Spin-Orbital Effects on the Excited-State Cycloaddition of 5-Acetoacenaphthylene to Cyclopentadiene[1,2]

Timothy E. O'Boyle,[3] Lou J. Scott,[4] and Benjamin F. Plummer*

Contribution from the Department of Chemistry, Trinity University, San Antonio, Texas 78284

P. S. Song*

Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

Received February 22, 1978

The compound 5-acetoacenaphthylene (aA) has been synthesized to study the effects of the influence of the n,π^* state on the photocycloaddition of aA to cyclopentadiene. Quantum yields of this reaction at 360 nm were studied as a function of cyclopentadiene concentration in the solvents cyclohexane, dibromomethane, and acetonitrile. Quenching of the cycloaddition reaction with ferrocene in the solvents dibromomethane and acetonitrile conformed to linear Stern–Volmer plots. The photocycloaddition of aA to cyclopentadiene was sensitized by the crown ether complex of Rose Bengal to yield product distributions similar to those found in the same solvent under direct irradiation. These results implicate the excited triplet state of aA as a reactive species. Kinetic parameters are derived from the data that suggest an intermediate role for spin-orbital perturbation by the carbonyl group. A heavy-atom effect is proposed to occur for compound aA when dibromomethane is used as an external perturbation.

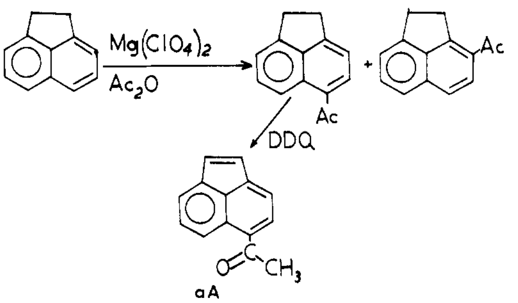
The interesting spectroscopic behavior of acenaphthylene[5] and its pronounced sensitivity to heavy-atom perturbation[6,7] make it an ideal molecule for the study of spin-orbital effects. We had previously determined that acenaphthylene (A) and 5-bromoacenaphthylene (bA) reacted from their excited triplet states in kinetically predictable ways to produce cycloadducts with cyclopentadiene (CP).[6b,c] We were curious to determine to what extent, if any, the triplet state population would be influenced if a chromophore containing a carbonyl group were incorporated into the basic acenaphthylene nucleus. Would the n,π^* state enhance triplet formation through the well-documented intersystem crossing efficiency characteristic of the carbonyl group?[8] Would this carbonyl-containing molecule show any external heavy-atom perturbation in a typical heavy-atom solvent?

To seek answers to these questions we chose for further study the target molecule 5-acetoacenaphthylene (aA).

Results

A. Synthesis and Spectroscopy of 5-Acetoacenaphthylene. The synthesis of 5-acetoacenaphthylene was achieved as shown in Scheme I. The overall yield is modest, but alternative synthetic schemes never reached fruition.

Scheme I



The acetylation method that proved to be the simplest involved reacting acenaphthene with refluxing acetic anhydride in the presence of magnesium perchlorate as a Lewis acid catalyst.[9] Although it was reported that this procedure produced nearly pure 5-acetoacenaphthene (H_2aA), we found that the isolated product was a mixture of about 75% of H_2aA and 25% of the 3-acetyl isomer. By the use of a room temperature crystallization of the mixture of isomers from a supersaturated methanol solution, we were able to achieve the preparation of pure H_2aA.

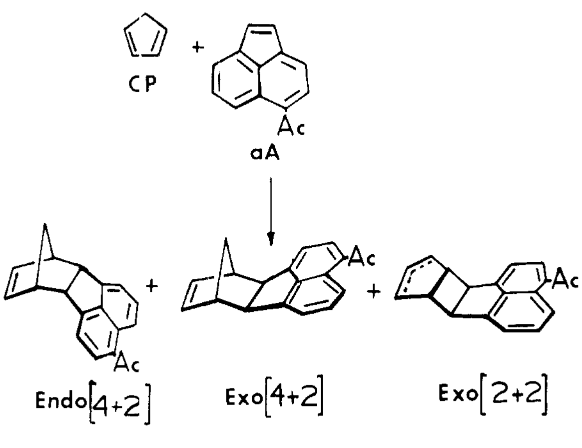
Unsaturation at the bridge of aA was produced by refluxing a mixture of H_2aA and the high potential quinone 2,3-dicyano-5,6-dichloro-1,4-benzoquinone (DDQ) in benzene.[10] We believe that our inability to reoxidize the recovered reduced DDQ may reflect the fact that much of the recovered substance is contaminated with some byproduct from the reaction of DDQ with H_2aA or with aA. This may explain the poor yield of pure aA during the dehydrogenation step.

A spectroscopic study of the photophysical properties of H_2aA and aA was undertaken. Compound H_2aA shows a broad absorption maximum at 328 nm and a narrow maximum at 244 nm. Corrected emission spectra in ethanol at 77 K show fluorescence maxima at 385, 405, and 425 nm and phosphoresence maxima at 510, 530, and 550 nm with the relative quantum yields of fluorescence and phosphorescence being about the same. The relatively strong fluorescence emission is indicative of the lowest emitting state being characterized predominantly as π,π^*. The phosphorescence emission from H_2aA is similar to that of naphthalene except for the red shift relative to that of the latter. Thus, the long wavelength band in H_2aA may be a combination of the π,π^* states characteristic of ${}^1L_a \leftarrow A$ transitions in naphthalene and acenaphthene.[11,12]

The absorption spectrum of aA in ethanol at 77 K shows maxima at 353, 335.5, and 233.5 nm. The room temperature spectrum is about the same, with the loss of resolution being the typically expected result. Concentrated solutions (0.01 M) of the ketone aA in ethanol show significant absorption out to 500 nm ($\epsilon \sim 19$). These spectra measured near 500 nm were found to obey a Beer's law plot upon dilution, thus ruling out significant self-association at high concentrations.

