

Photochemical Heavy-Atom Effects¹

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Transitions between pure spin states of different multiplicity are forbidden by the spin selection rule. There are, however, numerous examples in the literature of spin-forbidden or intercombinational transitions occurring in organic molecules. The occurrence of such transitions results from spin-orbit coupling, a relativistic phenomenon which induces a quantum mechanical mixing of states of different multiplicity. Thus, the spin states involved in an intercombinational transition are not pure states, but possess a small admixture of states of other multiplicities.² Qualitatively, spin-orbit coupling arises from the interaction of the spin magnetic moment of an electron and the magnetic field resulting from the apparent motion of the nucleus.³ Since the magnitude of the nuclear magnetic field is directly proportional to the nuclear charge and hence to the atomic number, spin-orbit coupling increases with increasing atomic number. Consequently, large increases in the rates of spin-forbidden radiative and radiationless transitions are often observed for molecules in the presence of atoms of high atomic number.⁴ This phenomenon, which has been extensively studied in recent years, is known as the heavy-atom (H-A) effect.

The presence of heavy atoms may influence both photophysical and photochemical processes in a molecule. For the purpose of discussion, a photophysical H-A effect is defined as one in which only photophysical processes are affected. A photochemical H-A effect is then defined as one in which changes in the photochemistry of the substrate are observed. In the latter case, changes in photophysical processes often occur as well.

The discovery of photophysical H-A effects predated that of photochemical H-A effects by nearly 20 years. The first example of the former was reported by McClure in 1949. McClure's work involved an attempt to correlate the phosphorescence lifetime of various H-A substituted (internal H-A effect) aromatic compounds in rigid matrices (77 K) with the spin-orbit coupling parameter, ξ , of the heavy atom. Although the quantitative results of this study were not good, McClure did observe a significant decrease in the phosphorescence lifetime, τ , of the compounds being investigated as the atomic number of the H-A substituent was increased.⁵ Further work by Ermolaev and Svitashv and later LaPaglia on the substrates originally investigated by McClure has revealed that in-

creases in the atomic weight of the H-A substituent not only produce a decrease in the triplet lifetime but also increase the ratio of the phosphorescence and fluorescence quantum yields, Φ_P/Φ_F .^{6,7} An analysis of these data by Birks has indicated that the observed decrease in phosphorescence lifetime results from increases in both the rate of phosphorescence and the rate of intersystem crossing for $T_1 \rightarrow S_0$. The increase in Φ_P/Φ_F on the other hand results from an increase in the rate of intersystem crossing for $S_1 \rightarrow T_1$.⁸ Thus internal heavy atoms appear to have a significant effect on both the rate of population of the triplet state and the rate of triplet decay.

Kasha was the first to suggest that fluorescence quenching of aromatic compounds in solution in the presence of alkyl halides was due to an increase in spin-orbit coupling resulting from collisional or external H-A perturbation.⁹ McGlynn later corroborated Kasha's results in a study on the external H-A perturbation of naphthalene in solid solutions at 77 K. Interestingly, McGlynn found that, while the rate of $S_1 \rightarrow T_1$ and phosphorescence increased with increasing atomic number of the solvent halogen substituent, little effect was observed on the rate of $T_1 \rightarrow S_0$.¹⁰ Clearly then, internal and external H-A perturbations do not manifest themselves in the same manner.

Although photophysical H-A effects are now well documented, reports of photochemical H-A effects have only recently grown to a respectable number. An early attempt by Wagner to observe an external H-A effect on the type II photoelimination of aliphatic ketones was unsuccessful.¹¹ It was concluded that this lack of H-A sensitivity resulted from the large spin-orbit coupling that is already inherent in the carbonyl group.¹² Subsequent studies on other compounds, however, have proven to be more fruitful.

(1) Photochemical Reactions. 15. For part 14, see J. C. Koziar and D. O. Cowan, *J. Am. Chem. Soc.*, **98**, 1001 (1976).

(2) (a) D. O. Cowan and R. L. Drisko, "Elements of Organic Photochemistry", Plenum Press, New York, N.Y., 1976, pp 250-262; (b) N. J. Turro, "Molecular Photochemistry", W. A. Benjamin, New York, N.Y., 1967, pp 27-29; (c) S. P. McGlynn, T. Azumi, and M. Kinoshita, "The Triplet State", Prentice-Hall, Englewood Cliffs, N. J., 1969, pp 183-284.

(3) I. N. Levine, "Quantum Chemistry", Vol. I, Allyn and Bacon, Boston, Mass., 1970, pp 306-310.

(4) (a) S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966); (b) M. A. El-Sayed, *Acc. Chem. Res.*, **1**, 8 (1968).

(5) (a) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949); (b) the spin-orbit coupling parameter is calculated from atomic spectral data; see ref 3 for the analytical expression for ξ .

(6) V. L. Ermolaev and K. K. Svitashv, *Opt. Spectrosc.*, **1**, 899 (1959).

(7) S. R. LaPaglia, *J. Mol. Spectrosc.*, **7**, 427 (1961).

(8) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, N.Y., 1970, pp 264-265.

(9) M. Kasha, *J. Chem. Phys.*, **20**, 71 (1952).

(10) S. P. McGlynn, M. J. Reynolds, G. W. Daigre, and N. D. Christodoyles, *J. Phys. Chem.*, **66**, 2499 (1962).

(11) P. J. Wagner, *J. Chem. Phys.*, **45**, 2335 (1966).

(12) M. A. El-Sayed, *J. Chem. Phys.*, **41**, 2464 (1964).

