arylethylene moiety) and/or the vertical energy gaps between the triplet at the relaxed geometry and the ground state are smaller than spectroscopic triplet energies. The rate constants  $(k_{q,DTBN}^{T})$ for quenching by DTBN show a trend opposite to that with ferrocene as the quencher. For rigid aromatic hydrocarbon triplets with  $E_{\rm T}$  lower than that of anthracene,  $k_{\rm q}^{\rm T}$ 's for quenching by nitroxy radicals are found to increase as the triplet energy is lowered.<sup>27</sup> This is explained<sup>27</sup> in terms of spin exchange interaction for which the energy gap law holds good. The (9anthryl)ethylene triplets appear to present a similar situation except that the progressive increase in  $k_{q,DTBN}^{T}$  along the series Me < Ph < 1N < 9A is considerably more pronounced. For example, on going from Me-9A to 9A-9A triplet, the increase in  $k_{a,DTBN}^{T}$  in toluene is more than 1 order of magnitude. In contrast, on going from anthracene ( $E_{\rm T} = 42.7$  kcal mol<sup>-1</sup>)<sup>18</sup> to tetracene ( $E_{\rm T} = 29$  kcal mol<sup>-1</sup>),<sup>18</sup> the increase in  $k_{\rm q,DTBN}^{-1}$  (in hexane) is only threefold (i.e., from  $1.2 \times 10^7$  M<sup>-1</sup> s<sup>-1</sup> for anthracene to  $3.5 \times 10$  $10^7 \text{ M}^{-1} \text{ s}^{-1}$  for tetracene).<sup>27a</sup> Again, the large values for  $k_{q,\text{DTBN}}$ may be attributed, at least partially, to the torsional distortion in the (9-anthryl)ethylene triplets. An analogous effect has been

noted<sup>28</sup> in the quenching of retinyl and diphenylpolyene triplets by nitroxy radicals. It is noted that  $k_{q,O_2}$ <sup>Ts</sup> for (9-anthryl)ethylene triplets (Table IV) are also larger than that for anthracene triplet, although the difference is not substantial.

In conclusion, the ground-state rotamerism, manifested in the anomalous photophysical behaviors of (2-anthryl)ethylenes (namely, excitation wavelength dependence of fluorescence and exciplex emission spectra and biexponential fluorescence decay), is not exhibited to any significant extent by (9-anthryl)ethylenes in fluid solutions.<sup>29</sup> However, the photoexcitation-induced geometric distortion related with planarity between anthracene and ethylene moieties affects both singlet and triplet properties in significant manners. As far as triplet lifetimes and triplet quenching behaviors are concerned, the effect of distortion about the single bond in (9-anthryl)ethylenes is analogous to, but smaller in magnitude than, that of twisting about the ethylene bond in smaller arylethylenes (e.g., stilbenes and naphthylethylenes).<sup>25</sup>

**Registry No.** Me-9A, 73568-80-6; Ph-9A, 42196-97-4; 1N-9A, 101932-91-6; 9A-9A, 3849-11-4.

(29) At low temperatures and in viscous solutions, excitation wavelength dependent fluorescence spectra have been noted<sup>4,5</sup> for 9A-9A.

# Photophysics, Photochemistry, and Kinetics of Photochromic Fulgides

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Nine different substituted bismethylene succinic anhydrides (fulgides) have been examined by microsecond and nanosecond laser flash techniques. In addition, fluorescence lifetimes have been determined for some fulgides. No triplet transients have been observed and oxygen (vs. nitrogen) has no effect on the spectra, or the kinetics of formation (<1 ns) or disappearance (>400  $\mu$ s) of the colored photoproduct. The relative quantum yield of photocoloration of one fulgide is observed to significantly *increase* with shorter wavelength excitation (266 nm) vs. longer wavelength (355 nm). This is discussed and considered in terms of earlier observations of a *decrease* in the quantum yield of fluorescence with increasing energy of excitation. All data strongly suggest that an excited singlet state of  $\pi,\pi^*$  character is the originating state for photochromism/photochemistry.