Luminescence studies using a spectrofluorometer (Model MPF3) showed no detectable emission from aA at room temperature. However, at 77 K using a single photon counting spectrometer an extremely weak emission (quantum yield $<10^{-4}$) was obtained. This broad emission peak centered near 440 nm is apparently due to phosphorescence since the phosphoroscope yields an almost identical spectrum. The lifetime of this emission is less than 6 ms. Phosphorescence polarization studies produced emissions monitored at 400, 440, and 530 nm that were about one-half the intensity relative to the excitation maximum. This indicates that the broad emission between 400 and 530 nm is in-plane polarized and probably originates in an n,π^* triplet. An excitation spectrum showed similarities with the absorption spectrum of aA, although the weak intensity of the emission makes the interpretation difficult.

Scheme II



The onset of the absorption band of aA at 500 nm is used to estimate the singlet energy of the presumed S_1 (π,π^*) state as 57 kcal. Triplet sensitization experiments using Rose Bengal (vide infra) place the lowest triplet state, T_1, at about 45 kcal. The phosphorescence emission maximum at 440 nm places another potential triplet state, T_2 perhaps, at 72 kcal, substantially higher than the nonemissive T_1 state. Our inability to locate the S_2 (n,π^*) state suggests that it is submerged under the long wavelength charge-transfer band characteristic of acenaphthylene derivatives. There are few examples of emission or energy transfer occurring from higher excited states. Azulene[13] emits from S_2, and Liu[14] has proposed that energy transfer can occur from a T_2 state of naphthalene. The low quantum efficiency of the 440-nm emission from aA at 77 K suggests that we are dealing with a relatively improbable event and that other nonradiative mechanisms are depopulating the excited state in competition with the population of T_2.

We subjected a hexane solution of aA to a pulsed nitrogen laser excitation (λ = 337.1 nm; bandwidth half-height = 8 ns) in the presence of a high concentration of naphthalene. No naphthalene T-T absorption, monitored at 430 nm,[15] could be detected. Since the triplet state of naphthalene is 60 kcal,[16] the presumed T_2 state of aA should be capable of transferring energy to naphthalene. The absence of detectable energy transfer from aA to naphthalene casts doubt on the 440-nm emission from aA as a legitimate state of aA and could suggest that the emission is impurity derived.

It is theoretically possible that emission could occur from a T_2 (n,π^*) state if it is highly localized and only weakly vibronically coupled to the acenaphthylene moiety. In an ethanol glass at 77 K that can impart structure and conformational restraints on the carbonyl chromophore, the possibility of such an uncoupled emission might be more probable. Phosphorescence from acenaphthylene has not been detected.[5,17,18] Thus, a weak uncoupled emission from carbonyl might have a slightly better probability of occurrence.

Calculations were performed for aA using the semiempirical π-electron SCF-CI Pariser-Parr-Pople method. Because of the extensive work of Michl,[18] we briefly outline our results here. The first excited singlet state is predicted to occur at 444 nm with a calculated dipole moment of 5.7 D. Configuration analyses of the P-P-P wave functions predicted that about 94% of this state (K band, $1 \rightarrow -1$ transition)[18] is localized on the acenaphthylene moiety with only 3.4% charge transfer from this moiety to the carbonyl group. The first excited triplet state shows 97% of the wave function localized on the acenaphthylene skeleton with only 2% charge transfer to carbonyl and a calculated dipole moment of 4.3 D. The calculated ground state dipole moment is significantly less, 3.2 D, and this difference is seemingly reflected in the kinetic data we have obtained (vide infra).

Table I. Product Distribution for Direct and Sensitized Photochemical Reactions between aA and CP [a]

solvent	endo [4 + 2]	exo [4 + 2]	exo [2 + 2]
cyclohexane	0.6 (0.5)	1.9 (2.0)	1.0
dibromomethane	0.7 (0.5)	1.9 (1.7)	1.0
acetonitrile	0.9 (0.5)	2.6 (2.2)	1.0

[a] Rose Bengal sensitized ratios are in parentheses; ratios are normalized to exo [2 + 2]; [CP] = 1 M.

According to the configuration analysis method,[19] the S_1 and T_1 states, while extensively restricted to the acenaphthylene moiety of aA, show large polarization effects. About 14% of the positive character of the first excited singlet state is localized on the ethylene unit of aA. The first triplet state shows a 35% localization of positive character at the ethylene unit of aA, indicating substantial activation of the ethylene bridge in the excited state.

These calculations support the observation of the electrophilic character associated with the attendant photochemistry of aA. The theoretical analysis similarly supports the spectroscopic interpretation of minimal interaction between the carbonyl chromophore and the hydrocarbon skeleton of aA.

B. Structure of Products. The three major stereoisomers that result from the photochemical cycloaddition of aA to CP are shown in Scheme II. They are the [4 + 2] products *endo*-7,10-methano-6b,7,10,10a-tetrahydro-3-acetofluoranthene (endo [4 + 2]) and the corresponding exo isomer (exo [4 + 2]) and the [2 + 2] product *exo*-4′-acetonaphtho[1′,8′]tricyclo[3.3.0.$0^{6,10}$]deca-2,7-diene.

The complete separation of the three stereoisomers by techniques available to us was not achieved. GLC analysis and separation was not totally satisfactory, in that baseline separation between peaks representing the endo and exo [4 + 2] isomers was not obtainable. Column temperatures were programmed to achieve optimal separations without concomitant thermal degradation. This allowed us to achieve a separation and purification of the exo [2 + 2] product, but the [4 + 2] isomers were collected as mixtures and analyzed accordingly.[6b] The spectroscopic properties of the pure exo [2 + 2] isomer and the [4 + 2] isomer mixture were corroborated by comparison with the spectra of the substituted derivatives available in our laboratories.

Our inability to assess accurately the separate areas for the endo [4 + 2] and exo [4 + 2] GLC peaks because of excessive tailing of the endo peak into the exo peak affected the accuracy of product ratios that were computed. This variability is reflected in the product ratios reported in Table I. We are not convinced that the deviation between product ratios obtained in direct and sensitized irradiations is necessarily a manifestation of a change in reaction mechanism.[20] We are more inclined to think that it is a result of difficulties arising from the analytical GLC integration of peak area.

