ *vs.* 1/(TND) was plotted and found to be linear (correlation coefficient = 1.00) (Figure 1). A least-squares calculation gave a limiting quantum yield of 0.18.

Determination of the Intersystem Crossing Efficiency (Φ_{isc}) to the Triplet Excited State of Compound 1a. The usual chemical method of determining Φ_{isc} devised by Lamola and Hammond[8] cannot be used for the determination of Φ_{isc} to the triplet excited state of thianaphthene 1,1-dioxide (**1a**); the energy level of triplet state **1a** (50 kcal/mol) is too low to sensitize the isomerization of any of the cis- or trans-substituted olefins (E_T required $\geqslant 58$ kcal/mol). The quantum yield of the reactions is a product of the Φ_{isc} and the yield of photodimers from the triplet state. Since the quantum yield for the photodimerization of compound **1a** is known, the determination of the yield of products from the triplet excited state would give Φ_{isc}.

In order to determine the yield of photodimers from the triplet state ($\Phi_t\Phi_c$ in Scheme I), the quantum yields of dimerization of **1a**, sensitized by benzophenone, were determined in benzene as a function of concentration. If the hypothesis of Wagner and Buchek[9] is applied to this photosensitized dimerization of compound **1a**, the mechanism shown in Scheme I results. From the mechanism shown in Scheme I the following relation-

Scheme I

	Rate
$\mathrm{B} \xrightarrow{h\nu} {}^1\mathrm{B}^a$	I
${}^1\mathrm{B} \xrightarrow{k_1} {}^3\mathrm{B}$	$k_1({}^1\mathrm{B})$
${}^1\mathrm{B} \xrightarrow{k_2} \mathrm{B}$	$k_2({}^1\mathrm{B})$
${}^3\mathrm{B} \xrightarrow{k_3} \mathrm{B}$	$k_3({}^3\mathrm{B})$
$\mathrm{TND} + {}^3\mathrm{B} \xrightarrow{k_4} {}^3\mathrm{TND} + \mathrm{B}$	$k_4({}^3\mathrm{B})(\mathrm{TND})$
${}^3\mathrm{TND} \xrightarrow{k_5} \mathrm{TND}$	$k_5({}^3\mathrm{TND})$
${}^3\mathrm{TND} + \mathrm{TND} \xrightarrow{k_6} \mathrm{H{-}{-}{-}H}^b$	$k_6({}^3\mathrm{TND})(\mathrm{TND})$
$\mathrm{H{-}{-}{-}H} \xrightarrow{k_7} \mathrm{TND}$	$k_7(\mathrm{H{-}{-}{-}H})$
$\mathrm{H{-}{-}{-}H} \xrightarrow{k_8} \mathrm{HH\ dimer}$	$k_8(\mathrm{H{-}{-}{-}H})$
${}^3\mathrm{TND} + \mathrm{TND} \xrightarrow{k_6'} \mathrm{H{-}{-}{-}T}^b$	$k_6'({}^3\mathrm{TND})(\mathrm{TND})$
$\mathrm{H{-}{-}{-}T} \xrightarrow{k_7'} \mathrm{TND}$	$k_7'(\mathrm{H{-}{-}{-}T})$
$\mathrm{H{-}{-}{-}T} \xrightarrow{k_8'} \mathrm{HT\ dimer}$	$k_8'(\mathrm{H{-}{-}{-}T})$

$$\Phi_{\mathrm{HH}}{}^c = k_8(\mathrm{H{-}{-}{-}H})/\mathrm{I}$$

[a] Benzophenone. [b] H---H and H---T are the metastable intermediates leading to the head-to-head photodimer **2** and head-to-tail photodimer **3**, respectively. [c] Φ_{HH} = the quantum yield for the formation of head-to-head dimer.

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(8) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(9) P. J. Wagner and D. J. Buchek, *J. Amer. Chem. Soc.*, **91**, 5090 (1969).

