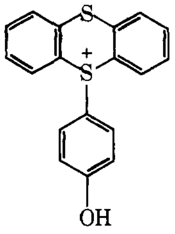
electrode compartment, reference electrode, inert gas supply, thermometer, and a Beckman rotating disk electrode. The temperature was controlled with tap water. The thianthrene cation radical solutions were prepared by partial oxidation of solutions of the compound in the solvent systems. Oxidations were carried out at constant current (25.0 mA) at a large area platinum gauze electrode. Current was passed for a time calculated to give the desired concentration of cation radical. The concentration of cation radical was determined exactly after oxidation by the magnitude of the limiting current at the rotating disk electrode. The limiting current was followed as a function of time for several minutes, and little or no decrease in cation radical concentration was observed before adding the phenol solution. The procedure used for carrying out the kinetic runs was that previously described.[10] $TH\cdot^{+}ClO_4$ (1.0 mmol), prepared according to a literature procedure,[11] was allowed to react with PHOH (1.0 mmol) in three solvents: acetonitrile, dichloromethane, and dichloromethane-TFA (49:1). The product, isolated as before,[3] was the same in all three cases and was identified as 5-(*p*-hydroxyphenyl)thianthrenium (**4**) perchlorate by its ultraviolet absorption spectrum.[3] The stoichiometry of the reaction was previously[3] shown to follow (17).

$2TH^{+\cdot} + PHOH \longrightarrow$  $+ TH + H^{+}$ (17)

4

References and Notes

(1) For other parts in the series, see (a) U. Svanholm, A. Ronlán, and V. D. Parker, *J. Am. Chem. Soc.*, **96**, 5108 (1974); (b) U. Svanholm, O. Hammerich, and V. D. Parker, *Ibid.*, **97**, 101 (1975); (c) U. Svanholm and V. D. Parker, *ibid.*, submitted for publication.

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(12) Very poor reproducibility was reported for the reactions of $TH\cdot^{+}$ with AN and acetanilide.[3] For example, the rate constants reported for acetanilide varied by a factor of about 5 and those for AN by a factor of about 6. At least some of this variation must be attributed to difficult to control background reactions.

(13) The value calculated by Shine[3] for their data was −16.7.

(14) Proton transfer reactions are discussed in detail in ref 8.

(15) Rate constants for the reaction of $TH\cdot^{+}$ with PHOD were difficult to reproduce This of course was due to the low PHOD concentrations used (5×10^{-4} M). The presence of trace amounts of water, which we were unable to avoid even though scrupulously dry solvent was used, markedly affects the PHOD/PHOH ratio and hence tends to diminish the apparent kinetic isotope effect. The isotope effect observed, $k_H/k_D = 2$, is much lower than the real value. After one run, the reaction mixture was evaporated under argon and the NMR spectrum showed that the isotopic purity was less than 50%.

Internal Heavy-Atom Effects on the Photodimerization of Acenaphthylene[1]

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Abstract: The quantum yields of dimerization of 5,6-dichloroacenaphthylene were measured at 365 nm as a function of ethyl iodide concentration, substrate concentration, and quencher concentration. The product distributions in each case were also determined. Except for the relative triplet efficiencies, the photochemistry of this compound appears to be analogous to that of acenaphthylene. The results of this study indicate that internal heavy atoms have a considerable influence on both $T_1 \leftarrow S_1$ and $S_0 \leftarrow T_1$, unlike the external heavy-atom case in which the former process was far more sensitive to heavy-atom perturbation. A mechanism consistent with the data is proposed, and the triplet rate constants for dimerization and the various decay modes have been determined.

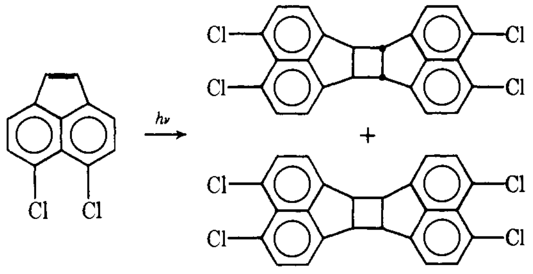
External heavy-atom effects on the dimerization and cycloaddition reactions of acenaphthylene have been the subject of a number of recent studies.[2] Solvents containing either bromine or iodine have been shown to produce a dramatic increase in the steady-state triplet population of acenaphthylene by increasing the rate of intersystem crossing, $T_1 \leftarrow S_1$.[3] As a result, numerous changes in the photochemistry of acenaphthylene in the presence of heavy-atom solvents have been observed.[4]

We recently reported a detailed mechanistic study on the effect of ethyl iodide on the photochemistry of acenaphthylene.[2g,h] As an extension of our studies on photochemical heavy-atom effects, we have now investigated the photochemistry of 5,6-dichloroacenaphthylene in order to compare internal and external heavy-atom perturbation.[5]

Results

(A) **Photoproducts.** The two major photoproducts resulting from the irradiation of 5,6-dichloroacenaphthylene have been identified as the cis cyclobutane dimer and the trans cyclobutane dimer, as illustrated in Chart I. Some difficulties were initially encountered in the separation, purification, and identification of these products as a result of both the relatively high-melting points of these dimers and their low solubilities in all organic solvents used, precluding the use of such analytical techniques as NMR, GLC, high-pressure liquid chromatography, and mass spectral analysis. By utilizing the knowledge of the photochemistry of acenaphthylene gained in previous studies, however, these difficulties were circumvented.