C. Photochemical Results. The influence of solvents, quenchers, and sensitizers upon the photochemical cycloaddition of aA to CP was studied in a fashion analogous to prior investigations (Figures 1–3).

The product distributions for direct and sensitized irradiations are listed in Table I. The direct irradiations were performed at 360 nm, while the sensitized irradiations used the 589-nm light from a sodium vapor lamp to selectively excite the crown ether complexes of disodium Rose Bengal as a triplet sensitizer.

The kinetic equation (1) derived from prior studies was used to verify the relationship between quantum yield of product formation and variation in concentration of cyclopentadiene in various solvents. In Table II, the parameters derived from the kinetic studies in cyclohexane, dibromomethane, and acetonitrile are enumerated.

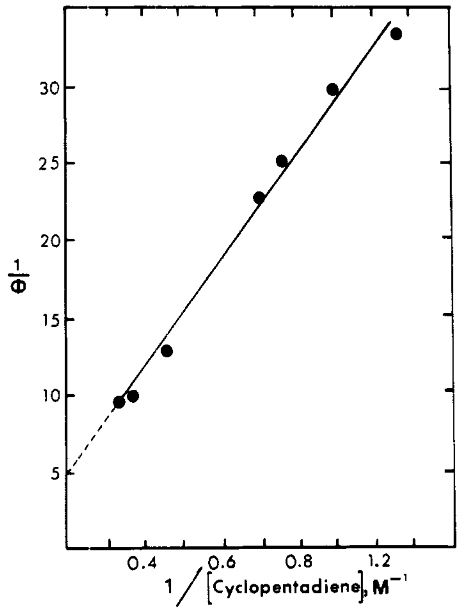


Figure 1. A plot of the concentration dependence of aA (0.005 M) reacting with CP in the solvent dibromomethane.

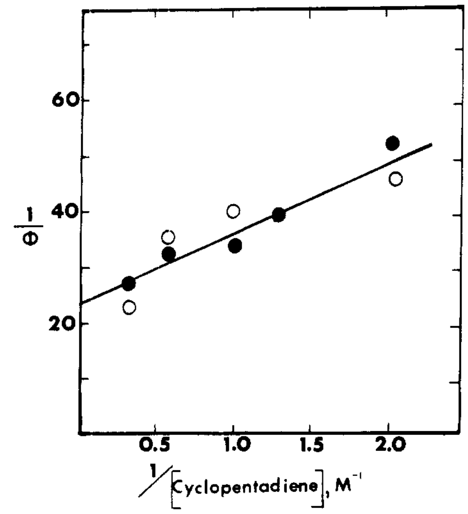


Figure 2. A plot of the concentration dependence of aA (0.007 M) reacting with CP in the solvent acetonitrile: ○ = nitrogen degassing run; ● = freeze–thaw degassing run.

Quenching data from the photoaddition of aA to CP were obtained using ferrocene as a triplet quencher.[6] The value used for k_q for ferrocene was chosen as 4×10^9 M^{-1} s^{-1} in acetonitrile and adjusted for viscosity effects in other solvents.[6b] The solvents dibromomethane and acetonitrile were investigated because the photochemical process occurred at a modest rate. Quenching in cyclohexane was not studied because the quantum yields for reaction between aA and CP in this solvent are very low. The data obtained conformed to Stern–Volmer relationships, and the results are found in Table III.

Discussion

The Triplet State. The triplet nature of the reaction of 5-acetoacenaphthylene with cyclopentadiene is indicated by the fact that the product ratios reflect similar sensitivity to solvent character in both direct and sensitized photochemical processes. The unsensitized reactions are quenched by ferrocene. Since ferrocene has been used successfully in prior studies[6] as a triplet quencher, we feel that the available data support the assumption of a triplet excited-state process.

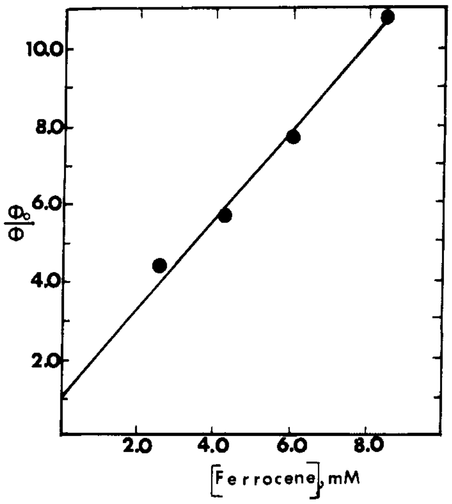


Figure 3. A typical plot of the ferrocene quenching concentration dependence of aA (0.0077 M) reacting with CP (1.80 M) in acetonitrile.

Table II. Kinetic Parameters Derived from Concentration Dependence of Reaction of aA with CP

solvent	slope ($k_d/\alpha\phi_{isc}k_r$)	intercept ($1/\alpha\phi_{isc}$)	correlation
cyclohexane	91 ± 6.1	16 ± 7.4	0.99
dibromomethane	18 ± 0.8	4.6 ± 0.8	0.99
acetonitrile	12 ± 1.6	24 ± 2.0	0.94

Table III. Ferrocene Quenching of the Reaction between aA and CP

solvent	slope, M^{-1}	intercept	correlation
dibromomethane[a]	3703 ± 635	1.2 ± 0.15	0.94
acetonitrile[b]	1143 ± 57	1.1 ± 0.3	0.99

[a] [aA] = 0.0053 M; [CP] = 3.8 M. [b] [aA] = 0.0077 M; [CP] = 1.8 M.

Proposed Mechanism. A mechanism consistent with the kinetic data is shown in Scheme III.