## Introduction

Stobbe<sup>1</sup> first discovered the photochromism of some phenylsubstituted bismethylene succinic anhydrides (fulgides) in the solid state. Becker et al.<sup>2</sup> first gave convincing evidence that the photochromism was a molecular phenomenon resulting from the formation of a dihydronaphthalene derivative (eq 1). This was



further confirmed by later studies of Heller<sup>3,4</sup> who demonstrated that the colored form arose by a conrotatory ring closure of the fulgide in accord with the Woodward–Hoffmann selection rules.

It has also been shown by one of  $us^2$  that, for at least two fulgides, the relative quantum yields of fluorescence emission decreased with increasing energy of excitation. There was evidence that this was the consequence of concurrent increased quantum yields of photochemistry for these and other molecular systems.<sup>2,5</sup> However, direct proof of this latter fact was not demonstrated. We now report direct proof of an increase in the quantum yields of photochemistry of one fulgide with increasing energy of excitation (that showed decreases in quantum yields of fluorescence).

To our knowledge, no attempt has been made (1) to characterize the multiplicity nature of the excited state(s) involved, (2) to identify the possible transients in the process and their origin, and (3) to determine kinetic data by microsecond and nanosecond flash techniques.

We thus performed the laser flash studies of nine fulgides (in various solvents at room temperature) which have possible application in optical memory storage, and in chemical actinometry.<sup>6</sup>

### **Experimental Section**

The fulgides have been synthesized as described before.<sup>2</sup> All the solvent used were spectrograde, dried, and kept over 3A

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TABLE I: Spectroscopic and Photochemical Properties of Various Fulgides

	fulgide	solvent	uncolored absorption $\lambda_{max}$ , nm	colored form longest $\lambda_{max}$ , nm
1	α,δ-diphenyl-	hexane	355	460
2	$\alpha, \alpha', \delta'$ -triphenyl	hexane	390	480
3	$\alpha, \alpha'$ -diphenyl- $\delta'$ -o- methoxyphenyl-	hexane	405	470
4	$\alpha, \alpha', \delta'$ -trimethyl-2,5 dimethyl-3-furyl-	toluene	350	$500 \ (\phi_{\rm PC}) = 20\%)$
5	$\alpha, \alpha'$ -dimethyl- $\delta$ -phenyl	hexane	325	470
6	$\alpha, \alpha', \delta, \delta'$ -tetraphenyl-	hexane	410	510
7	$\alpha, \alpha'$ -diphenyl- $\delta'$ -styryl-	hexane	425	500
8	$\alpha$ -phenyl- $\delta$ -piperonyl-	toluene	406	$417^a (\phi_{\rm PC} = 32\%)$
9	$\alpha, \alpha'$ -diphenyl- $\delta'$ - piperonyl-	toluene	420	510

 $^a$  The  $\lambda_{max}$  of the  $\Delta OD$  spectrum is 430 nm (see text). The value above is the true  $\lambda_{max}$  of the fulgide obtained by steady-state experiment.

molecular sieves and used without further purification. Absorption spectra were recorded on a Hewlett Packard 8450 A UV/visible spectrophotometer.

The microsecond laser flash experiments were carried out with a Q-switched Nd:YAG laser (11-ns pulse width). The rise time of the system is  $\sim 0.2 \ \mu$ s. The excitation source was the 355-nm third harmonic. The kinetic absorption spectrometer used to detect OD changes ( $\Delta$  OD) after excitation has been described previously.<sup>7</sup> The output of the laser was 80 mJ and the energy of the beam was controlled by the use of wire mesh screens. The common chosen energies were in the range of 1 to 20 mJ. Typical concentration employed were  $\sim 7 \times 10^{-4}$  M. Monitoring light levels were kept to a minimum by use of a venetian blind shutter.

The solutions were examined in rectangular quartz cell with a 5-mm pathlength along the monitoring light and degassed by bubbling nitrogen during each experiment. Also, oxygen was used to elucidate the presence of triplet excited-state transients.

The nanosecond experiments used the third harmonic generated from a mode-locked Nd:YAG laser (200 ps fwhm,  $\sim 24$  mJ output). The kinetic absorption spectrometer (for detection on the nanosecond time scale) consisted of a continuously operating 150-W xenon arc lamp, two electromechanical shutters, quartz lenses, target cell holder, a Spex Minimate monochromator, and a photomultiplier tube (Hamamatsu R928). Detector output waveforms were processed by a fast Tektronix R 7912 digitizer and computer combination (PDP 11/70). The rise time of the detection system (photomultiplier tube and digitizer) was 1 ns.