Table III. Dimerization of **1a** at Various Concentrations

Concn (C), mol/l. $\times 10^{-2}$	Φ_{TND}[a]	σ	$1/C$	$1/\Phi_{DIM} = 2/\Phi_{TND}$
2.41	0.035[b]	±0.001	41.5	57.1
3.61	0.051[b]	±0.001	27.7	39.2
4.82	0.063[b]	±0.001	20.7	31.7

[a] Thianaphthene 1,1-dioxide. [b] Weighted mean and average deviation for four determinations.

ship can be derived

$$1/\Phi_{DIM} = \frac{1}{(\Phi_c + \Phi_{c'})(\Phi_t + \Phi_{t'})\Phi_{isc}} + \frac{1}{(\Phi_c + \Phi_{c'})(\Phi_t + \Phi_{t'}h)\Phi_{isc}\tau k_4(\text{TND})} \quad (1)$$

where Φ_c = fraction of HH dimer formed from its metastable intermediate; Φ_{isc} = intersystem crossing of benzophenone singlet to benzophenone triplet; Φ_t = fraction of triplets attacking the ground state to form a metastable intermediate (H---H); $\Phi_{c'}$ = fraction of HT dimer formed from its metastable intermediate H---T; $\Phi_{t'}$ = fraction of triplets attacking the ground state to form a metastable intermediate (H---T).

The intercept of the plot $1/\Phi_{DIM}$ *vs.* 1/(TND) should give $1/(\Phi_c + \Phi_{c'})(\Phi_t + \Phi_{t'})\Phi_{isc}$. The Φ_{isc} for benzophenone has been shown to be equal to 1.0;[10] $\Phi_t + \Phi_{t'}$ can be shown to be unity if the thianaphthene 1,1-dioxide triplet state is relatively long lived and attack on the ground-state molecule by the triplet state is diffusion controlled (*i.e.*, $k_6 + k_6' = 10^9$ mol l.$^{-1}$ sec^{-1} and $k_5 \lesssim 10^5$ sec^{-1}). These assumptions are reasonable because the formation of the metastable intermediate should occur upon collision; the rate of encounters of triplet with ground-state molecules has been assumed to be 10^9–10^{10} mol l.$^{-1}$ sec^{-1}.[10] The results obtained in eq 2 (Figure 2) confirm the above assumptions made for compound **1a**. Therefore,

$$(\Phi_t + \Phi_{t'}) = \frac{(k_6 + k_{6'})(^3\text{TND})(\text{TND})}{k_5(^3\text{TND}) + (k_6 + k_{6'})(^3\text{TND})(\text{TND})} = \frac{(k_6 + k_{6'})(\text{TND})}{k_5 + (k_6 + k_{6'})(\text{TND})} = \frac{(10^9)(10^{-2})1}{10^5 + (10^9)(10^{-2})} = \frac{100 \times 10^5}{(1 + 100) \times 10^5} = \frac{100}{101} \simeq 1.0 \quad (2)$$

$$(\text{TND}) = 10^{-2}$$

$\Phi_c + \Phi_{c'}$ can be calculated from $1/\Phi_{isc}(\Phi_c + \Phi_{c'})(\Phi_t + \Phi_{t'})$ (eq 1).

If the relationship between Φ_{DIM} and monomer concentration for the nonsensitized photodimerization was utilized, Φ'_{isc} (thianaphthene 1,1-dioxide) can be calculated (eq 3).

$$1/\Phi_{DIM} = \frac{1}{\Phi'_{isc}(\Phi_c + \Phi_{c'})} + \frac{1}{(\Phi_c + \Phi_{c'})\Phi'_{isc}\tau'(k + k')(\text{TND})} \quad (3)$$