We define α as the ratio of the rate constants $k_T/(k_{-r} + k_T)$, reflecting the ability of the intermediate diradical [I] to partition among products or reactants. Defining ϕ_{isc} as the ratio $k_{isc}/(k_{ic} + k_{isc})$ and using the steady-state approximation lead to eq 1 when [Q] = 0.

$$1/\phi = 1/\alpha\phi_{isc} + (k_d/\alpha\phi_{isc}k_r)(1/[CP]) \qquad (1)$$

Scheme III[a]

	rate
$aA \xrightarrow{h\nu} {}^1aA$	Ia
${}^1aA \xrightarrow{k_{ic}} aA$	$k_{ic}[{}^1aA]$
${}^1aA \xrightarrow{k_{isc}} {}^3aA$	$k_{isc}[{}^1aA]$
${}^3aA \xrightarrow{k_d} aA$	$k_d[{}^3aA]$
${}^3aA + Q \xrightarrow{k_q} aA + {}^3Q$	$k_q[{}^3aA][Q]$
${}^3aA + CP \xrightarrow{k_r} [I]$	$k_r[{}^3aA][CP]$
$[I] \xrightarrow{k_{-r}} aA + CP$	$k_{-r}[I]$
$[I] \xrightarrow{k_T} \text{products}$	$k_T[I]$

[a] aA is 5-acetoacenaphthylene, CP is cyclopentadiene, and k_{ic}, k_{isc}, k_d, and k_q are, respectively, the rate constants for internal conversion ($S_1 \rightarrow S_0$), intersystem crossing ($S_1 \rightarrow T_1$), radiationless decay ($T_1 \rightarrow S_0$), and bimolecular quenching.

Table IV. Kinetic Parameters for Photocycloaddition of Acenaphthylene Derivatives to Cyclopentadiene in Different Solvents

substituent	H^a		$5\text{-}Br^a$	$5\text{-}CH_3CO$		
solvent	CH_2Br_2	CH_3CN	CH_3CN	CH_2Br_2	C_6H_{12}	CH_3CN
$\alpha\phi_{isc}$	0.21	0.0042	0.22	0.22	0.061	0.042
ϕ_{isc}	1	0.020	1	1	0.3^b	0.2^b
k_d/k_r, M^{-1}	2.2	0.36	31	3.9	5.5	0.50
k_r, $s^{-1}\,M^{-1}$	3.0×10^4	3.4×10^4	6.8×10^4	5.1×10^4	3.2×10^4	1.5×10^6
k_d, s^{-1}	6.6×10^4	1.2×10^4	2.1×10^6	2.0×10^5	$(1 \times 10^5)^c$	7.5×10^5

[a] These values are reported in ref 6b. [b] Values based on assumption $\alpha = 0.22$. [c] Estimated value for k_d.

The reciprocal of the intercept of plots of eq 1 yields values of $\alpha\phi_{isc}$, and the slope divided by the intercept produces ratios for k_d/k_r. To evaluate k_d and k_r, it is necessary to have the Stern–Volmer slope from quenching experiments.[6b]

In Table IV, we have listed the rate parameters derived from our prior studies on A and bA with those derived from this study for aA.

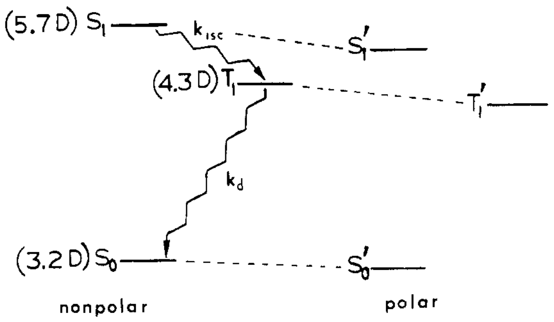
In previous studies, the value for α was found to be 0.22. Ideally, α can be determined by studying the quantum yield of sensitized cycloaddition of CP to aA. Experimentally, this proves to be difficult because sensitizers with accurately known values of ϕ_{isc} that absorb strongly beyond 500 nm are not readily available.[22] If we assume that $\phi_{isc} = 1$ for aA reacting in dibromomethane, then α is computed to be 0.22 for aA in this solvent. The agreement among the values derived for α for the different substituents when heavy-atom perturbation is present supports the assumption that ϕ_{isc} is close to unity. Implicit in this hypothesis is the further assumption that substituents remote from the position of photoreactivity have little influence on the partitioning of the intermediate diradical.[23]

We use the value of 0.22 for α in regular solvents to estimate the value for ϕ_{isc} in these systems. Thus, ϕ_{isc} for aA is between 0.2 and 0.3 in acetonitrile and cyclohexane. The standard deviation of the intercepts from the concentration studies for these solvents suggests that ϕ_{isc} is probably of similar magnitude in both solvents.

The effect of the carbonyl group upon the radiationless decay of the excited triplet is found by comparison of the values for the unimolecular decay constant k_d among the substituted acenaphthylenes. In acetonitrile solvent, the 5-Br substituent (internal heavy atom) is a factor of 3 more effective at enhancing $T_1 \rightarrow S_0$ than 5-acetyl in the same solvent. Still, it is interesting to note that the appended carbonyl causes k_d to be larger than the external heavy-atom effect.

The influence of substituents and solvents upon intercombinational radiationless transitions such as $S_1 \rightarrow T_1$ and $T_1 \rightarrow S_0$ is complex. Thus, the fact that k_d for aA in dibromomethane is one-fourth that of k_d for aA in acetonitrile is somewhat surprising. However, from first-order perturbation theory the probability that an intercombinational transition can occur is inversely proportional to the difference in energy between triplet and singlet states of the molecule.[25] Thus, the smaller the energy difference between singlet and triplet states, the more probable the intercombinational event becomes. Acetonitrile, having a high dielectric constant, is expected to stabilize dipolar states. Since the theoretical PPP-SCF-CI calculations suggest a larger dipole moment for both the excited singlet and triplet states of aA than the ground state, we surmise that the energy gaps between T_1, S_1, and S_0 are compressed as illustrated in Scheme IV.

Scheme IV



Ordinarily, carbonyl-containing molecules that contain the lowest n,π* triplet states are expected not to show significant heavy-atom perturbation.[26] Our data support the assumption that ϕ_{isc} in aA increases from 0.2 to 1 upon heavy-atom perturbation. This stands in contrast to the luminescence data that detects phosphorescence from an n,π* state of aA. Because we find a substantial heavy-atom effect upon k_{isc} for aA, we presume that the lowest triplet is a nonphosphorescent π,π* state that is very weakly coupled to the electronic states of the carbonyl chromophore. We note that the theoretical calculations suggested only a weak interaction.