Quantum yields of photochemistry,  $\phi_{PC}$ , were generally determined by a comparison method.<sup>8</sup> Benzophenone in benzene ( $\epsilon_{T-T} = 7630$ ,  $\phi_T = 1.0$ )<sup>9</sup> was used as an actinometer.

The  $\phi_{PC}$  of  $\alpha$ -phenyl- $\delta$ -piperonylfulgide was determined by two independent methods:

(1) A steady-state method employing a Cary 15 spectrophotometer was used. A medium-pressure Hg lamp and interference filters were used for irradiation. The  $\phi_{PC}$  was determined by a comparison method using the photochromic fulgide [ $\alpha$ -(2,5-dimethyl-3-furylethylidene)(isopropylidene)succinic anhydride] as the chemical actinometer ( $\phi_{PC} = 0.20$  and  $\epsilon_{494} = 8200$ ).<sup>10</sup>

(2) The  $\phi_{PC}$  was also measured by a laser flash experiment using benzophenone as a reference.

The fluorescence lifetime of the  $\alpha, \alpha'$ -diphenyl- $\delta'$ -styrylfulgide was determined by a photon-counting technique. The excitation was a Nd:YAG mode-locked laser pumping at 532 nm (60-ps pulse) a dye laser containing rhodamine B. The excitation wavelength tuned was 600 nm and then this was frequency doubled



**Figure 1.** Room temperature absorption spectrum of  $\alpha, \alpha', \delta'$ -triphenyl-fulgide in hexane.



**Figure 2.** Transient absorption spectrum ( $\Delta OD$  spectrum) of  $\alpha, \alpha', \delta'$ -triphenylfulgide in hexane recorded 1  $\mu$ s after the 355-nm laser flash.

(average power  $\sim 1 \ \mu$ W). The response time of the photoncounting detection system was 300 ps fwhm.

#### Results

Nine fulgides have been studied with laser flash techniques and all of them underwent photochemistry. Table I gives data on the absorption spectral properties of the fulgides and their photocolored forms.

A.  $\alpha,\delta$ -Diphenylfulgide (1),  $\alpha,\alpha',\delta'$ -Triphenylfulgide (2),  $\alpha,-\alpha'$ -Diphenyl- $\delta'$ -o-methoxyphenylfulgide (3), and  $\alpha$ -(2,5-Dimethyl-3-furylethylidene)(isopropylidene)succinic Anhydride (4). The three fulgides 1, 2, and 3 have been seen to give a colored photoproduct in 2MeTHF at 77 K.<sup>2</sup> Laser flash experiments (11-ns pulse,  $\sim 1-2$  mJ) at room temperature in hexane of those fulgides gave the spectrum of the colored product immediately after the pulse (see Figures 1 and 2). Thus, the colored form was produced in less than 200 ns. The shape of the absorption bands and the maxima of absorption corresponded to the steady-state experiment at 77 K. The red photoproducts were stable to >400  $\mu$ s time scale and their formation was not quenched by oxygen.

We also irradiated (at 355 nm) the  $\alpha$ , $\delta$ -diphenyl- and  $\alpha$ , $\alpha'$ ,- $\delta'$ -triphenylfulgides in hexane with a 200-ps laser pulse. The monitoring wavelengths were 400 and 480 nm respectively and positive  $\Delta$ OD values were obtained immediately after the flash. Thus, the rise time of the colored form was <1 ns as determined by the instrumental rise time. There was no further evolution of the initial OD at 400 nm and 480 to 800 ns. Therefore, from both flash experiments, the colored form arises in <1 ns and is stable to 400  $\mu$ s.