Chart I



As in the case of acenaphthylene,[6] two excited states appear to be involved in the dimerization of 5,6-dichloroacenaphthylene. The first excited singlet state yields predominantly the cis dimer while the first excited triplet state produces the trans isomer as the major product. The relative importance of each of these excited states depends on the nature of the solvent used.[2g,h,3,6] Each of the two dimers can therefore be isolated by adjusting the reaction conditions to favor either the singlet or the triplet intermediate.[7]

The cis dimer was prepared by irradiating the substrate in cyclohexane which had been saturated with oxygen prior to photolysis in an attempt to limit formation of the triplet intermediate.[8] The resulting product was recrystallized from benzene until no further changes were observed in the positions and relative intensities of the bands in the uv spectrum (300-350 nm).[9]

The trans dimer was prepared by the irradiation of 10 mol % ethyl iodide solutions of substrate, which had been degassed using five freeze-pump-thaw cycles. Under these conditions, the triplet state of 5,6-dichloroacenaphthylene should be the major intermediate in product formation. The isolated product was triturated with boiling benzene until no further changes in the uv spectrum (300-350 nm) were observed.

The elemental analysis of each of the products was found to be the same as that of the starting material, indicating that the photoreaction involved some type of cycloaddition or polymerization of the substrate. The ir spectra of the two products were almost identical, indicating that these products are very similar in structure. Their ir spectra were also very similar to that of 5,6-dichloroacenaphthene. In contrast, the uv spectra of these products, as illustrated in Figures 1 and 2, were significantly different. It is noteworthy that the long-wavelength band for the isomer identified as the trans dimer is considerably more intense than that of the cis dimer. The same spectral behavior was observed for the dimers of acenaphthylene.[10] One should also note that while the uv bands of the 5,6-dichloroacenaphthylene dimers occur at longer wavelengths, the band structure of these dimers is quite similar to that of the corresponding acenaphthylene dimers.[10] In addition, the fact that the absorption bands of these products occur in the same region as the B band of 5,6-dichloroacenaphthene[11] indicates that the naphthalene rings retain their aromaticity in both products.

To establish the stereochemistry of these products, each dimer was subjected to ozonolysis, oxidative decomposition, and esterification with diazomethane. This method of structural proof has been used to determine the stereochemistry of the acenaphthylene cis dimer,[12] a number of cyclobutane adducts formed from acenaphthylene,[2f] and cyclobutane adducts formed from phenanthrene.[13] Treatment of the cis dimer in the above manner yielded a product identified as *cis,cis,cis*-1,2,3,4-tetracarbomethoxycyclobutane by comparison of its ir and NMR spectra with those of an authentic sample.[14] Treatment of the trans dimer in the same manner yielded *cis,trans,cis*-1,2,3,4-tetracarbomethoxycyclobutane, identified by comparison of its NMR spectrum with that of an authentic sample.[14] Since rearrangements have not been observed in previous analyses of this type,[12] these results strongly suggest that the assigned stereochemistry is correct.

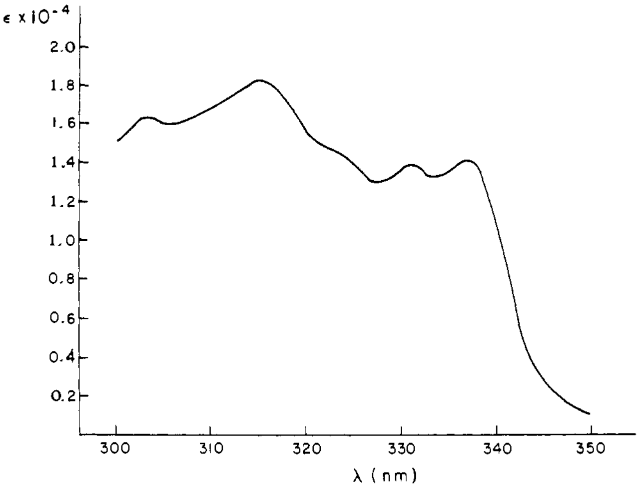


Figure 1. Uv spectrum of 5,6-dichloroacenaphthylene cis dimer.

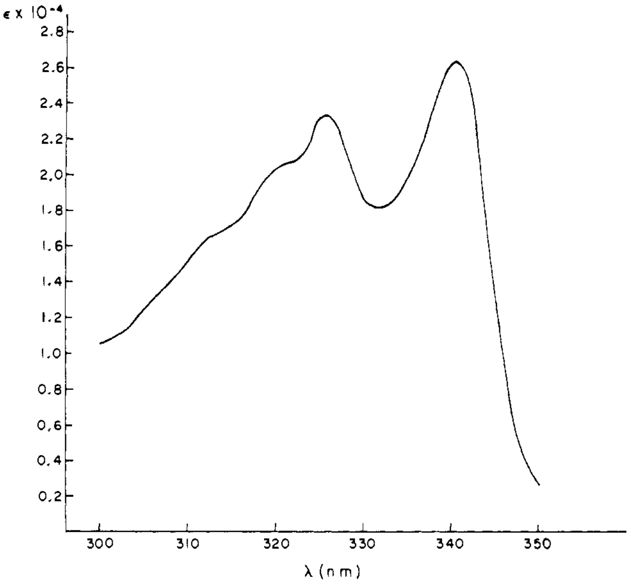


Figure 2. Uv spectrum of 5,6-dichloroacenaphthylene trans dimer.

(B) Effect of Ethyl Iodide. The quantum yield of dimerization of 5,6-dichloroacenaphthylene in cyclohexane is significantly larger than that of acenaphthylene. A determination of the quantum yield as a function of ethyl iodide concentration (Figure 3), however, indicates that while the behavior of 5,6-dichloroacenaphthylene is quite similar to that of the parent compound,[2g] the quantum yields in all cases are considerably smaller. Figure 4 illustrates a plot of the reciprocal of the quantum yield as a function of ethyl iodide concentration in the region in which the heavy-atom solvent quenches the dimerization. As in the case of acenaphthylene, a good linear relationship is obtained.