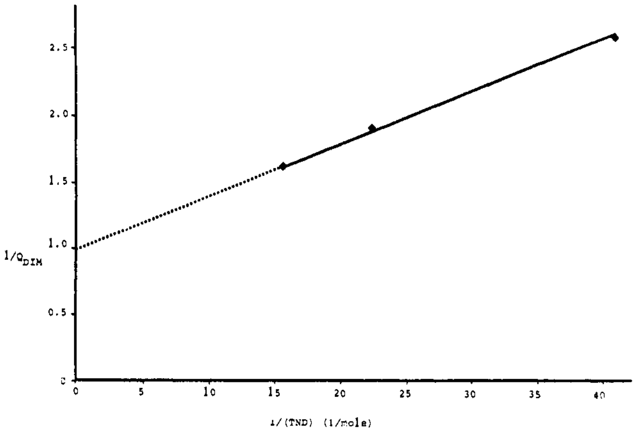

Figure 2. The photodimerization of thianaphthene 1,1-dioxide sensitized by benzophenone. The comparative insolubility of thianaphthene 1,1-dioxide precludes experimental points at concentrations greater than *ca.* 0.05 *M*.

Φ'_{isc} = intersystem crossing efficiency of TND
τ' = lifetime of TND

Each quantum yield at a given concentration of **1a** and a constant concentration of benzophenone was determined by parallel irradiation of our degassed samples with benzophenone–benzhydrol actinometer at 366 nm ($\Phi = 0.69$[11]). Dimer yields were determined using the same methods as that for the determination of quantum yields of the unsensitized dimerization. These results are tabulated in Table IV.

Table IV. Benzophenone[c]-Sensitized Dimerization of **1a** at Various Concentrations

(C), Concn, $M \times 10^{-2}$	Φ_{TND}[a]	σ	$1/C$	$1/\Phi_{DIM} = 2/\Phi_{TND}$
2.41	0.78[b]	0.01	41.5	2.56
3.61	1.03[b]	0.02	27.7	1.94
4.82	1.22[b]	0.00	20.7	1.64

[a] Thianaphthene 1,1-dioxide. [b] Weighted mean and average deviation for four determinations. [c] Benzophenone concentration 1.99 × 10^{-2} *M*.

A plot of $1/\Phi_{DIM}$ *vs.* 1/(TND) is linear with an intercept of 0.98 (Figure 2). This is indicative of $\Phi_c + \Phi_{c'}$ and $\Phi_t + \Phi_{t'}$ being unity. Therefore, using eq 3, ϕ'_{isc} is 0.18.

Solvent Effect. The product distribution as a function of solvent polarity was studied. The ratio of the head-to-head to head-to-tail dimer (HH/HT) was found to increase with the polarity of the solvents. Quantitative gas chromatography was used to determine dimer ratios. The plot of log HH/HT *vs.* the Kirkwood–Onsager parameter, $(D - 1)/(2D + 1) \cdot \rho/M$, was found to be linear, with a correlation coefficient of 0.90 (P = 0.02; *i.e.*, there is only a 1 in 50 chance that the points are random). This exceeds the generally adopted limit of $P = 0.05$[12] (Figure 3). In the Kirkwood–Onsager parameter, D is the dielectric constant, ρ is the density, and M is the molecular weight of the solvent (Table V). This result has been found to be

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(10) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 95.

(11) W. M. Moore and M. Ketchum, *J. Amer. Chem. Soc.*, **84**, 1368 (1962).

(12) H. D. Young, "Statistical Treatment of Experimental Data," McGraw-Hill, New York, N. Y., 1962.

Table V. Solvent Effects for the Dimerization of Thianaphthene 1,1-Dioxide

Solvent	Dielectric constant (D)	Density	$\frac{(D-1)\rho}{(2D-1)M}$	HH/HT	Log HH/HT	Yield, %
Benzene	2.27	0.8786	0.00229	2.70	0.4317	83
Chloroform	4.70	0.4832	0.00496	5.89	0.7701	85
Ethyl acetate	6.03	0.9003	0.00383	5.74	0.7589	77
1,2-Dichloroethane	10.37	1.2564	0.00573	6.50	0.8129	73
Acetic acid	6.15	1.0492	0.00675	7.35	0.8663	66
Dichloromethane	8.90	1.3266	0.00663	7.36	0.8669	82