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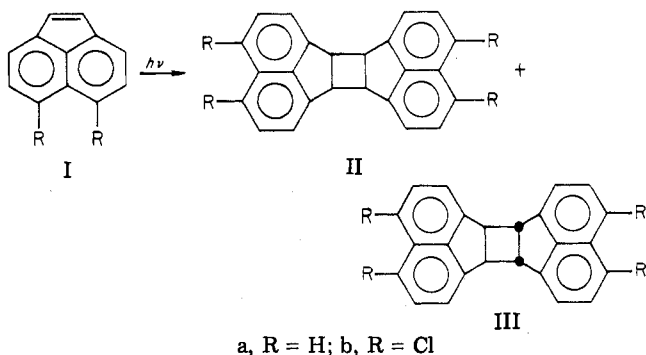
Table I
Dimerization of Acenaphthylene in the Presence of Heavy-Atom Solvents¹⁷

solvent ^a	solvent concn, mol %	dimer yield, g		
		cis	trans	total
cyclohexane	100	5.4	1.1	6.5
<i>n</i> -butyl chloride	100	5.0	2.1	7.1
<i>n</i> -propyl bromide	10	2.5	3.4	5.9
	25	3.0	5.0	8.0
	50	3.5	7.5	11.0
ethyl iodide	100	4.1	10.0	14.1
	5	2.0	8.4	10.4
	10	2.8	11.0	13.8
ethylene dibromide	10	1.8	4.3	6.1
carbon tetrachloride	100	2.8	2.7	5.5

^a Cyclohexane was used as a cosolvent in all cases in which the heavy-atom solvent concentration was less than 100 mol %.

Dimerization of Acenaphthylene

The presence of H-A solvents was shown by Cowan and Drisko to have a significant influence on the photochemistry of acenaphthylene (Ia), thus providing



one of the first examples of a photochemical H-A effect.^{13,14} Acenaphthylene is known to dimerize from both the first excited singlet state (S_1) and the first excited triplet state (T_1). Dimerization from T_1 yields the trans dimer as the major product, whereas dimerization from S_1 affords the cis dimer exclusively. In light-atom (L-A) solvents in which the transition $S_1 \rightarrow T_1$ is relatively inefficient ($\Phi_{isc} \approx 0.02^{15}$), the cis dimer predominates since dimerization occurs primarily from S_1 .¹⁶ In contrast, irradiation of acenaphthylene in the presence of various concentrations of H-A solvents such as propyl bromide and ethyl iodide resulted in a shift in the product distribution favoring the triplet-derived trans dimer. Both the proportion of trans dimer and the total dimer yield increased with increasing H-A solvent concentration. This behavior was attributed to an acceleration in the rate of $S_1 \rightarrow T_1$ resulting from external H-A perturbation.

Some of the results of this study are presented in Table I. These data indicate that both the atomic weight of the H-A perturber and the concentration of H-A solvent have a significant influence on the photochemistry of acenaphthylene. Interestingly, a comparison of the data for butyl chloride and propyl bromide with that for carbon tetrachloride and ethylene dibromide, respectively, suggests that the number of

Table II
Comparison of Trans Dimer Ratio with the Ratio of the Squares of the Spin-Orbit Coupling Parameters¹⁷

solvents ^a	ξ_{HA}^2/ξ_I^2	trans(HA)/trans(I) ^d
ethyl iodide	1	1
<i>n</i> -propyl bromide ^b	0.24	0.24
neopentyl bromide ^b	0.24	0.29
neopentyl bromide ^c	0.24	0.20
bromobenzene ^b	0.24	0.17
<i>n</i> -butyl chloride ^b	0.014	0.01

^a Heavy-atom solvent concentrations are either 5 or 10 mol % with cyclohexane as the cosolvent; the trans dimer obtained in each solvent is compared to the trans dimer obtained in the corresponding concentration of ethyl iodide. ^b 10 mol % heavy-atom solvent. ^c 5 mol % heavy-atom solvent. ^d Corrected for the amount of trans dimer formed in pure cyclohexane.

heavy atoms bonded to a perturbing molecule is also an important factor.

As evidence that spin-orbit coupling induced by the H-A solvent was responsible for the photochemical changes observed, Cowan and Drisko attempted to make a correlation between the spin-orbit coupling parameter, ξ , and the yield of trans dimer.¹⁷ There are two ways in which the external heavy atom can exert an influence on the spin-orbit coupling of the states:^{2,4} (1) direct coupling by means of penetration of the π -electron orbitals on the acenaphthylene molecule into the region of heavy-atom potential (collision complex)

$$k_{isc} \propto \langle {}^3A | H_{so} | {}^1A \rangle^2 \quad (1)$$

or (2) indirect coupling that involves mixing of the solvent wave functions with the acenaphthylene wave functions

$$k_{isc} \propto \frac{\langle {}^1A | H' | \psi_{sol}^a \rangle^2 \langle \psi_{sol}^a | H_{so} | \psi_{sol}^b \rangle^2 \langle \psi_{sol}^b | H'' | {}^3A \rangle^2}{(\Delta E_a \Delta E_b)^2} \quad (2)$$

where 1A and 3A represent the acenaphthylene wave functions, ψ the solvent wave functions, H' and H'' could be electron repulsion or vibronic operators, and H_{so} is the spin-orbit coupling operator.

For simple model systems this operator has the form

$$H_{so} \propto \xi(L \cdot S) \quad (3)$$

where L and S are the orbital and spin angular momentum operators and ξ is the spin-orbit coupling constant. If everything else remains constant, it is seen that the probability for intersystem crossing is related to the square of the spin-orbit coupling constant for both mechanisms. Thus in comparing the transition probabilities P_1 and P_2 in the presence of two different heavy atoms with coupling parameters ξ_1 and ξ_2 , the relationship given by eq 4 is obtained assuming that the

$$\frac{P_1}{P_2} = \frac{\xi_1^2}{\xi_2^2} \quad (4)$$

total perturbation results from the heaviest atom in the perturbing molecule. Since the yield of trans dimer is proportional to the transition probability of $S_1 \rightarrow T_1$, the ratio of trans dimer in two H-A solvents should equal the ratio of the squares of the coupling parameters of the heaviest atoms in those solvents. The

(13) D. O. Cowan and R. L. Drisko, *Tetrahedron Lett.*, 1255 (1967).

(14) D. O. Cowan and R. L. Drisko, *J. Am. Chem. Soc.*, **89**, 3068 (1967).

(15) D. O. Cowan and J. C. Koziar, *J. Am. Chem. Soc.*, **97**, 249 (1975).