In a previous study, Becker et al.<sup>2</sup> found that, in the case of the  $\alpha, \alpha', \delta'$ -triphenylfulgide and the  $\alpha, \alpha'$ -diphenyl- $\delta'$ -styrylfulgide, the relative quantum yield of fluorescence emission decreased upon excitation into the second electronic transition compared to the

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(10) Heller, H.; Langon, J. J. Chem. Soc., Perkin Trans. 2 1981, 1, 341-343.</sup> 

first. We performed an experiment where two solutions of  $\alpha$ ,- $\alpha', \delta'$ -triphenylfulgide in hexane of identical absorbance at 355 and 266 nm respectively were irradiated with the third and fourth harmonic of the Nd:Yag laser. The energy output was controlled with a wire mesh screen in order to have essentially the same number of photons in both experiments. We determined the relative quantum yield of photocoloration with 355-nm excitation (using benzophenone in benzene actinometry) to that with 266-nm excitation (using biphenyl in hexane actinometry). The ratio of  $\phi_{PC}$  at 266 nm to that at 355 nm was 3:1. The earlier work assigned the decrease in the quantum yield of fluorescence resulting from excitation into the second excited state to be the result of increased photochemistry. This idea was expanded a short time later into a more general quantitative consideration based on vibronic effects in photochemistry.<sup>5</sup> The results found here completely corroborate the idea that the photochemistry is more efficient when excitation occurs to an excited state higher than the lowest one. Moreover, the results are in complete harmony with the mechanism suggested earlier for the decrease in the fluorescence yield that can occur upon excitation into higher excited singlet states whereby photochemistry competes with internal conversion at each step in the vibronic ladder during the relaxation process to the lowest excited singlet state.

The heterocyclic fulgide 4 was studied in toluene. The maximum of absorption and the shape of the band of the photoproduct indicated that we obtained the same photoproduct as in the previous steady-state study<sup>10</sup> in toluene. We determined the  $\phi_{PC}$  by the comparison method using benzophenone in benzene actinometry and found a value of 20% which is in excellent agreement with the earlier steady-state value.<sup>10</sup> No oxygen quenching was observed.

B.  $\alpha, \alpha'$ -Dimethyl- $\delta$ -phenylfulgide (5),  $\alpha, \alpha', \delta, \delta'$ -Tetraphenylfulgide (6), and  $\alpha, \alpha'$ -Diphenyl- $\delta'$ -styrylfulgide (7). The three fulgides 5, 6, and 7 were not seen to be photochromic in 2MeTHF at 77 K<sup>2</sup>, although in another study<sup>6</sup> it was found that the tetraphenyl derivative was photochromic. We were able to detect the colored photoproducts of all three compounds in very low yield in toluene. In order to observe a colored form, the energy of the laser pulse had to be increased to 5–20 mJ which is 5 to 20 times greater than required for the compounds discussed in section A. The principal differences found for these compounds compared to the fulgides examined in section A were a red shift of the longest wavelength band of the colored form (to 500 nm from ~470 nm) and a significantly lower quantum yield for coloration.

No oxygen quenching was observed and the photoproducts were stable to >400  $\mu$ s as observed for the compounds in section A. The emission lifetime of the  $\alpha, \alpha'$  diphenyl- $\delta'$ -styrylfulgide was determined by a photon-counting method in 2MeTHF at 77 K. The excitation wavelength was 300 nm and the fluorescence lifetime was measured in the region of the maximum of fluorescence ( $\lambda = 570$  nm). We found a single exponential decay corresponding to a lifetime of 4.6 ns.

C.  $\alpha$ -Phenyl- $\delta$ -piperonylfulgide (8) and  $\alpha, \alpha'$ -Diphenyl- $\delta'$ -piperonylfulgide (9). The  $\alpha$ -phenyl- $\delta$ -piperonylfulgide (8) ( $\lambda_{max}$  = 406 nm,  $\epsilon_{406}$  = 9500 M<sup>-1</sup> cm<sup>-1</sup>) gave a positive  $\Delta$ OD spectrum immediately after the pulse which reached a maximum 430 nm in toluene (see Figure 4). The small red shift of the absorption maximum of the photoproduct compared to the original fulgide made us believe that formation of the naphthylidene derivative corresponding to the ring closure did not occur and what we observed, in fact, was an E-Z isomerization of the phenyl group.





Figure 3. Absorption spectra of  $\alpha$ -phenyl- $\delta$ -piperonylfulgide in toluene: (a) absorption spectrum, room temperature; (b) absorption spectrum, room temperature, after 5 min of irradiation at 400 nm.