The 5-acetyl substituent produces the largest value for k_r in acetonitrile among the three compounds studied. Since k_r is a bimolecular rate constant reflecting the rate of reaction of excited triplet aA with CP, we presume that there exists some activation energy barrier for this process. We surmise that the transition state for the reaction may reflect increased polar character as the excited triplet of aA begins to associate with CP. Since aA is an electron acceptor and CP a typical electron donor, the transition state polarity may be accentuated through charge transfer from diene to π acceptor. The polar solvent, acetonitrile, would enhance the charge transfer interaction and in turn lower the energy content of the transition state. This charge transfer stabilization would enhance the magnitude of k_r, as is seen in the data.

The extensive studies by Cowan and Koziar[6e,f] provide additional information as a basis for comparison of k_d values. We choose the reciprocal of k_d as the nonradiative lifetime, τ, of the excited triplet state of various acenaphthylene derivatives. This differs from the Stern–Volmer lifetime because additional processes are involved in deactivating the excited triplet in these studies. In Table V we summarized various triplet lifetimes obtained from different investigations and different laboratories. The experimental uncertainties associated with kinetic data of this type require that comparisons be drawn cautiously. However, the lifetime for triplet A in heavy-atom solvents is found to be about 10^{-5} s by two different laboratories studying quite different reactions.[6b,e,f] While this may be fortuitous, we prefer to believe that it supports the assumption that valid comparisons can be made. Thus, the compound having the heavy internal atom perturbation is the one with the shortest nonradiative triplet lifetime of about 5×10^{-7} s. The 5-acetoacenaphthylene has a k_d of 10^{-6} s in the solvents dibromomethane and acetonitrile, while 1,2-dichloroacenaphthylene has a similar magnitude for k_d in ethyl iodide.

Table V. Excited Triplet Lifetimes of Acenaphthylene Compounds (τ), s^{-1}

compd	ICH_2CH_3	CH_2Br_2	CH_3CN
acenaphthylene	1.0×10^{-5} [a]	1.5×10^{-5} [b]	8.0×10^{-5} [b]
1,2-dichloroacenaphthylene	1.5×10^{-6} [a]		
5-bromoacenaphthylene			4.7×10^{-7} [b]
5-acetoacenaphthylene		5×10^{-6}	1.3×10^{-6}

[a] Dimerization reaction.[6e,f] [b] Cycloaddition reaction to CP.[6b]

The values for the reaction rate constant, k_r, of triplet excited state reacting with substrate vary from 3×10^4 to 1.5×10^6 M^{-1} s^{-1} with the rate constant for aA in acetonitrile being the largest.[27] Thus, a shortened triplet lifetime is compensated for by an increase in k_r, and the overall quantum yield is substantially larger than the similar system in A or bA.

Summary

The photochemical reaction of aA with cyclopentadiene is used as a tool to delineate the affect of carbonyl perturbation on the chemistry of acenaphthylene. The absence of some emissive states in the acenaphthylene system requires the use of reaction kinetics to determine some of the rate parameters for excited states. This study has shown that intramolecular carbonyl perturbation is not as effective as internal and external heavy atoms in maximizing ϕ_{isc} in the acenaphthylene family.

Experimental Section

Materials. Benzophenone (Eastman) was recrystallized from 95% ethyl alcohol, mp 46.6–46.9 °C. Tetradecane (Baker, Practical Grade) was distilled through a spinning band column, bp 101–103 °C (4.0 mm). 1,3-Cyclohexadiene (Aldrich, 99%) was stored under refrigeration and passed over a short column of Al_2O_3 prior to use. Acenaphthene (Aldrich, 99%) was recrystallized from benzene. Benzene (Mallinckrodt, Analytical Reagent) used for actinometry was distilled from CaH_2 through a 1-m Vigreux fractionating column. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (Aldrich, 98%) and benzene that was stored over $MgSO_4$ were used in dehydrogenations. Dibromomethane (Aldrich), ethyl iodide (Aldrich), acetonitrile (Aldrich), and cyclohexane (Baker, Spectro Grade) were distilled immediately prior to use through a 1-m Vigreux column. A 5% $AgNO_3$–silica gel mixture was prepared by dissolving 5 g of reagent grade $AgNO_3$ in 50 mL of CH_3CN and adding to this solution 100 g of silica gel (Curtin, 60–200 mesh) followed by additional CH_3CN to make a mobile slurry. After rotary evaporation, the dry powder was transferred to a brown bottle and placed in a 100 °C oven for 18 h. Crude triphenylmethanol was recrystallized twice from methanol and analyzed by GLC, mp 159–160 °C. Aluminum oxide for chromatography was Sargent-Welch alumina F-20, 80–200 mesh. The bis(dicyclohexyl-18-crown-6 ether) complex of disodium Bengal Red was the product obtained by Plummer and Ferree[6b] and was used without further purification. Ferrocene (Eastman Practical), mp 174–175 °C, was purified by vacuum sublimation. Acetic anhydride (Baker, Reagent) was used without purification.

Instrumentation. A Varian T-60 NMR spectrometer was used to obtain spectra from dilute solutions of solute dissolved in CCl_4 at 34 °C with internal tetramethylsilane. Infrared spectra of thin films of liquid samples or of KBr pellets of solid samples were obtained on a Perkin-Elmer 337 spectrometer. A Finnigan 1015 C System/150 computer-controlled ensemble with gas chromatograph was used to generate mass spectra at 70 eV. GLC analyses were performed with a Varian 2400 Hi-F1 connected to a Sargent SR recorder equipped with a disc integrator. Column A was a 2 ft × 0.125 in. 1.5% OV-101 on Chromosorb G column. Preparative scale GLC separations were performed on a Varian 920 using column B, a 4 ft × 0.25 in. column of 3% OV-1 on 80–100 mesh Chromosorb W. Melting points were obtained from a Fisher-Johns apparatus and are uncorrected. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, Tenn. Ultraviolet measurements were obtained from a Cary 118 C recording spectrometer. Luminescence measurements at 77 K were measured on a Perkin-Elmer spectrophotofluorometer (Model MPF-3). Single photon detection experiments were obtained from an instrument as previously described.[28]

Irradiation Procedures. Direct irradiations were performed with a 450-W Hanovia lamp in a Pyrex immersion well with circulating copper nitrate solution (0.7 M) and surrounded by filters of Corning Glass CS-7-60 so that only a narrow band of light between 360 and 390 nm was transmitted.[29] This was placed in the center of Rayonet MGR-500 merry-go-round apparatus contained in a box specially designed to seal out stray light. The actinometer solutions were irradiated in parallel with the reaction mixtures. All runs were carried to less than 10% conversion of reactant, and concentrations of reactants were chosen so that the molar absorbance of aA was always greater than 3.0 after the cessation of the reaction. Samples were degassed with nitrogen purge for 30 min or were freeze-thaw degassed several times at 10^{-2} mm.