(16) D. O. Cowan and R. L. Drisko, *J. Am. Chem. Soc.*, **92**, 6286 (1970).

(17) D. O. Cowan and R. L. Drisko, *J. Am. Chem. Soc.*, **92**, 6281 (1970).

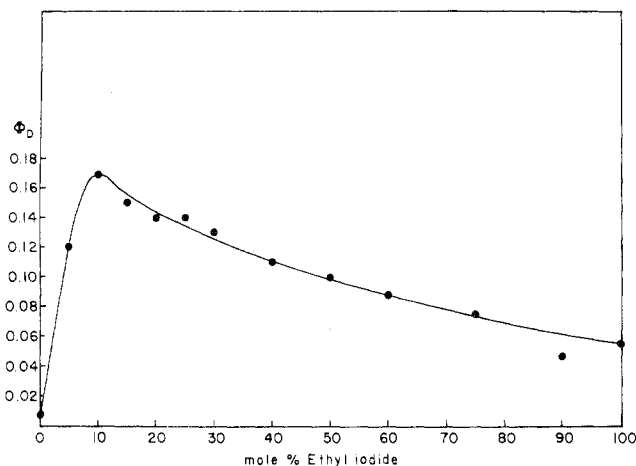


Figure 1. The dependence of Φ_D on the concentration of ethyl iodide.

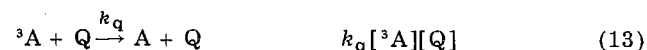
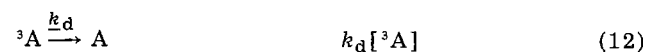
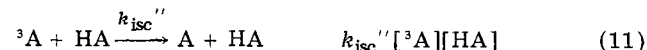
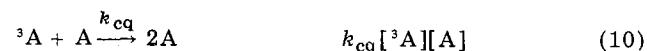
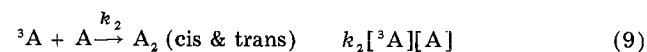
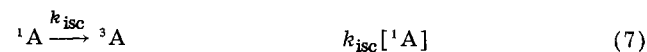
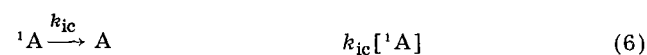
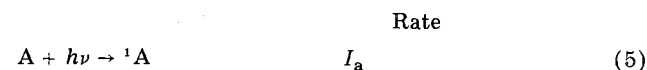
results of this correlation, which are given in Table II, were quite good.

This early work suggested that external H-A perturbation influenced the transition $S_1 \rightarrow T_1$ to a much greater extent than any of the remaining intercombinational transitions of acenaphthylene. Clearly the absence of new absorption bands and the absence of phosphorescence precluded any significant effect on direct absorption to the triplet or radiative decay of the triplet state.¹⁷ In order to arrive at more definitive conclusions concerning the other intercombinational transitions, a more quantitative study was undertaken.

Irradiation of acenaphthylene in various brominated solvents indicated that large increases in the quantum yield of dimerization (Φ_D) could be obtained under appropriate conditions.^{17,18} It was recognized, however, that if the behavior of acenaphthylene in H-A solvents was due entirely to an increase in $S_1 \rightarrow T_1$, then Φ_D must have an asymptotic limit at which the quantum yield for intersystem crossing (Φ_{isc}) approaches unity. Once this limit is reached, further increases in external H-A perturbation should have no effect on Φ_D unless other intercombinational transitions are being influenced. To establish the limiting value of Φ_D and to examine the possible influence of H-A solvents on other less sensitive transitions, the dimerization of acenaphthylene was studied in the highly perturbing solvent ethyl iodide.

As expected, the quantum yield of dimerization was found to increase dramatically in going from 0 to 10 mol % ethyl iodide using cyclohexane as a co-solvent. In contrast, further increases in the concentration of ethyl iodide resulted in a gradual decrease in Φ_D , as indicated in Figure 1. This behavior suggested that at least two competing processes were being affected by the H-A solvent. At low concentrations of ethyl iodide in which $\Phi_{isc} \ll 1.0$, $S_1 \rightarrow T_1$ is the transition most sensitive to H-A perturbation, thus resulting in a large increase in Φ_D . At high concentrations of ethyl iodide in which $\Phi_{isc} \approx 1.0$, H-A effects on the less sensitive transition $T_1 \rightarrow S_0$ become significant, and Φ_D is gradually reduced.¹⁹ The fact that $S_1 \rightarrow T_1$ is considerably more sensitive than $T_1 \rightarrow S_0$ to external perturbation is consistent with earlier photophysical studies previously discussed.

The behavior of acenaphthylene at high concentrations of ethyl iodide allows one to use this solvent as a mechanistic probe. For example, the simplified mechanism given by eq 5-13 has been proposed for the



dimerization of acenaphthylene. In the above mechanism A = acenaphthylene, A_2 = acenaphthylene dimer, HA = ethyl iodide, and Q = triplet quencher (ferrocene in this study). By utilizing the steady-state approximation, one arrives at the following expression for Φ_D .

$$\Phi_D = \Phi_{isc} \frac{k_2[A]}{k_2[A] + k_q[Q] + k_{cq}[A] + k_d + k_{isc}''[HA]} \quad (14)$$

At high concentrations of ethyl iodide, $\Phi_{isc} \approx 1.0$, and one then obtains the following relationships for Φ_D^{-1} .

$$\frac{1}{\Phi_D} = \frac{k_2[A] + k_{cq}[A] + k_d + k_q[Q]}{k_2[A]} + \frac{k_{isc}''[HA]}{k_2[A]} \quad (15)$$

$$\frac{1}{\Phi_D} = \frac{k_2 + k_{cq}}{k_2} + \frac{k_d + k_q[Q] + k_{isc}''[HA]}{k_2} \frac{1}{[A]} \quad (16)$$

These equations indicate that $1/\Phi_D$ is a linear function of both $[HA]$ and $[A]^{-1}$. Plots of the appropriate data yielded linear relationships as predicted. As also predicted by the above mechanism, a linear Stern-Volmer plot for the dimerization of acenaphthylene was obtained.