A determination of the product distribution[5] by uv analysis, as given in Table I, indicates that as the concentration of ethyl iodide is increased, there is a moderate increase in the proportion of cis dimer formed. The product distributions observed for 5,6-dichloroacenaphthylene are virtually identical with those determined for acenaphthylene under the same experimental conditions.[2h]

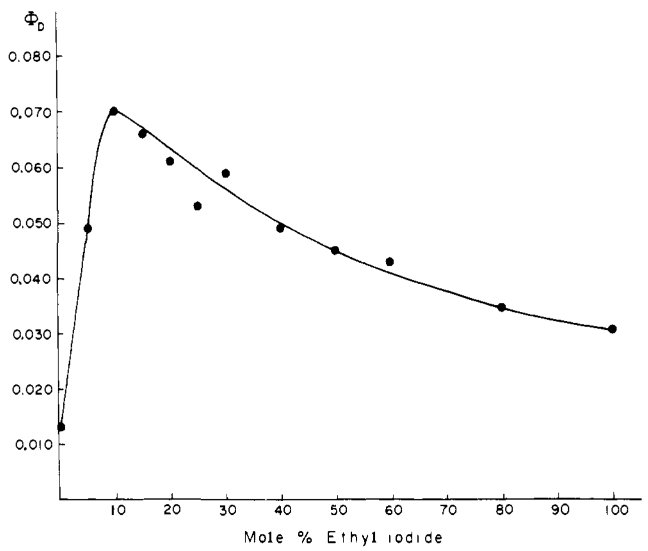


Figure 3. The dependence of Φ_D on the concentration of ethyl iodide.

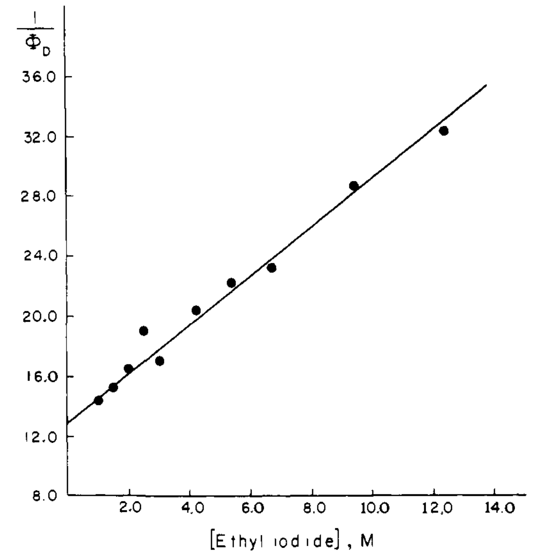


Figure 4. The dependence of $1/\Phi_D$ on the concentration of ethyl iodide.

Table I. Solvent Dependence of Quantum Yields and Product Distributions for 0.10 M 5,6-Dichloroacenaphthylene Solutions

Mol % EtI[a]	Φ_D	% cis	% trans
0	0.013	30	70
5	0.049	22	78
10	0.070	19	81
15	0.066	20	80
20	0.061	21	79
25	0.053	20	80
30	0.059	24	76
40	0.049	24	76
50	0.045	26	74
60	0.043	29	71
80	0.035	31	69
100	0.031	36	64

[a] Cyclohexane was used as a cosolvent in all samples containing less than 100 mol % EtI.

(C) Concentration Effects. Figure 5 illustrates the effect of 5,6-dichloroacenaphthylene concentration on the quantum yield of dimerization in 25 mol % ethyl iodide. A linear relationship between the reciprocal of the quantum yield and the reciprocal of substrate concentration is observed.

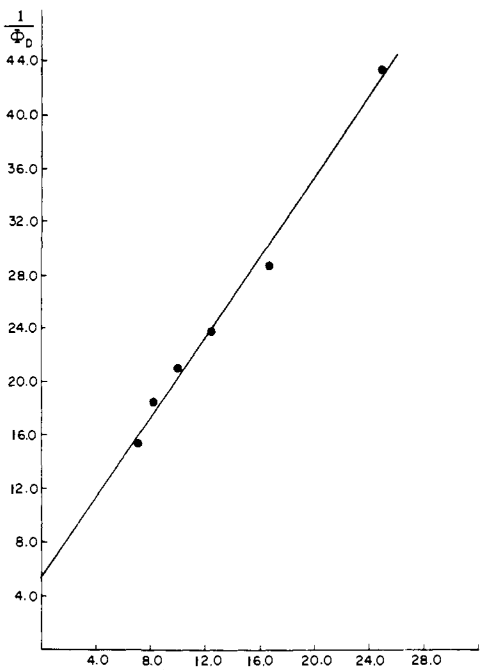


Figure 5. The dependence of $1/\Phi_D$ on the reciprocal of the concentration of 5,6-dichloroacenaphthylene in 25 mol % ethyl iodide.

Table II. Dependence of Quantum Yields and Product Distributions on the Concentration of 5,6-Dichloroacenaphthylene in 25 Mol % Ethyl Iodide

[DiCl-A]	Φ_D	% cis	% trans
0.0400	0.023	19	81
0.0599	0.035	20	80
0.0800	0.042	21	79
0.1003	0.048	20	80
0.1198	0.054	24	76
0.1399	0.065	20	80

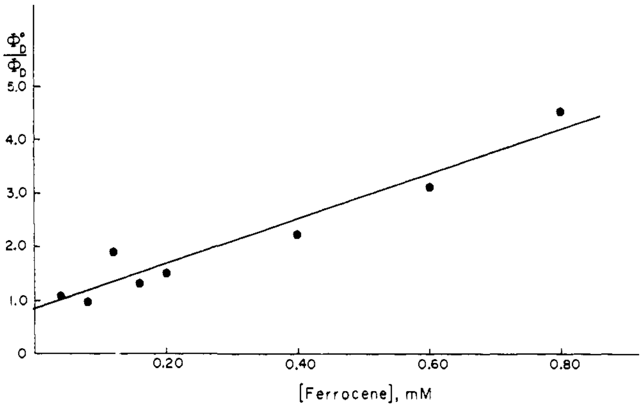


Figure 6. A Stern-Volmer plot of the dimerization of 5,6-dichloroacenaphthylene as a function of the concentration of ferrocene in 25 mol % ethyl iodide.

The data in Table II indicate that in the range of concentrations studied (0.04 to 0.14 M), the product distribution remains constant for a given concentration of ethyl iodide.