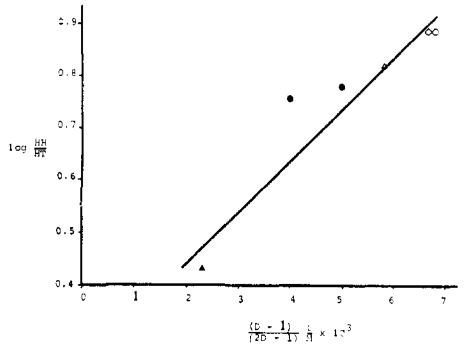

Figure 3. Solvent effect: (▲) benzene, (■) ethyl acetate, (●) chloroform, (△) 1,2-dichloroethane, (□) dichloromethane, (O) acetic acid.

consistent with preferential solvation of the head-to-head transition state. The above (Figure 3) correlation of the HH/HT ratios has been used as evidence for polarity differences in the transition states leading to the endo and exo adducts of cyclopentadiene to methyl acrylate and methyl *trans*-crotonate.[13]

Discussion

The above results are consistent for the photodimerization which involves attack on the ground-state molecule by the triplet excited state as illustrated by the mechanism in Scheme II.

Scheme II

	Rate
$\mathrm{TND} \xrightarrow{h\nu} {}^1\mathrm{TND}$	I
${}^1\mathrm{TND} \xrightarrow{k_1} \mathrm{TND}$	$k_1({}^1\mathrm{TND})$
${}^1\mathrm{TND} \xrightarrow{k_2} {}^3\mathrm{TND}$	$k_2({}^1\mathrm{TND})$
${}^3\mathrm{TND} \xrightarrow{k_3} \mathrm{TND}$	$k_3({}^3\mathrm{TND})$
$\mathrm{TND} + {}^3\mathrm{TND} \xrightarrow{k_4} \mathrm{H{-}{-}{-}H}$	$k_4({}^3\mathrm{TND})(\mathrm{TND})$
$\mathrm{TND} + {}^3\mathrm{TND} \xrightarrow{k_4'} \mathrm{H{-}{-}{-}T}$	$k_4'({}^3\mathrm{TND})(\mathrm{TND})$
$\mathrm{H{-}{-}{-}H} \xrightarrow{k_5} \mathrm{TND}$	$k_5(\mathrm{H{-}{-}{-}H})$
$\mathrm{H{-}{-}{-}T} \xrightarrow{k_5'} \mathrm{TND}$	$k_5'(\mathrm{H{-}{-}{-}T})$
$\mathrm{H{-}{-}{-}H} \xrightarrow{k_6} \mathrm{HH\ dimer}$	$k_6(\mathrm{H{-}{-}{-}H})$
$\mathrm{H{-}{-}{-}T} \xrightarrow{k_6'} \mathrm{HT\ dimer}$	$k_6'(\mathrm{H{-}{-}{-}T})$

From the above mechanism the relationship between Φ_{DIM} and the concentration of thianaphthene 1,1-dioxide (**1a**) (eq 3) is derived.

The formation of head-to-head and head-to-tail dimers from two triplet states is not supported by observations of constant HH/HT ratios with decreasing triplet energy level of the sensitizer (Table I). If two triplet states were intermediates in this photodimerization reaction, the HH/HT ratio would be expected to change as the triplet energy level of the sensitizer approaches that of thianaphthene 1,1-dioxide.[14a]

The observation of a limiting quantum yield of unity for the dimerization of **1a** sensitized by benzophenone implies that the formation of dimers from a metastable intermediate of the type proposed by Wagner and Buchek[9] was 100% efficient (*i.e.*, $\Phi_t = 1.0$). Therefore, the increase of HH over HT dimers with an increase in solvent polarity was due to the selective formation of these intermediates rather than their selective decomposition.[15]