These data not only lend credence to the proposed mechanism but also allow one to calculate the triplet lifetime τ of acenaphthylene and the rate constants for dimerization, k_2 , concentration quenching, k_{cq} , unimolecular decay, k_d , and intersystem crossing to the ground state, k_{isc}'' . These values, which are presented in Table III,²⁰ would not have been readily accessible in the absence of H-A perturbation. Although singlet dimerization is relatively inefficient, it is nonetheless competitive with triplet dimerization in L-A solvents due to the low value of Φ_{isc} .¹⁵ In order to separate these

(18) D. O. Cowan and J. C. Koziar, unpublished results.

(19) D. O. Cowan and J. C. Koziar, *J. Am. Chem. Soc.*, **96**, 1229 (1974).

(20) J. C. Koziar and D. O. Cowan, *J. Am. Chem. Soc.*, **98**, 1001 (1976).

Table III
Triplet Lifetimes and Rate Constants for
Acenaphthylene and 5,6-Dichloroacenaphthylene²⁰

	Acenaphthylene	5,6-Dichloroacenaphthylene
τ , s	2.2×10^{-6}	6.6×10^{-7}
k_2 , $M^{-1} s^{-1}$	6.6×10^5	9.1×10^5
k_{cqq} , $M^{-1} s^{-1}$	1.6×10^6	4.0×10^6
k_d , s^{-1}	9.2×10^4	6.8×10^5
k_{isc} , $M^{-1} s^{-1}$	6.7×10^4	1.5×10^5

two modes of dimerization, the use of a triplet sensitizer would be required, thus introducing the possibility of additional photochemical reactions. Since the H-A solvent if properly chosen is not an absorbing species, the possibility of side reactions is greatly reduced. Furthermore, the presence of a triplet sensitizer would have rendered the determination of the Stern-Volmer plot, which was necessary in the subsequent calculations of the rate constants, extremely difficult. The use of H-A solvents thus provides a convenient and simple mechanistic probe for compounds which undergo relatively inefficient intersystem crossing and which may react from more than one excited state. While this technique has not as yet been extensively utilized, there is little doubt that many systems would be amenable to this approach.

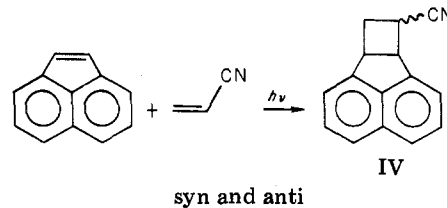
Since photophysical studies have indicated that internal H-A perturbation does not affect the various intercombinational transitions of a compound to the same relative degree as does external perturbation, an examination of the photochemistry of 5,6-dichloroacenaphthylene (Ib) was subsequently undertaken. As one might predict, the photochemistry of the halogenated compound was analogous to that of acenaphthylene. Similar kinetic data were obtained which allowed for the determination of the triplet lifetime and various intercombinational rate constants presented in Table III. Not surprisingly, the product distributions for 5,6-dichloroacenaphthylene were to within experimental error also identical with those obtained for the parent compound under corresponding conditions. The sensitivity of Φ_D of the halogenated substrate to external H-A perturbation was, however, significantly different.

Although the dimerization quantum yield of 5,6-dichloroacenaphthylene in cyclohexane was, as expected, greater than that of the parent compound under the same conditions, the maximum value of Φ_D for the halogenated substrate obtained in 10 mol % ethyl iodide was found to be less than half that of acenaphthylene. This behavior clearly indicates that internal perturbation does not affect the various intercombinational transitions of acenaphthylene in the same manner as does external perturbation. The following interpretation is consistent with both the results of this study and with those of earlier photophysical studies. Both internal and external heavy atoms appear to have a very large effect on $S_1 \rightarrow T_1$. While external heavy atoms also produce a small but significant increase in the rate of $T_1 \rightarrow S_0$, internal heavy atoms have a considerably larger effect on this transition. As a result, the rates of intersystem crossing and triplet decay to the ground state are much more competitive in the presence of internal H-A perturbation.²⁰ Thus, under conditions in which internal and external perturbations are comparable, H-A substitu-

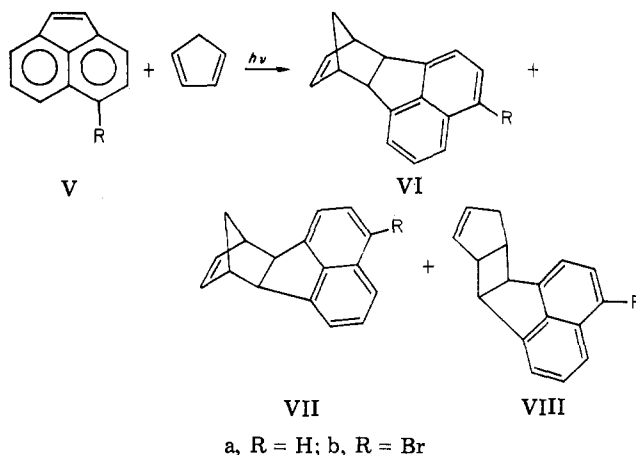
ents lead to a reduced quantum yield of dimerization.

Cycloaddition Reactions of Acenaphthylene

Cycloaddition reactions of acenaphthylene to a number of olefins have also been shown to be susceptible to H-A perturbation. Plummer first demonstrated that the rate of cycloaddition of acenaphthylene to acrylonitrile dramatically increased in the presence of various halogenated solvents.²¹



One of the most extensively studied reactions involved the cycloaddition of acenaphthylene to cyclopentadiene in which endo and exo [4 + 2] adducts as well as a single [2 + 2] adduct are formed. In this



study, as much as a 50-fold increase in the quantum yield of cycloaddition (Φ_r) was obtained in going from cyclohexane to dibromoethane.^{22,23}

As was observed in acenaphthylene dimerization, substitution of a heavy atom directly onto the substrate significantly altered the sensitivity of acenaphthylene to external perturbation. Although Φ_r of 5-bromoacenaphthylene was approximately 5 times larger than that of the parent compound in cyclohexane, the quantum yield was significantly smaller than that of acenaphthylene in H-A solvents.²⁴