(D) Quenching Studies. Figure 6 illustrates a Stern-Volmer plot of the quenching of 5,6-dichloroacenaphthylene dimerization in 25 mol % ethyl iodide by ferrocene. The slope of this plot is considerably smaller than that of acenaphthylene,[2h] indicating that the triplet lifetime for the halogenated compound is shorter. The plot remains linear throughout the concentration range used, establishing that only one ex-

Table III. Quantum Yields and Product Distributions in the Presence of Ferrocene in 25 Mol % Ethyl Iodide[a]

[Ferrocene]	Φ_D	% cis	% trans
0	0.060	19	81
4.0×10^{-5}	0.056	22	78
8.0×10^{-5}	0.062	18	82
1.2×10^{-4}	0.032		
1.6×10^{-4}	0.046	20	80
2.0×10^{-4}	0.040	16	84
4.0×10^{-4}	0.027	15	85
6.0×10^{-4}	0.019	17	83
8.0×10^{-4}	0.013	17	83

[a] 5,6-Dichloroacenaphthylene concentration: 0.10 M.

cited state intermediate is being quenched. At the maximum concentration (8.0×10^{-4} M) of ferrocene used, approximately 80% of the dimerization is quenched.

Table III indicates that the product distribution is independent of ferrocene concentration. The product distribution is identical with that determined in the absence of quencher (Table II).

Discussion

(A) Comparison of Photochemistry. With the exception of the relative rates of the various triplet processes, the photochemistry of 5,6-dichloroacenaphthylene parallels that of acenaphthylene. This conclusion is supported by both the kinetic results obtained in this study and the product distributions determined under various experimental conditions.

The linearity of the Stern-Volmer plot in Figure 6, as well as the invariance of the product distribution to changes in ferrocene concentration, indicates that the dimerization of 5,6-dichloroacenaphthylene occurs from a single excited-state intermediate in the presence of heavy-atom solvent. The triplet nature of this excited state is indicated by the following observations. Increases in the heavy-atom solvent concentration from 0 to 1.0 M produce a concomitant increase in the efficiency of dimerization. A reduction in dimerization efficiency, however, is observed with further increases in ethyl iodide concentration. These results are analogous to those obtained for acenaphthylene.[2g] The proportion of cis dimer of 5,6-dichloroacenaphthylene increases moderately with increasing solvent polarity, as does that of the cis dimer of the unsubstituted compound.[2h,6,15] Furthermore, the distribution of products of 5,6-dichloroacenaphthylene at various concentrations of ethyl iodide is, within experimental error, identical with that of acenaphthylene under corresponding reaction conditions.[2h] Lastly, the kinetic data for the halogenated compound is consistent with the mechanism originally proposed for the dimerization of acenaphthylene in heavy-atom solvents. These results clearly indicate that both compounds undergo dimerization from the same excited state, namely the triplet state.

In light-atom solvents in the presence of a triplet quencher such as oxygen, acenaphthylene has been shown to dimerize from the singlet state producing cis dimer as the exclusive product.[6] Irradiation of 5,6-dichloroacenaphthylene in cyclohexane saturated with oxygen led to the formation of a product mixture containing approximately 90% cis dimer and 10% trans dimer. Although singlet dimerization of the halogenated compound was not examined in detail, this experiment clearly suggests that the singlet state of 5,6-dichloroacenaphthylene also undergoes dimerization, yielding the cis dimer as the major or perhaps exclusive product.[16]

(B) Mechanism. The simplified mechanism[29] shown in Chart II is consistent with all of the kinetic data, where A = 5,6-dichloroacenaphthylene, A_2 = 5,6-dichloroacenaphthylene dimer, HA = ethyl iodide, and Q = ferrocene. This mechanism is essentially the same as that proposed for the dimerization of acenaphthylene.[2h] The steps involving possible singlet excimer formation and singlet dimerization have been excluded since they were not studied in detail and are at best relatively unimportant processes in heavy-atom solvents. Using the steady-state approximation, one can derive the following expression for Φ_D, the quantum yield of dimerization.

Chart II

	Rate	
$A + h\nu \longrightarrow {}^1A$	I_a	(1)
${}^1A \xrightarrow{k_{ic}} A$	$k_{ic}[{}^1A]$	(2)
${}^1A \xrightarrow{k_{isc}} {}^3A$	$k_{isc}[{}^1A]$	(3)
${}^1A + HA \xrightarrow{k'_{isc}} {}^3A + HA$	$k'_{isc}[{}^1A][HA]$	(4)
${}^3A + A \xrightarrow{k_2} A_2$ (cis and trans)	$k_2[{}^3A][A]$	(5)
${}^3A + A \xrightarrow{k_{cq}} 2A$	$k_{cq}[{}^3A][A]$	(6)
${}^3A + HA \xrightarrow{k''_{isc}} A + HA$	$k''_{isc}[{}^3A][HA]$	(7)
${}^3A \xrightarrow{k_d} A$	$k_d[{}^3A]$	(8)
${}^3A + Q \xrightarrow{k_q} A + Q$	$k_q[{}^3A][Q]$	(9)

$$\Phi_D = \Phi_{isc} \frac{k_2[A]}{k_2[A] + k_{cq}[A] + k''_{isc}[HA] + k_q[Q] + k_d} \qquad (10)$$

By setting Φ_{isc} equal to unity,[17] one can obtain the following relationships:

$$\frac{1}{\Phi_D} = \frac{(k_2 + k_{cq})[A] + k_d + k_q[Q]}{k_2[A]} + \frac{k''_{isc}}{k_2[A]}[HA] \qquad (11)$$

$$\frac{1}{\Phi_D} = \frac{k_2 + k_{cq}}{k_2} + \frac{k''_{isc}[HA] + k_d + k_q[Q]}{k_2} \frac{1}{[A]} \qquad (12)$$

Equations 11 and 12 are the analytical expressions for the plots in Figures 4 and 5, respectively.