Actinometry and Sensitized Irradiations. Benzophenone-sensitized photodimerization of 1,3-cyclohexadiene[6a,b,30] was used as a chemical actinometer.

Sensitized irradiations were performed with a Sargent-Welch sodium vapor lamp placed at the center of a Rayonet photochemical reactor. The photolysis tubes were suspended around the lamp by use of a MGR-100 merry-go-round reactor. The reaction conditions were similar to those reported for prior studies in these laboratories.[6a-c]

Quenching. Ferrocene quenching studies were performed as previously described.[6b]

Analyses. Photolysis mixtures were analyzed by GLC using linear temperature programming of the oven temperature from 160 to 165 °C at a rate of 1 °C/min and then from 165 to 250 °C at a rate of 4 °C/min. The helium and hydrogen flow rates were both 25 mL/min, and the injector and detector temperatures were 255 and 265 °C, respectively. Triphenylmethanol was used as an internal standard in these analyses.

Isomer distributions were obtained by measuring peak areas using a disc integrator. Areas for endo [4 + 2] and exo [4 + 2] isomers were determined by dropping a perpendicular from the saddle point to the baseline. The response factor was determined and checked after each set of analyses using a standard equimolar solution of exo [2 + 2] and triphenylmethanol in chloroform. The response factor (R) for the flame ionization detector was calculated using eq 2. The R factor was found to be 0.70 ± 0.08.

$$R = (\text{exo } [2+2]/Ph_3COH)_{\text{peak area}}/(\text{exo } [2+2]/Ph_3COH)_{\text{mol}} \quad (2)$$

Purification of 1,3-Cyclopentadiene. Into a 500-mL separatory funnel was added 300 mL of technical grade dicyclopentadiene (Aldrich). This was washed consecutively with 3 × 50 mL of 25% concentrated KOH, 1 × 50 mL of distilled water, 1 × 2 g of $NaIO_4$ in 10 mL of concentrated acetic acid and 50 mL of distilled water, and 1 × 50 mL of saturated NaCl. The remaining dicyclopentadiene was dried over anhydrous sodium sulfate and passed through a 0.5 × 8 in. silica gel (Curtin) column. The collected dicyclopentadiene was cracked under a nitrogen atmosphere using a 2-ft vacuum-jacketed fractionating column packed with 0.25 in. Berl Saddles. The resultant monomeric cyclopentadiene was distilled a second time under nitrogen immediately before use, bp 38.5–39.5 °C.

5-Acetoacenaphthene. A mixture of 46 g (0.30 mol) of acenaphthene (Aldrich), 3.3 g (0.015 mol) of anhydrous magnesium perchlorate and 45 mL (0.48 mol) of acetic anhydride was refluxed for 1 h as described previously.[9] After workup and vacuum distillation, the crude viscous yellow oil was added to 75 mL of absolute methanol with thorough mixing. Overnight crystallization at room temperature produced a crop of off-white crystals that was collected by decantation of the mother liquor. The crude crystals of H_2aA were twice recrystallized from hot absolute methanol followed by ice cooling. A yield of 23 g (40%) of pure 5-acetoacenaphthene containing less than 1% of the 3 isomer (GLC analysis) was obtained, mp 68.5–70.0 °C.[31]

5-Acetoacenaphthylene. Into a 500-mL round-bottom flask was added 6.0 g (30.6 mmol) of 5-acetoacenaphthene, 13.6 g (60 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and 250 mL of benzene (Eastman). After vigorous mixing the resultant greenish solution was then refluxed under a nitrogen atmosphere for 12 h. Following this period of reflux, the brown precipitate of 2,3-dichloro-5,6-dicyanohydroquinone (DDQH) was removed by suction filtration and washed with 4 × 100 mL of hot benzene. The combined benzene solutions were rotary evaporated to about 100 mL and added to a 1 × 18 in. acid-washed Al_2O_3 (Baker) column. Elution with ethyl ether with positive nitrogen pressure produced about 1250 mL of yellow solution. After rotary evaporation was performed, the resultant oil was dissolved in a minimal amount of warm pentane and the mixture was allowed to crystallize at −5 °C for 3 days. Gas chromatographic analysis of the collected yellow crystals using an OV-101 column (5 ft × 1/8 in.) (oven temperature 180–200 °C, injector 280 °C, detector 290 °C) revealed no detectable impurities. A 33.7% yield (2.0 g) of pure 5-acetoacenaphthylene was obtained: mp 54.0–54.5 °C; NMR (CCl_4) δ 2.7 (s, 3 H, $COCH_3$), 7.0 (dd, 2 H, –CH=CH–, J = 6 Hz), 7.5 (m, 3 H, ArH), 8.0 (d, 1 H, J = 7 Hz), 8.8 (m, 1 H, ArH); IR (KBr) 1680, 1480, 1350, 1260, 1225, 1190, 1075, 835 cm^{-1}; UV (C_6H_{12}) λ_{max} (ϵ) 353 (4800), 334 (10 300), 278 (2190), 268 (3570), 232 (28 000), 205 (25 200) nm; mass spectrum (70 eV), *m/e* (rel intensity) 194 (43), 170 (100), 165 (5), 163 (5), 151 (89), 150 (35), 99 (5), 98 (5), 97 (5), 76 (10), 75 (22), 74 (8). Anal. Calcd for $C_{14}H_{10}O$: C, 86.57; H, 5.19. Found: C, 86.78; H, 5.23.