Plummer originally rationalized the behavior of this reaction in a manner essentially the same as that presented for the dimerization of acenaphthylene. A detailed mechanistic study of both acenaphthylene and 5-bromoacenaphthylene has verified this conclusion.^{23,24}

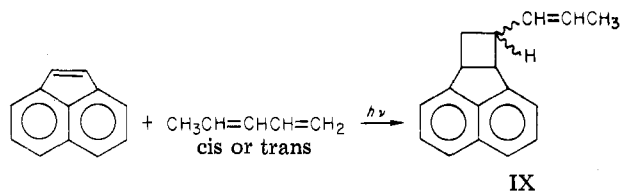
The rate of cycloaddition of acenaphthylene to *cis*- or *trans*-1,3-pentadiene is also enhanced in the presence of H-A solvents. Unlike cyclopentadiene, these acyclic olefins yielded exclusively [2 + 2] adducts, with the major products resulting from reaction with the terminal double bond of the olefin. As with the earlier examples, large increases in Φ_r of up to 40-fold were

(21) B. F. Plummer and R. A. Hall, *Chem. Commun.*, 44 (1970).

(22) B. F. Plummer and D. M. Chihal, *J. Am. Chem. Soc.*, **93**, 2071 (1971).

(23) W. I. Ferree, Jr., and B. F. Plummer, *J. Am. Chem. Soc.*, **95**, 6709 (1973).

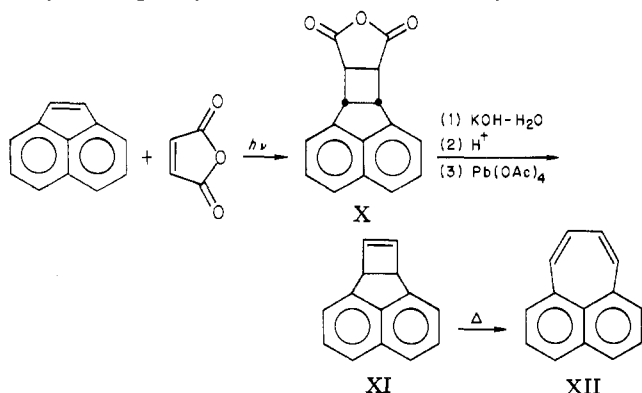
(24) B. F. Plummer and W. I. Ferree, Jr., *J. Chem. Soc., Chem. Commun.*, 306 (1972).



obtained in H-A solvents.²⁵

One of the more interesting examples of the photochemical H-A effect involved a study by Meinwald in which external H-A perturbation was used to induce the cycloaddition of acenaphthylene to maleic anhydride. This work is particularly significant in that the adduct (anti isomer) was used as an intermediate in the synthesis of pleiadiene, thus providing the first example of a synthetic utilization of the H-A effect. Although pleiadiene is obtainable by other routes, the H-A assisted photochemical procedure afforded a 4-fold increase in the final yield.²⁶

The synthetic utility of this reaction led to detailed studies by a number of other workers. While attempts to induce the cycloaddition in L-A solvents have yielded only acenaphthylene dimers and a copolymer, irradi-



ation of acenaphthylene and maleic anhydride in various halogenated solvents afforded both the desired adduct and L-A solvent products. Furthermore, the adduct yield was found to increase proportionally with the atomic number of the halogen in the solvent at the expense of the other products.²⁷ The anti adduct of citraconic anhydride has also been prepared in H-A solvents. Attempts to synthesize the adduct from dimethylmaleic anhydride under a variety of conditions, however, were unsuccessful.²⁸

The success in the use of H-A solvents in synthesizing this adduct suggested the possibility of incorporating a heavy atom into one of the addends. The irradiation of acenaphthylene in the presence of several halogenated maleic anhydrides was therefore examined. Although adducts were obtained in halogenated solvents, the cycloaddition failed to proceed in the presence of L-A solvents, presumably because the concentrations of the halogenated maleic anhydrides were not sufficient to induce significant external H-A perturbation.^{28,29}

(25) W. I. Ferree, Jr., B. F. Plummer, and W. W. Schloman, *J. Am. Chem. Soc.*, **96**, 7741 (1974).

(26) J. Meinwald, G. E. Samuelson, and M. Ikeda, *J. Am. Chem. Soc.*, **92**, 7604 (1970).

(27) W. Hartmann and H.-G. Heine, *Angew. Chem., Int. Ed. Engl.*, **10**, 272 (1971).

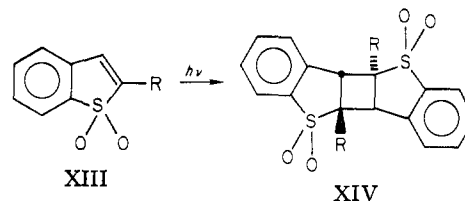
(28) J. E. Shields, D. Gavrilovic, J. Kopecky, W. Hartmann, and H.-G. Heine, *J. Org. Chem.*, **39**, 515 (1974).

(29) J. E. Shields, D. Gavrilovic, and J. Kopecky, *Tetrahedron Lett.*, **271** (1971).

Cycloaddition Reactions of Other Substrates

Although acenaphthylene has received a great deal of attention, other substrates have been found to be susceptible to photochemical H-A effects. For example, the quantum yield for the formation of the 2:1 adduct of maleic anhydride and benzene increased significantly in the presence of methylene bromide. Sensitized irradiation indicated that this effect was due to an increase in S₁ → T₁ of the excited-state precursor leading to the intermediate 1:1 adduct.³⁰

The dimerization of thianaphthene 1,1-dioxide (XIIIa) is susceptible to both internal and external H-A