(C) Rate Constants. The Stern-Volmer plot illustrated in Figure 6 is represented by the equation

$$\Phi_D{}^0/\Phi_D = 1 + k_q\tau[Q] \qquad (13)$$

where k_q is the rate constant for the quenching of triplet 5,6-dichloroacenaphthylene, τ is the triplet lifetime, and [Q] is the concentration of ferrocene. Assuming that k_q is diffusion controlled,[18] the slope of the Stern-Volmer plot yields an estimate of the 5,6-dichloroacenaphthylene triplet lifetime.

The value of k_2, the rate constant for dimerization, can then be calculated according to the equation

$$(\Phi_D{}^0/\tau)(1/[A]) = k_2 \qquad (14)$$

By substituting this value of k_2 into the analytical expression for the intercept given in eq 12 and setting this expression equal to 5.4, the calculated value of the intercept, an estimate of k_{cq}, the rate constant for concentration quenching, may be determined. The rate constant for unimolecular decay, k_d, was obtained by setting the intercept given in eq 11 equal to 12.9, the calculated value of this intercept, and by substituting the values of k_2, k_{cq}, and [A] into the expression for the intercept. Since no quencher was present, k_q[Q] was set equal to zero. The rate constant for heavy-atom quenching, k''_{isc}, was determined by substituting the values for k_2 and [A] into the expression for the slope in eq 11, which was then set equal to the calculated value of 1.61. The results of these calculations are presented in Table IV.

The relative triplet efficiencies for concentration quench-

Table IV. Evaluation of Data

EtI Dependence			
Slope, M^{-1}	1.61 ± 0.05		
Intercept	12.9 ± 0.3		
Correlation coefficient	0.996		
Concentration Dependence			
Slope, M	1.49 ± 0.05		
Intercept	5.4 ± 0.8		
Correlation coefficient	0.996		
Ferrocene Dependence			
Slope, M^{-1}	4200 ± 400		
Intercept	0.85 ± 0.13		
Correlation coefficient	0.969		
Triplet Lifetime and Rate Constants			
	5,6-Dichloroacenaphthylene	Acenaphthylene[2h]	
τ, sec	6.6×10^{-7}	2.15×10^{-6}	
k_2 M^{-1} sec^{-1}	9.1×10^{5}	6.58×10^{5}	
k_{cq}, M^{-1} sec^{-1}	4.0×10^{6}	1.58×10^{6}	
k_d, sec^{-1}	6.8×10^{5}	9.20×10^{4}	
k''_{isc}, M^{-1} sec^{-1}	1.5×10^{5}	6.71×10^{4}	
Relative Triplet Efficiencies[a]			
[EtI]	0	1.0 M	12.4 M
Φ_D	0.078	0.069	0.030
Φ_{cq}	0.34	0.30	0.13
Φ_{ST}	0.58	0.63	0.84

[a] These values were calculated using a 5,6-dichloroacenaphthylene concentration of 0.10 M.

ing and intersystem crossing to the ground state are given by the equations

$$\Phi_{cq} = \frac{k_{cq}[A]}{k_2[A] + k_{cq}[A] + k_d + k''_{isc}[HA] + k_q[Q]} \qquad (15)$$

$$\Phi_{ST} = \frac{k_d + k''_{isc}[HA]}{k_2[A] + k_{cq}[A] + k_d + k''_{isc}[HA] + k_q[Q]} \qquad (16)$$

Estimates of these relative efficiencies have been calculated for several concentrations of heavy-atom solvent and are given in Table IV.

One will note that, in contrast to the results obtained for acenaphthylene, intersystem crossing to the ground state is the major process leading to depopulation of the triplet state of 5,6-dichloroacenaphthylene even in light-atom solvents. The value of Φ_{ST} increases further upon addition of heavy-atom solvent, reaching a maximum value of 0.84 in 100 mol % ethyl iodide. This is very close to the value of Φ_{ST} obtained for acenaphthylene under the same conditions.[2h,19]

(D) Heavy-Atom Sensitivity. Recent studies in this laboratory[20] involving external heavy-atom effects on the photophysical processes of anthracene indicate that $k'_{isc} \gg k''_{isc}$ for this system, in agreement with our qualitative results on acenaphthylene. It was noted, however, that the sensitivity of $S_0 \leftarrow T_1$ to external perturbation was much greater than that of $T_1 \leftarrow S_1$, where sensitivity was defined by

$$\frac{f_{TS}'}{f_{ST}} = \frac{k'_{isc}/k_{isc}}{k''_{isc}/k_d} \qquad (17)$$

In this expression, the rate constants have the same meaning as previously described and f_{TS}' and f_{ST} represent the sensitivity of $T_1 \leftarrow S_1$ and $S_0 \leftarrow T_1$, respectively, to external heavy-atom perturbation. While this expression is useful in comparing rate constants, it provides no information about the relative rates of the two intersystem crossing processes. Furthermore, this definition of heavy-atom sensitivity is not useful in the acenaphthylene system since we have not determined the unperturbed and heavy-atom assisted rate constants for $T_1 \leftarrow S_1$. Therefore, in this paper we define sensitivity to heavy-atom perturbation in terms of the effect on the quantum yield of dimerization. By defining sensitivity in this more pragmatic manner, we are in essence comparing $k_{isc} + k'_{isc}[HA]$ and $k_d + k''_{isc}[HA]$ rather than rate ratios.