Photoproducts *endo*-7,10-Methano-6b,7,10,10a-tetrahydro-3-acetofluoranthene (Endo [4 + 2], Exo [4 + 2]) and *exo*-4′-Acetonaphtho[1′,8′]tricyclo[3.3.0.0^{6,10}]deca-2,7-diene (Exo [2 + 2]). Solutions of 40 mg of aA, 10 mL (0.123 mol) of freshly cracked cyclopentadiene, and 5 mL of a 10 mol % solution of ethyl iodide in cyclohexane were placed in Pyrex tubes (Rayonet RPV-8). The tubes were purged with a purified nitrogen stream for 30 min and irradiated for 1 h in a Rayonet MGR-500 merry-go-round using a 450-W Hanovia lamp in a Pyrex immersion well with circulating cold copper nitrate solution. The solutions from all tubes were combined and rotary evaporated to a volume of 2 mL. The viscous oil was added to a 12 × 1 in. aluminum oxide (Sargent-Welch alumina F-20, 80–200 mesh) column and eluted with a total of 8 L of ligroin (bp 85–95 °C). The progress of the photoproducts down the column was monitored by their fluorescence emission when excited by a UV lamp. Each 200-mL fraction was analyzed by GLC. The fractions containing the photoproducts were rotary evaporated to a viscous oil. This purified mixture of photoproducts was chromatographed on a 2 in. × 1 ft $AgNO_3$–silica gel column according to the procedure of Baker and Mason.[32] Using 50% purified ligroin–benzene as the eluting solvent, fractions of 50 mL were collected. The first fractions eluted contained primarily exo [2 + 2] with a small amount of endo [4 + 2] as determined by GLC. After rotary evaporation, the oil was taken up in 2 mL of hexane and subjected to preparative GLC on column B at 215 °C. A yellow oil was collected, dissolved in 0.5 mL of hexane, and subjected to a second preparative GLC purification. After dissolving the collected oil in 1 mL of hexane and cooling to −10 °C, the white cyrstals were collected by suction filtration to yield 7 mg of exo [2 + 2]: mp 85.5–86.5 °C; NMR (CCl_4) δ 2.8 (s, 3 H, CH_3CO), 2.70–2.85 (3 H, allylic, overlapped by CH_3CO), 3.1 (m, 1 H), 3.8 (m, 2 H, benzylic), 6.0 (m, 2 H, vinylic), 7.2–7.8 (m, 3 H, ArH), 8.0 (d, 1 H, J = 7 Hz, ArH), 8.8 (d, 1 H, J = 8 Hz, ArH); IR (KBr) 1680, 1600, 1500, 1240, 1200, 1175, 950 cm^{-1}; mass spectrum (70 eV), *m/e* (rel intensity) 260 (2), 202 (5), 195 (10), 194 (68), 179 (100), 152 (10), 151 (60), 150 (15), 101 (7), 66 (14), 65 (8), 43 (40), 39 (12). Anal. Calcd for $C_{19}H_{16}O$: C, 87.69; H, 6.15. Found: C, 87.43; H, 6.10.

The fractions rich in endo [4 + 2] and exo [4 + 2] were rotary evaporated to a viscous yellow oil. This oil was subjected to a molecular distillation at 80 °C and 0.1 mmHg and analyzed as a mixture because of the difficulty of separation of the stereoisomers:[6b] exo [4 + 2] NMR (CCl_4) δ 0.8 (m, 1 H), 1.28 (m, 1 H), 2.65 (s, 3 H, $COCH_3$), 2.85 (m, 2 H), 3.49 (m, 2 H), 6.3 (m, 2 H, CH=CH); endo [4 + 2] NMR (CCl_4) δ 1.75 (m, 2 H), 2.65 (s, 3 H, $COCH_3$), 3.2 (m, 2 H), 4.02 (m, 2 H), 5.32 (m, 2 H, CH=CH); IR (CCl_4) mixture 3080, 3060, 2970, 2930, 1685, 1600, 1550, 1500, 1350, 1270, 1260, 1250, 1240, 1235 cm^{-1}; mass spectrum (70 eV) exo, *m/e* (rel intensity) 260 (8), 215 (7), 205 (5), 195 (15), 194 (78), 180 (18), 179 (100), 151 (48), 150 (12), 101 (5), 66 (11); mass spectrum (70 eV) endo, *m/e* (rel intensity) 260 (80), 215 (7), 205 (5), 195 (15), 194 (78), 180 (17), 179 (100), 151 (47), 150 (12), 75 (10), 66 (10). Anal. Calcd for $C_{19}H_{16}O$: C, 87.65; H, 6.19. Found: C, 87.48; H, 5.97.

Acknowledgment. We appreciate the support of the Robert A. Welch Foundation for the investigation described and thank the National Science Foundation for matching funds to purchase the Cary 118 C spectrophotometer. This work was also supported in part by the NIH (GM 23089).

Registry No.—aA, 68399-52-0; H_2aA, 10047-18-4; endo [4 + 2], 68399-53-1; exo [4 + 2], 68422-66-2; exo [2 + 2], 68399-54-2; 1,3-cyclopentadiene, 542-92-7; dicyclopentadiene, 77-73-6; acenaphthene, 83-32-9.

References and Notes

(1) Photochemical Heavy-Atom Effect. 9. Part 8: *J. Am. Chem. Soc.*, accepted for publication.

(2) Presented in part at the 12th Informal Conference on Photochemistry, Washington, D.C., 1976.

(3) Robert A. Welch Undergraduate Scholar.

(4) Taken in part from the M.S. Thesis of L. J. Scott, Robert A. Welch Postgraduate Fellow, Trinity University, San Antonio, Tex., 1976.