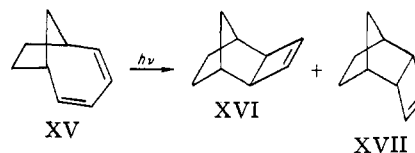


a, R = H; b, R = Br

perturbation. H-A effects on this compound differed somewhat from those observed for acenaphthylene.³¹ In the parent compound, the rate of T₁ → S₀, as well as that of S₁ → T₁, was increased in the presence of ethyl bromide. Furthermore, the relative H-A effect on the dimerization of thianaphthene 1,1-dioxide was smaller than that obtained for acenaphthylene under corresponding conditions. Studies of the dimerization of 2-bromothianaphthene 1,1-dioxide (XIIIb) have indicated that internal and external perturbation do have the same relative effect on S₁ → T₁ and T₁ → S₀ as were observed for acenaphthylene.³²

Electrocyclic Rearrangements and Related Reactions

Recent studies have indicated that a number of electrocyclic rearrangements are affected by the presence of heavy atoms. Bicyclo[4.2.1]nona-2,4-diene (XV) isomerizes photochemically to *exo*- and *endo*-



tricyclo[4.2.1.0^{2,5}]non-3-enes, with a product distribution containing 30% of the *exo* isomer, XVI, and 70% of the *endo* isomer, XVII. Examination of a series of chloro derivatives indicated a dramatic change in the product distribution, with the percent *exo* isomer increasing with increasing chlorine substitution. Product distributions were found to be approximately the same for the entire series under sensitized conditions and were quite similar to those obtained for the di- and tri-substituted compounds. It was concluded that the substitution of chlorines increased the rate of inter-system crossing of the diene, leading to isomerization from both the singlet and triplet states. When sufficient

(30) D. Bryce-Smith, R. R. Deshpande, and A. Gilbert, *Tetrahedron Lett.*, 1627 (1975).

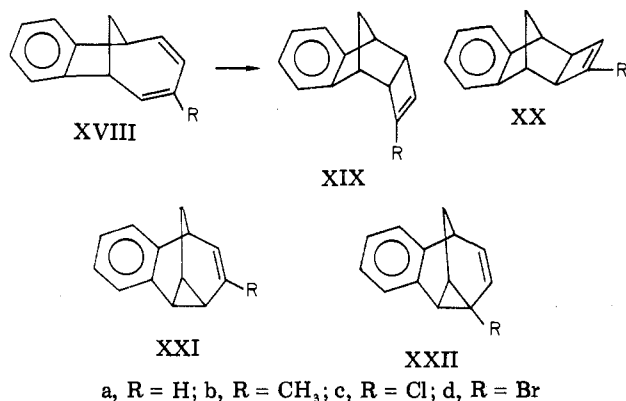
(31) W. W. Schloman and B. F. Plummer, *J. Chem. Soc., Chem. Commun.*, 705 (1974).

(32) W. W. Schloman and B. F. Plummer, *J. Am. Chem. Soc.*, **98**, 3254 (1976).

perturbation is present, as in the case of the di- and trisubstituted derivatives, isomerization appears to result predominantly from the triplet state. Direct irradiation of the parent compound in the presence of ethyl iodide also led to a significant increase in the amount of *exo* isomer formed, indicating that this substrate is susceptible to external as well as internal H-A perturbation. In contrast, the presence of ethyl bromide had little effect on the product distribution.³³

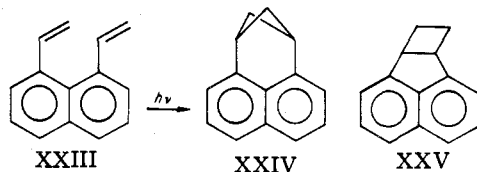
Internal H-A perturbation has a significant effect on the photorearrangement of benzo[7,8]bicyclo[4.2.1]nona-2,4,7-trienes (XVIII). Although the strikingly different product distributions obtained for XVIIIa,b and XVIIIc,d, presumably resulting from steric and polar effects, render the analysis of this system somewhat difficult, the data strongly suggest a change in the multiplicity of the excited-state intermediate in going from XVIIIa,b to XVIIId apparently resulting from an internal H-A effect.

Both XVIIIa and XVIIIb yield the di- π -methane rearrangement products and cyclobutenes upon direct irradiation. Additional experimental data indicate that



these reactions occur from the excited singlet state. Photorearrangement of XVIIIc,d by either direct or sensitized conditions yielded the cyclobutenes as the sole products. In the case of the 3-bromo derivative, the product distributions for direct and sensitized irradiation were essentially the same, suggesting that isomerization during direct irradiation occurred via the triplet state.³⁴

The internal dimerization of the vinyl moieties of 1,8-divinylnaphthalene (XXIII) has also been shown to be subject to H-A perturbation. The presence of



bromocyclopropane was found to produce a decrease in the fluorescence quantum yield of the starting material with a concomitant increase in the rate of triplet derived product formation. This behavior clearly suggests that the H-A solvent produces an increase in $S_1 \rightarrow T_1$. Virtually no effect was observed on $T_1 \rightarrow S_0$, consistent with most of the results obtained in other studies.³⁵

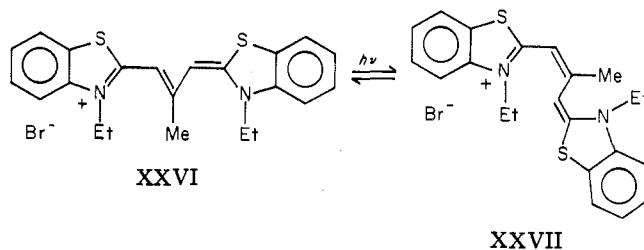
(33) C. W. Jefford and F. Delay, *J. Am. Chem. Soc.*, **97**, 2272 (1975).

(34) R. C. Hahn and R. P. Johnson, *J. Am. Chem. Soc.*, **97**, 212 (1975).

(35) R. H. Fleming, F. H. Quinn, and G. S. Hammond, *J. Am. Chem. Soc.*, **96**, 7738 (1974).