Figure 4. Transient absorption spectrum ( $\Delta$ OD spectrum) of  $\alpha$ -phenyl- $\delta$ -piperonylfulgide in toluene recorded 1  $\mu$ s after the 355-nm laser flash.

conjugated with the chromophore.

In order to obtain an estimation of the quantum yield of E–Z isomerization, we first performed a steady-state experiment in toluene to measure the extinction coefficient of the photoproduct at room temperature (see Figure 3). The photoproduct was found to be stable during the time of the experiment. Since the absorption and of the fulgide and its photoproduct are overlapping, we applied the method of Fischer<sup>11</sup> to determine the extinction coefficient. We found an extinction coefficient of 15 000 (±150) M<sup>-1</sup> cm<sup>-1</sup>. We calculated the quantum yield by two independent methods involving steady-state and flash techniques (see Experimental Section) and found a value of 32% for the quantum yield by both methods. The determination of the  $\phi_{PC}$  was more difficult in the laser flash experiment because the colored form could also be bleached by the laser pulse. Consequently, very low energy pulses of ~0.6 mJ were employed.

As a matter of comparison, we studied  $\alpha, \alpha'$ -diphenyl- $\delta$ -piperonylfulgide in toluene. In this case, a photoproduct was produced in low yield which reached a maximum at 510 nm. This is in good agreement with what would be expected from the formation of the classical colored form since ring closure is now possible with the phenyl ring in the  $\alpha'$ -position.

For both fulgides, no oxygen quenching was found and no decay of the photoproducts occurred over 400  $\mu$ s.

## Discussion

In laser flash experiments, the colored forms generated by ring closure, eq 1, are the same as those seen in steady-state experiments at low or room temperature. Moreover, at least in the case of the  $\alpha$ , $\delta$ -diphenyl and  $\alpha$ , $\alpha'$ , $\delta$ -triphenyl derivatives, the colored form arises in <1 ns and appears not to evolve into a discernibly different form for at least 400  $\mu$ s (based on nanosecond and microsecond kinetic studies). In other cases, the rise time is <0.2  $\mu$ s and no evolution occurs for at least 4000  $\mu$ s. We believe, based on the nanosecond kinetics of the  $\alpha$ , $\delta$ -diphenyl and  $\alpha$ , $\alpha'$ , $\delta$ -triphenyl derivatives, that the colored form of all the compounds studied probably arise in <1 ns. The spectra of the colored forms are

<sup>(11)</sup> Fischer, E. J. Phys. Chem. 1967, 71, 3704-3706.

unaffected by the presence of oxygen (vs. nitrogen). Moreover, the OD changes at any given wavelength are unaffected by the presence of oxygen relative to nitrogen and do not evolve in time up to 400  $\mu$ s. No triplet transients were observed. Also, recall that no phosphorescence has been observed for the compounds studied nor was it possible to sensitize the formation of the colored form of  $\alpha$ , $\delta$ -diphenylfulgide with known triplet sensitizers (at low temperature).<sup>2</sup> The summation of all of these facts strongly suggest that the photochemical ring closure is exclusively initiated in the excited singlet-state manifold.

On the basis of the results of the relative yield of fluorescence and photochemistry as a function of the energy of the excited singlet state initially formed (see section A), it is clear that photochemistry competes with internal conversion among the excited singlet states. Considering this, the rate constant for photochemistry must be of the order of  $10^{11}-10^{13}$  s.

In the case of the  $\alpha$ -phenyl- $\delta$ -piperonylfulgide, E–Z isomerization occurred but no ring closure was observed. This was no affected by the presence of oxygen (vs. nitrogen); therefore, the isomerization process appears to originate exclusively in a sinlet excited state. Recall that the  $\alpha, \alpha'$ -diphenyl- $\delta'$ -piperonyl derivative behaves as all the other fulgides giving a photoproduct resulting from ring closure.