(5) (a) E. Heilbronner, J. P. Weber, J. Michl, and R. Zahradnik, *Theor. Chim. Acta*, **6,** 141 (1966); (b) A. Bree, C. Y. Fan, and R. A. Kydd, *Spectrochim. Acta, Part A*, **25,** 1375 (1969); (c) J. Michl, *J. Am. Chem. Soc.*, **98,** 4546 (1976); (d) J. Michl and J. F. Muller, *ibid.*, **98,** 4550 (1976).

(6) (a) W. I. Ferree, B. F. Plummer, and W. W. Schloman, *J. Am. Chem. Soc.*, **96,** 7741 (1974); (b) W. I. Ferree and B. F. Plummer, *ibid.*, **95,** 6709 (1973); (c) B. F. Plummer and D. M. Chihal, *ibid.*, **94,** 6428 (1972); (d) B. F. Plummer and R. A. Hall, *Chem. Commun.*, 44 (1970); (e) D. O. Cowan and J. Koziar, *J. Am. Chem. Soc.*, **98,** 1001 (1976); (f) *ibid.*, **97,** 249 (1975); (g) *ibid.*, **96,** 1229 (1974); (h) D. O. Cowan and R. L. Drisko, *ibid.*, **92,** 6281 (1970).

(7) D. O. Cowan and R. L. Drisko, "Elements of Organic Photochemistry", Plenum Press, New York, 1976, Chapter 10.

(8) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83,** 2739 (1961).

(9) B. A. Rosenberg, R. D. Bodnarcheck, G. N. Dorofeenko, and E. P. Babin, *Zh. Obshch. Khim.*, **33,** 1489 (1963).

(10) E. A. Braude, A. G. Brook, and R. P. Linstead, *J. Chem. Soc.*, 3569 (1954).

(11) J. R. Platt, *J. Chem. Phys.*, **18,** 1168 (1950).

(12) J. R. Platt, *J. Chem. Phys.*, **19,** 263 (1951).

(13) (a) M. Beer and H. C. Longuet-Higgins, *J. Chem. Phys.*, **23,** 23, 1390 (1955); (b) C. Viswanath and M. Kasha, *ibid.*, **24,** 574 (1956); (c) J. Sidman and D. S. McClure, *ibid.*, **24,** 757 (1956); (d) R. Praiser, *ibid.*, **25,** 1112 (1957); (e) S. P. McGlynn, F. J. Smith, and G. Cilento, *Photochem. Photobiol.*, **3,** 269 (1964); (f) J. B. Birks, *Chem. Phys. Lett.*, **17,** 370 (1972).

(14) C. C. Ladwig and R. S. H. Liu, *J. Am. Chem. Soc.*, **98,** 8093 (1976), and references therein.

(15) D. P. Craig and I. G. Ross, *J. Chem. Soc.*, 1589 (1954).

(16) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66,** 2100 (1944).

(17) We are currently studying the fluorescence characteristics of A and its derivatives using a pulsed nitrogen laser. An anomalous emission near 420 nm as well as an emission near 540 nm has been found in all compounds. We believe that these results will have an important bearing on the detailed understanding of the photophysical properties of aA. A report of these results will be forthcoming.

(18) (a) E. W. Thulstrup and J. Michl, *J. Am. Chem. Soc.*, **98,** 4533 (1976); (b) J. W. Kenney, D. A. Herold, J. Michl, and J. Michl, *ibid.*, **100,** 6884 (1978).

(19) (a) H. Baba, S. Suzuki, and T. Takemura, *J. Chem. Phys.*, **50,** 2078 (1969); (b) P. S. Song, C. A. Chin, I. Yamazaki, and H. Baba, *Int. J. Quantum Chem., Quantum Biol. Symp.*, **No. 2,** 1 (1975).

(20) A referee is concerned with the disparity between the product ratios determined for sensitized and direct irradiation photolyses of aA with CP in acetonitrile. The suggestion is made that in acetonitrile under direct irradiation a radical ion process could be occurring, thus vitiating the kinetic data obtained in this solvent. We have not detected the presence of any other products that might reflect the intervention of radical ions. Recent results on the photochemistry of radical ions[21] suggest that the differences in oxidation and reduction potentials for aA and CP are not large enough to facilitate this process. It is not readily apparent to us, for example, which molecule, aA or CP, would be the radical cation and which the radical anion.

(21) A. J. Maroulis, Y. Shigemitsu, and D. R. Arnold. *J. Am. Chem. Soc.*, **100,** 535 (1978), and references therein.

(22) S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, 1973.

(23) A referee objects to these assumptions because of the potential for a heavy-atom effect occurring on intersystem crossing in the proposed 1,4-biradical. Prior kinetic studies of photodimerizations of A and its derivatives and cycloaddition reactions of A have not produced evidence that α is profoundly influenced by solvents.[6] Experiments on the mechanism of photodimerization of benzo[*b*]thiophene 1,1-dioxides in heavy-atom solvents suggest that a heavy-atom effect on intersystem crossing in a 1,4-biradical occurs rarely, and usually when steric hindrance to ring closure is an important energy consideration.[1,24]

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

(25) (a) See ref 7, pp, 250–255; (b) M. A. El-Sayed, *Acc. Chem. Res.*, **1,** 8 (1968); (c) S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, **66,** 199 (1969); (d) G. W. Robinson and R. Frosch, *J. Chem. Phys.*, **38,** 1187 (1963).

(26) (a) P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, **87,** 4009 (1965); **88,** 1245 (1966); (b) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **46,** 2333 (1967).

(27) Cowan[6e,f] has found the rate constant for the similar step in the photodimerization of A and 1,2-dichloro A to be on the order of 10^5 M^{-1} s^{-1}.

(28) W. W. Manutlin and P. S. Song, *J. Am. Chem. Soc.*, **95,** 5122 (1973).

(29) B. F. Plummer, *Mol. Photochem.*, **6,** 241 (1974).

(30) (a) G. S. Hammond and G. F. Vesley, *Mol. Photochem.*, **5,** 367 (1973); (b) *J. Am. Chem. Soc.*, **89,** 3482 (1967).

(31) L. F. Fieser and E. B. Hersherb, *J. Am. Chem. Soc.*, **61,** 1272 (1939).

(32) R. Baker and T. J. Mason, *J. Chem. Soc. C*, 596 (1970).