The electrostatic free-energy change, when a dipole is transferred from a vacuum to a solvent, is given by

$$G_{\mathrm{solvent}} - G_{\mathrm{vac}} = \Delta G = -u^2(D-1)/a^3(2D+1)^{13}$$

The free-energy difference for two different dipoles (HH and HT transition states) is then

$$\Delta G^{\ddagger}_{\mathrm{HH}} - \Delta G^{\ddagger}_{\mathrm{HT}} = -(u^2_{\mathrm{HH}} - u^2_{\mathrm{HT}})/a^3(D-1)/(2D+1)^{13}$$

A good correlation between ΔG and solvent polarity is obtained when "a," the "cavity radius," is identified with the molar volume (M/ρ) of the solvent.[13] Since the photodimerization of thianaphthene 1,1-dioxide (**1a**) does not involve an equilibrium between the products and starting material, the reaction is kinetically controlled. Therefore, the following relationship holds.

$$\log \mathrm{HH/HT} = \log k_{\mathrm{HH}}/k_{\mathrm{HT}} = -2.303(\Delta G^{\ddagger}_{\mathrm{HH}} - \Delta G^{\ddagger}_{\mathrm{HT}})/RT$$

A linear plot of log HH/HT *vs.* $(D-1)/(2D+1)\cdot\rho/M$ can be taken as evidence that an increase in log HH/HT with increasing solvent polarity corresponds to an increase in the difference of free energies of activation, $\Delta G^{\ddagger}_{\mathrm{HH}} - \Delta G^{\ddagger}_{\mathrm{HT}}$. This result is easily accepted if it is assumed that the total dipole moment of the head-to-head transition state is greater than that of the head-to-tail transition state (Scheme II). This assumption is quite reasonable if the transition state is imagined

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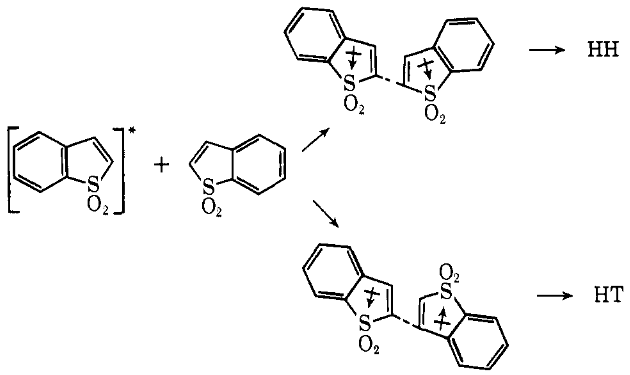
[13] J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Amer. Chem. Soc.*, **84**, 297 (1962).

[14] (a) It has been observed[14b] that the rate constant for energy transfer decreases as the triplet energy level of the donor approaches that of the acceptor. Therefore, the rate of energy transfer to the substrate triplet of higher energy would decrease at a faster rate with decreasing sensitizer triplet energy level, thus favoring the formation of one dimer over the other. (b) E. F. Ullman and W. A. Henderson, *ibid.*, **88**, 4942 (1966).

[15] The formation of a metastable intermediate (H---H or H---T) from the reaction of ground state and triplet excited state of thianaphthene 1,1-dioxide involves a net loss of energy. Therefore, the decomposition of the metastable intermediate would lead to the ground state (reaction 5 and 5′) rather than triplet state plus ground state (reverse of reactions 4 and 4′).

to consist of an aggregate of two thianaphthene 1,1-dioxide molecules as shown in Scheme III. In the head-to-head transition state, the component dipoles point in the same direction and the net moment would be expected to be greater than that of the head-to-tail transition state where the component dipoles lie in opposite directions. Therefore, the solvent effect appears due to the polarity difference in the transition state leading to the head-to-head and head-to-tail dimers.