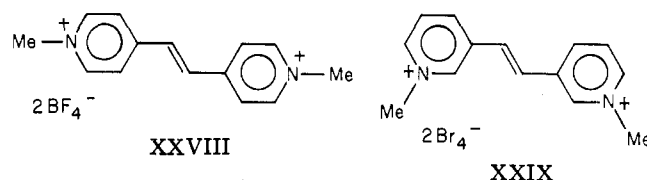
Photochemical Cis-Trans Isomerizations

H-A effects on photoisomerization reactions illustrates further the scope of this phenomenon. The rate of cis-trans isomerization of 3,3'-diethyl-9-methyl-



thiacarbocyanine bromide in EPA (ethyl ether, isopentane, and ethanol 5:5:2 by volume) matrices at -125°C was found to increase significantly in the presence of ethyl halides. As predicted, the triplet isomerization rate increased with both the H-A solvent concentration and the atomic weight of the halogen. Furthermore, the presence of ethyl iodide increased the rate of $T_1 \rightarrow S_0$ as well as that of intersystem crossing leading to the triplet state. Consistent with earlier results, the presence of ethyl chloride and ethyl bromide appeared to have little effect on the triplet lifetime. The photoisomerization of this cyanine dye was also shown to be sensitive to internal H-A perturbation. Examination of the selenium and oxygen analogues indicated that the rate of photoisomerization increased in the following order: $\text{O} < \text{S} < \text{Se}$.³⁶

Isomerization of the dimethyl fluoroborates of *trans*-1,2-bis(4-pyridyl)ethylene (XXVIII) and *trans*-1,2-bis(3-pyridyl)ethylene (XXIX) has also been shown to be subject to external H-A perturbation. While direct irradiation of XXVIII and XXIX in degassed aceto-



nitrile solutions led to little or no reaction, air-equilibrated solutions yielded very rapid isomerization. These results, which indicated that the presence of oxygen induced intersystem crossing to the triplet state from which isomerization occurred, suggested that this system might be susceptible to H-A effects. Although direct irradiation of XXVIII in degassed acetonitrile solutions containing organic halides led to complex and unusual behavior, XXIX isomerized quite rapidly with concurrent fluorescence quenching.^{37,38}

The isomerization of stilbene is susceptible to both internal and external H-A effects.^{39,40} The presence of bromine in the para position of one of the benzene rings of stilbene greatly enhances intersystem crossing to the triplet state. Substitution of bromine in the meta position, however, had little effect on this intercombinational transition. This positional dependence

(36) W. Cooper and K. A. Rome, *J. Phys. Chem.*, **78**, 16 (1974).

(37) A. R. Gutierrez and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 7128 (1974).

(38) A. R. Gutierrez and D. G. Whitten, *J. Am. Chem. Soc.*, **98**, 6233 (1976).

(39) J. Saltiel, D. Chang, and E. D. Megarity, *J. Am. Chem. Soc.*, **96**, 6521 (1974).

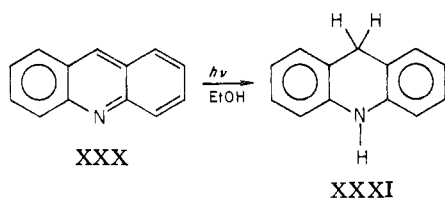
(40) G. Fischer, K. A. Muszkat, and E. Fischer, *Isr. J. Chem.*, **6**, 965 (1968).

appears to be related to the difference between the meta and para coefficients of the highest occupied and lowest unoccupied molecular orbitals of stilbene. In the Hückel approximation, $C_{\text{meta}} = 0.0791$ and $C_{\text{para}} = 0.3138$. The same positional dependence was observed for H-A effects on $T_1 \rightarrow S_0$.³⁹

Although H-A solvents are generally employed to promote facile intersystem crossing to the triplet state following singlet absorption, a rare case was reported in which H-A perturbation was used to enhance the excitation of stilbene directly to the triplet state. In the presence of either methyl iodide or ethyl iodide, irradiation at the appropriate wavelength led to direct absorption to the stilbene triplet, yielding a cis-trans isomerization rate 10-fold greater than that obtained in L-A solvents.⁴⁰

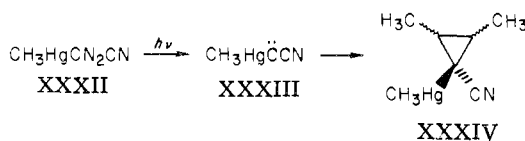
Further Examples

The photoreduction of acridine provides an unusual example of H-A effects on a singlet reaction. In the



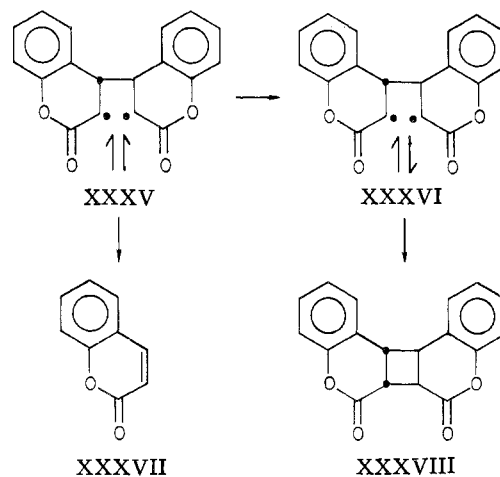
presence of NaI, the rate of photoreduction was found to decrease by an amount corresponding to the decrease in fluorescence under the same conditions. Triplet quenchers and sensitizers had no effect on the photoreduction, clearly suggesting a singlet process. Flash photolysis studies further confirmed the singlet nature of the reactive species by demonstrating that the quenching of reactivity and fluorescence led to an increase in triplet absorption.⁴¹

While halogens have been most frequently employed in H-A studies, other atoms of high atomic weight have also produced similar effects. α -Methylmercuriodiazoacetonitrile (XXXII) is subject to an internal H-A effect resulting from the presence of the mercury atom. Direct irradiation of XXXII in *cis*-2-butene afforded



a nonstereospecific 1:1 mixture of *cis* and *trans* products. In contrast, the reaction of diazoacetonitrile was stereospecific, suggesting that the presence of mercury allowed the initially formed singlet carbene to intersystem-cross to the ground-state triplet before reaction occurred.⁴²

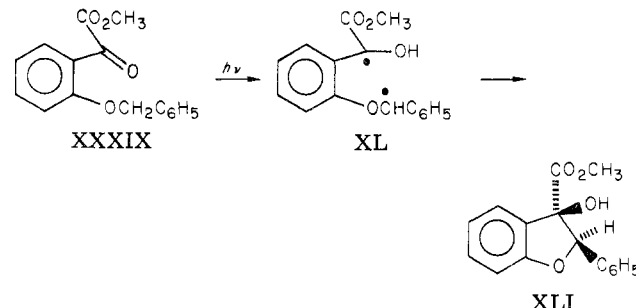
Intercombinational transitions of the triplet intermediate can also be influenced by H-A solvents, as exemplified by the dramatic increase in the quantum yield of anti dimer formation of coumarin in the presence of carbon tetrachloride. Triplet counting measurements indicated little increase in the rate of $S_1 \rightarrow T_1$ in the presence of the H-A solvent. Furthermore, even under sensitized conditions, Φ_r for anti dimer formation was found to be significantly greater in



carbon tetrachloride than in L-A solvents.