The cyclization reactions have been proposed to occur by  $n,\pi^*$  excitation of one of the carbonyl chromophores in the molecule.<sup>4</sup> Heller et al.<sup>4</sup> found that for the diphenylmethylene(iso-propylidene)-*N*-phenylsuccinimide (a fulgimide) at room temperature in hexane, the change in "sensitivity" of ring closure as a function of exciting wavelength did not relate to the main absorption band of the imide. Furthermore, the wavelength at which the photochemical sensitivity was greatest was partly outside

the main absorption band. However, there is no spectral evidence for an  $n,\pi^*$  transition buried under the main absorption band of the fulgide where the extinction coefficients are far greater than expected for an  $n,\pi^*$  transition. An excitation spectrum done on the  $\alpha, \alpha', \delta'$ -triphenylfulgide in 2MeTHF at 77 K showed the relative fluorescence quantum yield was constant even in the long wavelength portion of the first absorption band and only changed, became lower, in the second transition.<sup>2</sup> Also, the short fluorescence lifetime (4.6 ns) found in the case of the  $\alpha, \alpha'$ -diphenyl- $\delta'$ -styrylfulgide strongly suggests that a state of  $\pi,\pi^*$ character is most likely for the lowest excited singlet state. It would not be expected that the fulgimide would be significantly different. Finally, in the case of the published work<sup>4</sup> where the "sensitivity" varied in the first transition and was finite outside of the absorption, it is not clear, for one thing, whether the variation of the number of exciting photons as a function of input energy at various exciting wavelengths was taken into account (no information was supplied). If this was not considered, this alone could contribute to the observed result.

Based on all of the foregoing, we believe that the photocyclization of the fulgides (succinic anhydride derivatives) is not caused by  $n,\pi^*$  excitation but rather by a  $\pi,\pi^*$  excitation; that is, a  $\pi,\pi^*$  singlet excited state is the originating state for photochemical ring closure. We believe this applies to the fulgimides as well.

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# Emission Properties of Acetaldehyde Vapor in Relation to Photodissociation

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The quantum yield and decay of emission from acetaldehyde vapor at various pressures have been obtained for excitation in the  $S_0 \rightarrow S_1(n\pi^*)$  absorption region from 340 to 270 nm. Excitation energy dependence of the quantum yield and decay of fluorescence varies with pressure. At low pressure (<1 Torr), both the quantum yield and the decay of fluorescence drastically change as the excitation wavelength becomes shorter than a photodissociation threshold which is known to be located near 320 nm. It is shown that the fluorescence characteristics suddenly change at 317 nm; the characteristics correspond to those of a molecule with an intermediate case level structure and to those of a statistical limit molecule with a quasi-continuous level structure respectively for excitation above and below 317 nm. The phosphorescence quantum yield obtained at 10 Torr exhibits a sudden drop when the excitation wavelength is shortened beyond the photodissociation threshold. These results suggest that photodissociation occurs via higher vibrational levels of T<sub>1</sub> reached via intersystem crossing from the initially excited S<sub>1</sub> vibrational level which lies above the threshold energy of the photodissociation.

### Introduction

Aliphatic carbonyl compounds are well-known to undergo photodissociation in low-lying electronically excited states.<sup>1</sup> Photodissociation of acetaldehyde, one of the simplest aliphatic aldehydes, has received special attention in connection with air pollution.<sup>2</sup>

Emission properties of acetaldehyde vapor have also attracted much attention in relation to photodissociation. Parmenter and Noyes investigated the pressure dependence of the emission quantum yield of acetaldehyde vapor, with the excitation wavelength changing from 334 to 253.7 nm.<sup>3</sup> They suggested that

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- (2) See, e.g., Finlayson, B. J.; Pitts, Jr., J. N. Science 1976, 192, 111.

over 99% of the photoexcited molecules relax to the triplet state when excitation is made at the longer wavelengths, and that dissociation from high vibrational levels of  $S_1$  becomes important for excitation at the shorter wavelengths. Their experiments, made at moderately high pressures above 25 Torr, showed that the fluorescence quantum yield is independent of the acetaldehyde pressure. Further, the quantum yield and lifetime of fluorescence which were measured at 10 Torr as a function of the excess vibrational energy in  $S_1^{4.5}$  were both found to decrease monotonously with increasing excitation energy. This merely indicates that nonradiative processes, which may include a dissociation

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