(E) Comparison of Triplet Efficiencies. The quantum yield of dimerization of 5,6-dichloroacenaphthylene in cyclohexane is approximately twofold larger than that of acenaphthylene[2g] under identical conditions. Since the calculated triplet dimerization efficiency of the halogenated compound in cyclohexane is less than half of that of the unsubstituted compound,[21] the observed increase in Φ_D has been attributed to an increase in Φ_{isc} resulting from internal heavy-atom perturbation. The triplet nature of the intermediate in the dimerization of the substituted compound was further established by oxygen quenching studies.[22]

In contrast, the quantum yields of dimerization of 5,6-dichloroacenaphthylene in various concentrations of ethyl iodide were considerably smaller than the corresponding values of Φ_D for acenaphthylene.[2g] An analysis of the kinetic data indicates that the triplet decay efficiency, Φ_{ST}, of 5,6-dichloroacenaphthylene in cyclohexane is 0.58, as compared to a value of 0.42[2h] for acenaphthylene in 1.0 M ethyl iodide. The quantum yield of intersystem crossing, however, is estimated to be ~0.13,[23] a value significantly smaller than that of ~1.0[2h] for acenaphthylene in 1.0 M ethyl iodide. These results clearly indicate that the relative effects of internal heavy-atom perturbation on $T_1 \leftarrow S_1$ and $S_0 \leftarrow T_1$ are not the same as those resulting from external perturbation. Thus, for corresponding values of Φ_{isc}, Φ_{ST} is much greater for 5,6-dichloroacenaphthylene than for acenaphthylene. We therefore conclude that $T_1 \leftarrow S_1$ and $S_0 \leftarrow T_1$ are affected to a more comparable extent by internal heavy-atom perturbation than by external perturbation.[24]

It is not unreasonable that the substitution of chlorines onto the acenaphthylene ring should have such a significant influence on the intersystem crossing processes discussed above. It is somewhat surprising, however, that the other processes involving spin-inversion were affected to such a small extent. The rate constants for dimerization, concentration quenching, and heavy-atom quenching undergo an approximately twofold increase as a result of heavy-atom substitution, as compared to the sevenfold increase observed for k_d.

Summary and Conclusions

We have shown that the photochemistry of 5,6-dichloroacenaphthylene is analogous to that of acenaphthylene. Both compounds undergo dimerization primarily from the triplet state in heavy-atom solvents yielding a trans cyclobutane dimer as the major product and a cis cyclobutane dimer as the minor product. Singlet dimerization, although occurring to some extent, is a relatively inefficient process in each compound.

Both internal and external heavy-atom perturbation have been shown to increase the rate of population of the triplet state. Internal heavy atoms, however, enhance the rate of triplet decay to a comparable degree. As a result, the values of Φ_D for 5,6-dichloroacenaphthylene in ethyl iodide are significantly smaller than the corresponding values of acenaphthylene.

This work again demonstrates the limits inherent in the use of heavy-atom perturbation to enhance a photochemical reaction. Thus, while internal heavy atoms produced the expected increase in Φ_D in light-atom solvents, their presence greatly limited the sensitivity of Φ_D to further perturbation.

Experimental Section

Materials. Ethyl iodide (Eastman Kodak) was distilled at 72° on a column (46 × 2 cm) packed with glass helices. Ferrocene (Alfa Inorganics) was recrystallized once from hexane, mp 173–175°. Acenaphthene (Eastman Kodak) and Eastman spectrograde cyclohexane were used without further purification.

Irradiation Procedure. The irradiation procedure was identical with that described in a previous paper.[2h]

Quantum Yields of Dimerization. The quantum yields were determined in a manner similar to that previously described.[2h] The optical densities of the irradiated and corresponding unirradiated solutions of 5,6-dichloroacenaphthylene were measured at a wavelength of 361.5 nm. Neither of the dimers of 5,6-dichloroacenaphthylene absorb at this wavelength.

Product Distribution. Solutions of pure cis and pure trans dimers of 5,6-dichloroacenaphthylene in benzene were prepared, and the molar absorptivities at 340 and 316 nm for each were determined: (cis) ϵ_{340}, 1.07×10^4 M^{-1} cm^{-1}, ϵ_{316}, 1.80×10^4 M^{-1} cm^{-1}; (trans) ϵ_{340}, 2.63×10^4 M^{-1} cm^{-1}, ϵ_{316}, 1.74×10^4 M^{-1} cm^{-1}. The composition of the product dimer mixtures was determined by measuring the optical densities of benzene solutions of these dimers at 340 and 316 nm. From these optical densities and the corresponding molar absorptivities, the concentrations of the cis and trans dimers were calculated.

The product dimer mixtures were prepared for dimer analysis as described previously.[2h]

5,6-Dichloroacenaphthene.[25] To a solution containing 5.0 g (33.0 mmol) of acenaphthene and 0.15 g of aluminum chloride in 100 ml of carbon tetrachloride, cooled in an ice-water bath, was added over a period of 5 min 7.0 ml (12 g, 80 mmol) of sulfuryl chloride. The reaction mixture was kept in the ice-water bath for 4 h. The reaction was then allowed to proceed at room temperature for 2 days. The crude product, which precipitated out of solution during this period, was collected by suction filtration and recrystallized from 95% ethanol, yielding 1.57 g (7.0 mmol, 21%) of 5,6-dichloroacenaphthene: mp 167.5–169.5° (lit.[25] mp 168–169°); NMR (CCl_4) δ 7.46 (d, 2 H, aromatic), 7.08 (d, 2 H, aromatic), 3.32 (s, 4 H); ir (KBr) 2920, 1850, 1600, 1570, 1410, 1350, 1330, 1260, 1230, 1110, 1025, 915, 870, 830, 810, 740, 720, 700 cm^{-1}.

Anal. Calcd for $C_{12}H_8Cl_2$: C, 64.60; H, 3.62; Cl, 31.78. Found: C, 64.48; H, 3.75; Cl, 32.00.

5,6-Dichloroacenaphthylene.[26] A solution containing 5.00 g (22.3 mmol) of 5,6-dichloroacenaphthene and 7.64 g (33.7 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 50 ml of benzene was refluxed for a period of 26 h. The reaction mixture was diluted with 100 ml of ligroin (bp 63–75°), filtered, passed through a column (10 × 1 cm) of Alcoa F-20 alumina, and evaporated in vacuo yielding 2.03 g (9.19 mmol, 41%) of a bright yellow solid. Recrystallization from 95% ethanol followed by sublimation (130°, 0.02 Torr) yielded 1.69 g (7.64 mmol, 34%) of pure 5,6-dichloroacenaphthylene: mp 163–164° (lit.[27] mp 162.5–163.5°); NMR (CCl_4) δ 7.58 (d, 2 H, aromatic), 7.42 (d, 2 H, aromatic), 6.90 (s, 2 H); ir (KBr) 3080, 1580, 1495, 1470, 1440, 1420, 1240, 1200, 1110, 1085, 1060, 1030, 900, 830, 745, 730, 640 cm^{-1}.