Scheme III



Summary

The results stated above indicate that the photodimerization of thianaphthene 1,1-dioxide occurs *via* an attack on the ground-state molecule by a triplet excited-state molecule ($E \simeq 50$ kcal/mol) according to the mechanism written in Scheme II.[16] The intersystem crossing efficiency (Φ_{isc}) from singlet to triplet excited-state was found to be equal to 0.18 and the efficiency of dimerization from metastable intermediate, $\phi_c + \phi_{c'}$, was unity.

A solvent dependency (Kirkwood–Onsager) of the photodimerization of cyclopentenone similar to that of the photodimerization of thianaphthene 1,1-dioxide (**1a**) has been reported.[17] It is suggested that other similar solvent effects, observed by Eaton,[18] Hammond,[19] and Chapman,[20,21] for the dimerization of cyclopentenone, cyclohexenone, and isophorone, respectively, may well be attributed to the polarity differences in the transition states leading to head-to-head and head-to-tail dimers. Berson and coworkers[13] have observed that the logarithms of the ratio of the stereoisomers in the kinetically controlled Diels–Alder addition to methyl methacrylate and methyl *trans*-crotonate are linearly related to the Kirkwood–Onsager parameter and have attributed this effect to a difference of the polarity in the transition state, thus lending credence to the above proposals.

Experimental Section

Solvents. Spectrograde benzene, ethyl acetate, methylene chloride, and reagent grade 1,2-dichloroethane were fractionally distilled twice through a 100-cm Vigreux column in which the middle 50% was collected. Spectrograde chloroform was washed twice with distilled water to remove ethanol, dried over anhydrous calcium chloride, fractionally distilled twice, and used immediately. Acetic anhydride (10 ml) was added to 1 l. of reagent grade glacial acetic acid and the mixture was fractionally distilled collecting the middle 50%.

Substrate. Thianaphthene 1,1-dioxide was prepared according to the method of Davies and James.[22] It was recrystallized three times in absolute ethanol and dried *in vacuo* at 50° (mp 142.5–143°).

Sensitizers. Benzophenone, chrysene, benzil, fluoren-9-one, and pyrene (Baker sensitizer grade reagents) were all recrystallized from absolute ethanol and dried *in vacuo*.

Quenchers. *trans*-α-Methylstilbene (Aldrich Chemical Co.) was recrystallized from petroleum ether (bp 60–90°) and dried *in vacuo*.

Solvent Effects. A solution (250 ml) of thianaphthene 1,1-dioxide (1.0 g, 2.4×10^{-2} *M*), previously purged with dry nitrogen for 45 min, was irradiated with a Hanovia mercury vapor lamp (type L 450 W) in the usual water-cooled quartz immersion apparatus with a Pyrex filter for 2 hr at room temperature. After solvent evaporation, starting material **1a** was removed by extraction with boiling water. The mixture of dimers (0.400 g) was dissolved in 25.0 ml of reagent grade DMSO. The dimer ratios were determined by gas chromatography on a Hewlett-Packard F & M 5750 flame ionization instrument equipped with a calibrated $^1/_8$ in. × 6 ft column of 10% Apiezon L on Chromosorb W. The column temperature was 300°.

Calibration of Apiezon L Column. Mixtures of dimers (0.40 g) of HH/HT ratios 0.165, 0.997, 1.65, 2.99, and 6.28 were dissolved in 25.0 ml of reagent grade DMSO. The ratios of the areas were found to be 0.208, 0.313, 0.583, 1.01, and 2.10, respectively. The calibration constant $K = (\mathrm{HH/HT})_{\mathrm{wt}}/(\mathrm{HH/HT})_{\mathrm{area}}$ was found to be equal to 2.98 ± 0.06.