This quantum yield increase was attributed to an increase in the rate of spin inversion of XXXV to yield XXXVI. In the absence of H-A perturbation, rotation about the initially formed bond in XXXV followed by spin inversion and cleavage to yield XXXVII is much more competitive with dimer formation, thus resulting in reduced dimer yield.⁴³

Similar results have been reported on the photoabstraction-cyclization of methyl *o*-(benzyloxy)-phenylglyoxalate. Although the stereoselectivity of this



reaction is quite low in L-A solvents, the *cis* isomer (with respect to the geometric relationship of the 2-phenyl and 3-hydroxy groups) was found to be the predominant product in the presence of chloroform, bromoform, and bromobenzene. These results appear to implicate a favored geometry for the initial hydrogen abstraction regardless of the nature of the solvent. In H-A solvents, the intermediate XL may then undergo rapid spin inversion and cyclization, affording XLI. In the absence of H-A perturbation, rotation about the C-O bond is competitive with spin inversion, yielding a mixture of isomers.⁴⁴

While the number of literature examples of photochemical H-A effects is still limited, it is apparent from the above discussion that the scope of this phenomenon is quite broad. Many different types of systems appear to be susceptible to H-A perturbation. Both quantum yields of reaction and product distributions may be influenced. Although $S_1 \rightarrow T_1$ has generally been found to be more sensitive than other spin-forbidden transitions, clearly any spin-forbidden process may be affected, sometimes leading to very unusual results. As was demonstrated in photophysical studies, internal and external photochemical H-A effects do not always

(41) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **48**, 2651 (1968).

(42) P. S. Skell, S. J. Valenty, and P. W. Humer, *J. Am. Chem. Soc.*, **95**, 5041 (1973).

(43) R. Hoffman, P. Wells, and H. Morrison, *J. Org. Chem.*, **36**, 102 (1971).

(44) S. P. Pappas and R. D. Zehr, *J. Am. Chem. Soc.*, **93**, 7112 (1971).

manifest themselves in precisely the same manner. Internal heavy atoms often produce a much greater effect on triplet decay, which can lead to lower product yields.

The photochemical H-A effect is, however, more than simply an interesting phenomenon to be explored for

purely academic reasons. The utility of the H-A effect has clearly been demonstrated both as a synthetic tool and as a mechanistic probe. Undoubtedly, as the list of compounds which are susceptible to this effect continues to increase, so too will the exploitation of this phenomenon.

Studies of the Temporary Anion States of Unsaturated Hydrocarbons by Electron Transmission Spectroscopy

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The concept of occupied and unoccupied orbitals has provided a useful means for visualizing many of the most important properties of molecular systems. Yet, there is a curious imbalance in our experimental knowledge of the energies of occupied and unoccupied orbitals. Whereas photoelectron spectroscopy has provided a wealth of data on positive ion states and has established that they can be associated, within the context of Koopmans' theorem, with the occupied orbitals of the neutral molecule, the corresponding information for the negative ion states, associated with the normally unoccupied orbitals, is sparse. In part this reflects the experimental difficulties connected with measuring the electron affinities of molecules which possess stable anions. A more interesting aspect, in our view, is that for many molecules even the ground state of the anion lies *above* the ground state of the neutral molecule and thus is unstable with respect to auto-detachment of the additional electron. The temporary anions which we will discuss in this Account possess lifetimes in the range from 10^{-12} to 10^{-15} s in the gas phase. Ephemeral as these anions might appear, their existence is amply demonstrated in electron-scattering experiments. At energies in which an impacting electron may be temporarily captured into a normally unoccupied orbital, the electron-scattering cross section undergoes a pronounced change in magnitude, commonly referred to as a "resonance" by those in the scattering field.¹

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A number of electron-scattering techniques may be used to investigate temporary anion formation. In this article we will describe only one, the electron transmission method in the format devised by Sanche and Schulz.² This technique has numerous assets: it is both conceptually and experimentally straightforward, and it is likely the most sensitive means for detection of temporary anions.

During the last few years, electron transmission spectroscopy has seen increasing application to organic molecules. In the following sections, we discuss our results and those of other workers which bear on the characteristics of the temporary anion states associated with low-lying π^* orbitals in a number of classes of hydrocarbons. In addition we will describe briefly the relationship of this work to other chemical studies, such as optical absorption measurements on anions in solution, molecular orbital theories of reactivity, and studies of low-lying electronic states of neutral molecules.

Temporary Anion Formation

A conceptually useful picture of temporary anion formation has been developed from studies on atoms and diatomic molecules.¹ The essential ideas may be carried over to the hydrocarbons we will discuss here. Let us first consider electron scattering from the spherically symmetric potential field of an atom. The incident beam of electrons may be represented as a plane wave containing all components of angular momentum. If the atom possesses an energetically accessible unfilled orbital, characterized by a particular value of the orbital angular momentum quantum number l , then an incident electron with this appropriate orbital symmetry may be temporarily "captured". Both the energy and lifetime of such an anionic state are determined by the total potential in which the

(1) G. J. Schulz, *Rev. Mod. Phys.*, **45**, 378, 423 (1973).

(2) L. Sanche and G. J. Schulz, *Phys. Rev. A*, **5**, 1672 (1972).