Anal. Calcd for $C_{12}H_6Cl_2$: C, 65.19; H, 2.74; Cl, 32.07. Found: C, 65.42; H, 2.64; Cl, 31.92.

Preparation and Isolation of Dimers. (A) Cis Dimer. A solution containing 1.09 g of 5,6-dichloroacenaphthylene in 150 ml of cyclohexane was irradiated for a period of 44 h with a 450-W Hanovia medium-pressure mercury arc lamp in a water-cooled Hanovia Vycor immersion vessel fitted with a uranium glass filter sleeve to absorb all radiation of wavelengths shorter than 325 nm. The water-cooled arc was immersed in the reaction vessel which was magnetically stirred. The solution was flushed with oxygen for 0.5 h prior to irradiation.

Following irradiation, the solution was filtered yielding 0.358 g of photoproduct. After two recrystallizations from benzene, 0.063 g of cis dimer was obtained: mp 315–317°; ir (KBr) 3040, 2940, 1600, 1565, 1410, 1330, 1235, 1210, 1110, 1065, 1035, 920, 820, 730, 670 cm^{-1}.

Anal. Calcd for $C_{24}H_{12}Cl_4$: C, 65.19; H, 2.74; Cl, 32.07. Found: C, 64.92; H, 2.83; Cl, 31.84.

(B) Trans Dimer. Solutions of 5,6-dichloroacenaphthylene in 10 mol % ethyl iodide[28] containing a total of 0.199 g of starting material were degassed with five freeze-pump-thaw cycles and irradiated on the merry-go-round apparatus previously described[26] for a period of 155 h.

Following irradiation, the solutions were combined and filtered yielding 0.071 g of photoproduct. Trituration of this product with boiling benzene produced 0.042 g of trans dimer: mp 354–356°; ir (KBr) 3040, 2940, 1600, 1570, 1415, 1350, 1330, 1265, 1230, 1210, 1110, 1040, 930, 865, 820, 730, 650 cm^{-1}.

Anal. Calcd for $C_{24}H_{12}Cl_4$: C, 65.19; H, 2.74; Cl, 32.07. Found: C, 65.25; H, 2.64; Cl, 32.02.

Ozonolysis of Cis Dimer. Ozone was bubbled at a rate of ~4 g/h through a suspension of 0.208 g of cis dimer in 100 ml of 90% aqueous acetic acid for 11 h at 20°. To the resulting clear solution was added 10 ml of 30% H_2O_2, and the reaction mixture was allowed to stand at room temperature with stirring for 4 days. Two additional 5-ml aliquots of H_2O_2 were added to the solution during this period at 36-h intervals. The solution was evaporated under reduced pressure, and the resulting residue was treated with an ethereal solution of diazomethane until a yellow color persisted. An NMR spectrum of the product contained singlets at δ 3.95 and 4.02, as did the NMR spectrum of an authentic sample of *cis,cis,cis*-1,2,3,4-tetracarbomethoxycyclobutane. Recrystallization of the product from benzene yielded 3.0 mg (2%) of the pure ester. The ir spectrum of this material was identical with that of an authentic sample.

Ozonolysis of Trans Dimer. Treatment of 0.107 g of the trans dimer with ozone, as described above, afforded a product with an NMR spectrum containing singlets of δ 3.80 and 3.75, as did the NMR spectrum of an authentic sample of *cis,trans,cis*-1,2,3,4-tetracarbomethoxycyclobutane. Attempts to recrystallize this product from benzene were unsuccessful. It was therefore not possible to obtain an ir spectrum of the pure ester.

Material Balance. For most of the determinations, the amount of isolated dimer accounts for more than 90% of the consumed starting material as determined by uv spectra. Those cases in which the material balance was less than 90% were randomly distributed, indicating that experimental error rather than the formation of new products was responsible for the discrepancies that occurred.

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References and Notes

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(4) Heavy-atom perturbation can alter either the quantum yield or the product distribution of a given photochemical reaction.

(5) For a recent study on internal heavy-atom effects on acenaphthylene cycloaddition to cyclopentadiene, see W. I. Ferree and B. F. Plummer, *J. Am. Chem. Soc.*, **95**, 6709 (1973).

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(7) The same method was used to successfully isolate the acenaphthylene dimers.

(8) Oxygen is known to be a very efficient quencher of triplet acenaphthylene.

(9) Since the solubilities of the cis and trans dimers of 5,6-dichloroacenaphthylene are sufficiently different, this criterion of purity is reasonable only in showing that each isomer is free of contamination by the other. Our conclusion that these dimers are relatively pure is based on their elemental analyses and their ir and uv spectra.

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(16) No attempt was made to ensure that the solution remained saturated

with oxygen throughout the entire irradiation period as was done in a similar experiment with acenaphthylene.[6] As a result, some triplet dimerization leading to the trans product may have occurred.

(17) For the purposes of discussion, Φ_{isc} is assumed to be 1.0. The linearity of the plot in Figure 4 indicates that Φ_{isc} remains relatively constant throughout the concentration range of ethyl iodide used. If Φ_{isc} is less than unity, a systematic error in our calculated rate constants will result, but the conclusions will not be affected.

(18) For a diffusion-controlled reaction, $k_q = 8RT/3000\eta$. The viscosity of cyclohexane was used in the calculation of this rate constant.

(19) This result is not unreasonable since Φ_{ST} for both the substituted and unsubstituted compounds should asymptotically approach unity at high concentrations of heavy-atom solvent. For acenaphthylene in 100 mol % ethyl iodide, $\Phi_{ST} = 0.81$.

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(21) The triplet dimerization efficiency for 5,6-dichloroacenaphthylene in cyclohexane is 0.078 (see Table IV). A value of 0.21[2h] was obtained for acenaphthylene under the same conditions.