Sensitized Dimerization of Thianaphthene 1,1-Dioxide. A series of benzene solutions of thianaphthene 1,1-dioxide (0.100 g, 2.40×10^{-2} *M*), each with one of benzophenone, chrysene, benzil, fluoren-9-one, or pyrene (2.41×10^{-2} *M*), was pipetted into Pyrex test tubes (25 × 150 mm) which were constricted to facilitate sealing. One sample contained no sensitizer, only a solution of thianaphthene 1,1-dioxide (2.40×10^{-2} *M*) which was used as a blank. These were then degassed using three freeze–thaw cycles and sealed under pressures of the order of 2×10^{-2} Torr. The tubes were put on the quantum yield "merry-go-round apparatus" and irradiated for 24 hr at 366 nm using the Hanovia medium-pressure lamp (type L, 450 W) and the Alizarine Red, aluminum sulfate, and calcium chloride filter.[23] After the sample tubes were opened and the reaction mixtures freed from benzene, the reaction mixtures were filtered from boiling cyclohexane to remove the sensitizer and then from boiling water to remove starting material **1a**. The dimer ratios were determined by gas chromatography using the same methods and apparatus as that for HH/HT ratios for solvent effects.

Thianaphthene 1,1-Dioxide (1a) as a Sensitizer. Benzene solutions (25.0 ml) of *trans*-α-methylstilbene (0.05 *M*), thianaphthene 1,1-dioxide (**1a**, 0.05 *M*), *trans*-α-methylstilbene (0.05 *M*), benzoquinone (purified by sublimation, 0.05 *M*), *trans*-α-methylstilbene (0.05 *M*), and pyrene (0.05 *M*) were pipetted into Pyrex test tubes (constricted on top to facilitate sealing) (two of each acceptor–

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[16] (a) McCullough and Ramachandran[16b] have investigated the photocycloaddition of 2-phenylcyclohex-2-enone to tetramethylethylene (TME) which occurs by direct irradiation and sensitization by Michler's ketone. A plot, $[\Phi]^{-1}$, for cycloadditions by direct irradiation and sensitization against the $[\text{tetramethylethylene}]^{-1}$ gave two straight lines having the same intercept but with different slopes. These observations were attributed to a triplet excited state for cycloaddition by sensitization and a singlet state intermediate by direct irradiation. However, the above observations could well be consistent with a triplet state as intermediate for photocycloaddition both by direct and sensitized irradiation as shown in eq 1 and 3. While, for direct irradiation, the slope of $[\Phi]^{-1}$ *vs.* $[\text{tetramethylethylene}]^{-1}$ plot is dependent on the product of Φ (product formation) and the rate of decay of the excited state to rate of attack of the excited on the ground state,[16b] the slope for sensitized irradiation should depend on $[\Phi]$ for product formation and the triplet lifetime of the sensitizer (eq 1). Thus, the different slopes obtained[16b] could be attributed to the different lifetimes of the two different triplets involved (sensitizer and substrate). A choice between a triplet or singlet excited state intermediate could be made by appropriate quenching experiments. (b) J. J. McCullough and B. R. Ramachandran, *Chem. Commun.*, 1180 (1971).

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donor pair). These samples were degassed by four freeze–thaw cycles and sealed under a pressure of 2 × 10^{-2} Torr. These solutions were then irradiated on the merry-go-round apparatus with the ultraviolet lamp used previously at 313 nm using the K_2CrO_4–K_2CO_3 filter.[9] The isomerization of *trans*-α-methylstilbene was followed by gas chromatography on a $^1/_8$ in. × 6 ft column of 10% LAC 728 on Chromosorb W until cis/trans ratios were constant (60 hr of irradiation).

Quantum Yield of Photodimerization of Thianaphthene 1,1-Dioxide (1a). The sample tubes were 25 × 150 mm Pyrex test tubes attached to 19/24 ground glass female joints provided with a constriction for sealing. Benzene solutions (25.0 ml at concentrations of 2.41 × 10^{-2}, 3.62 × 10^{-2}, and 4.82 × 10^{-2} *M*) were degassed (four freeze–degas–thaw cycles) and sealed at a pressure of 2 × 10^{-2} Torr. Four sample tubes with solutions at one concentration were placed on the merry-go-round apparatus in the presence of four tubes with uranyl oxalate actinometer solution and irradiated with the lamp previously used at 313 nm. The amount of thianaphthene 1,1-dioxide reacted was determined by quantitative uv spectrophotometric analysis using an extinction coefficient, ϵ (304 nm), of 2.32 ± 0.06 l. mol^{-1} cm^{-1}. Tubes containing 0.05 *M* uranyl oxalate (made from 0.05 *M* uranyl sulfate and 0.05 *M* of oxalic acid) in distilled water were irradiated simultaneously with solutions of compound **1a** during the determination of quantum yields of all nonsensitized dimerizations. The amount of oxalate reacted was determined by titrating an acidified solution of actinometer solution with standardized $KMnO_4$ solution (0.06 *N*) at 50°. The quantum yield for oxalate decomposition was taken at 0.56 at 313 nm.[17] Total periods of irradiation (1.75 hr) were adjusted so that 35–40% of actinometer and 9–11% of thianaphthene 1,1-dioxide reacted.

Determination of the Molar Extinction Coefficient of Thianaphthene 1,1-Dioxide (1a). Benzene solutions of compound **1a** at concentrations of 6.566 × 10^{-4}, 5.253 × 10^{-4}, 3.940 × 10^{-4}, 2.626 × 10^{-4}, and 1.313 × 10^{-4} *M* were prepared. The absorbance, *A*, of these solutions was measured in 1-cm cells on a Unicam SP 800 uv spectrophotometer at 304 nm. The molar extinction coefficient of 2.32 ± 0.06 × 10^3 l. mol^{-1} cm^{-1} was calculated by the Beer–Lambert equation using the method of least squares.

Quantum Yield of the Sensitized Dimerization of Thianaphthene 1,1-Dioxide (1a). The sample cells used in this procedure were identical with those used in the determination of the quantum yields of the nonsensitized reaction. Benzene solutions (25.0 ml at concentrations of 2.41 × 10^{-2}, 3.62 × 10^{-2}, and 4.82 × 10^{-2} *M* of thianaphthene 1,1-dioxide and 1.99 × 10^{-2} *M* of benzophenone in all three samples) were degassed (four freeze–degas–thaw cycles) and sealed at a pressure of 2 × 10^{-2} Torr. Four samples at one concentration of **1a** were placed on the merry-go-round apparatus and irradiated in the presence of four samples of benzophenone–benzhydrol actinometer at 366 nm. The amount of **1a** reacted was determined in the presence of sensitizer by uv spectrophotometric measurements at a wavelength of 310 nm in which compound **1a** has a molar extinction coefficient of 2.28 ± 0.06 × 10^3 l. mol^{-1} cm^{-1}. This extinction coefficient was determined in the same way as previously described. For a concentration of 0.1 *M* benzhydrol and 0.1 *M* benzophenone, the quantum yield for the photoreduction of benzophenone has been found to be 0.69.[11] The amount of benzophenone reacted was determined by uv spectrophotometry using extinction coefficient at 344 nm equal to 1.36 × 10^2 l. mol^{-1} cm^{-1}.[11] Total periods of irradiation were adjusted so that 50% of actinometer and 5% of thianaphthene 1,1-dioxide reacted.

Filter Solutions for the Isolation of the 313- and 366-nm Bands. In both cases (wavelength = 313 and 366 nm) the emission from a Hanovia medium-pressure lamp (type L, 450 W), positioned in the center of the turntable, was filtered by a Pyrex sleeve. When uv light of wavelength = 313 nm was needed, an aqueous solution of 0.2 g of potassium chromate and 10 g of potassium carbonate per liter of solution was put in the Pyrex sleeve.[9] When a wavelength of 366 nm was needed, an aqueous solution of 0.37 g of Alizarine Red, 0.015 g of aluminum sulfate·18 H_2O, and 0.25 g of calcium chloride per liter of solution was used. A pH of 4.64 was maintained with acetic acid–sodium acetate buffer (0.1 *N* acetic acid and 0.1 *N* sodium acetate).[23]

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