(22) The quantum yield of dimerization of 5,6-dichloroacenaphthylene in air-saturated cyclohexane is 0.003 as compared to a value of 0.013 in degassed cyclohexane.

(23) The quantum yield of intersystem crossing, Φ_{isc}, is equal to the quantum yield of dimerization from the triplet state divided by the triplet dimerization efficiency, as given in eq 18, where the terms in the denominator have the same meaning as previously given. The triplet dimerization efficiency is given in Table IV. The value of $\Phi_D{}^1$ was assumed to be 0.010, the difference between Φ_D in degassed cyclohexane and air saturated cyclohexane.

$$\Phi_{isc} = \frac{\Phi_D{}^t}{k_2[A]/(k_2[A] + k_{cq}[A] + k''_{isc}[HA] + k_d + k_q[Q])} \qquad (18)$$

(24) (a) This same type of behavior was observed by Plummer for the cycloaddition of 5-bromoacenaphthylene to cyclopentadiene; see ref 5. (b) We have observed similar behavior in a preliminary study of 5,6-dibromoacenaphthylene. Quantum yields of 0.033, 0.011, and 0.0086 in cyclohexane, 10 mol % ethyl iodide-90 mol % cyclohexane, and ethyl iodide, respectively, were obtained indicating that $S_0 \leftarrow T_1$ is more sensitive than $T_1 \leftarrow S_1$ to internal heavy-atom perturbation when bromine is used.

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(26) (a) E. A. Braude, A. G. Brook, and R. P. Linstead, *J. Chem. Soc.*, 3569 (1954). (b) The reaction conditions for the dehydrogenation of acenaphthene as given by Braude were not optimized. The resulting reaction mixture contained both acenaphthylene and starting material which are very difficult to separate. We have found that by increasing the amount of quinone used to 1.5 equiv and by increasing the reaction time to 26 h, all of the starting material is consumed, thus eliminating this separation problem.

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(28) Cyclohexane was used as the cosolvent.

(29) A referee has commented that dimerization probably occurs through a stepwise reaction involving a dimeric triplet intermediate, $^3A_2$. Our data neither support nor disprove the existence of such an intermediate. If one replaces steps 5 and 6 of the mechanism in Chart II with the following,

$$^3A + A \xrightarrow{k_I} {}^3A_2,\ {}^3A_2 \xrightarrow{k_1} A_2, \text{ and } {}^3A_2 \xrightarrow{k_A} 2A$$

one obtains a mechanism which is kinetically indistinguishable from the one presented here. In the triplet intermediate mechanism, $k_I = k_2 + k_{cq}$ while k''_{isc} and k_d remain unchanged. Hence, this mechanistic choice does not alter the conclusions regarding the effects of heavy-atom perturbation.

Effect of ^{13}C–^{14}N Dipolar Interactions on Spin–Lattice Relaxation Times and Intensities of Nonprotonated Carbon Resonances

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Abstract: Spin-lattice relaxation times (T_1) and integrated intensities of the resonances in proton-decoupled natural-abundance ^{13}C Fourier transform NMR spectra of adenosine 5′-monophosphate and guanosine 5′-monophosphate (in H_2O and D_2O, at 40-44 °C, at 15.18 MHz, in 20-mm sample tubes) are compared with calculated values that take into account ^{13}C-^1H and ^{13}C-^{14}N dipolar relaxation. In each case, T_1 values of methine carbons of the base were used to obtain a rotational correlation time, which was then used, together with interatomic distances from crystallographic data, to compute T_1 values of nonprotonated carbons. Nonprotonated carbons which are directly bonded to nitrogens and which have no hydrogens two bonds removed yield theoretical T_1 values strongly affected by ^{13}C-^{14}N dipolar interactions. For carbons in this category, calculated T_1 values which include ^{13}C-^{14}N dipolar interactions are in much better agreement with experimental values than calculated values which consider only ^{13}C-^1H interactions. Integrated intensities were calculated by considering variations in the nuclear Overhauser enhancement that result from differences in relative contributions to $1/T_1$ from ^{13}C-^1H and ^{13}C-^{14}N dipolar relaxation. The calculated intensities are in excellent agreement with the experimental ones.

Measurements of ^{13}C spin-lattice relaxation times (T_1) of protonated carbons have yielded detailed information about overall rotation and internal motions of large molecules in solution.[1-4] The interpretation of T_1 values of protonated carbons of large molecules is relatively simple, because the relaxation of such carbons is overwhelmingly dominated by ^{13}C-^1H dipole-dipole interactions with the directly bonded hydrogens.[2] The contribution of dipole-dipole relaxation to $1/T_1$ is proportional to the inverse of the sixth power of the distance (r) between the nuclei involved. Values of r^{-6} are about 60 times greater for directly bonded C-H groups ($r \approx 1.09$ Å) than for the closest nonbonded C-H interactions.[5] Therefore, in general, the T_1 values of nonprotonated carbons are much longer than those of protonated ones.[2] One must investigate the possibility that contributions from relaxation mechanisms other than the ^{13}C-^1H dipolar one can be significant for nonprotonated carbons. There is evidence[2] that the lone nonprotonated carbon of sucrose (in H_2O) and the three nonprotonated carbons of cholesteryl chloride (in CCl_4) exhibit only ^{13}C-^1H dipolar relaxation at a resonance frequency of 15.1 MHz. On the other hand, there is also evidence[2,6] that mechanisms other than the ^{13}C-^1H dipolar one contribute significantly to the relaxation of two of the three nonprotonated carbons of adenosine 5′-monophosphate (AMP) in H_2O.

A knowledge of the relative importance of various contributions to the relaxation of nonprotonated carbons will facilitate the use of ^{13}C T_1 values for making spectral assignments,[7] and the use of integrated intensities of nonprotonated carbon resonances for making carbon counts and for quantitative analysis. Carbon-13 NMR spectra of large molecules are nearly always recorded under conditions of proton decoupling, in order to remove complex splitting pat-