J. Phys. Chem. A **1999,** *103,* 5477−5484

Wavelength- and Isomer-Dependent Photochemistry of Styryl- and (Phenylethynyl)fluorenones

S. J. Weininger,* Y. Ren, Z. Wang, L. Chen, and W. G. McGimpsey*

Department of Chemistry, Worcester Polytechnic Institute, Worcester, Massachusetts 01609

Received: January 12, 1999; In Final Form: May 17, 1999

Fluorenones substituted with *cis*- and *trans*-styryl and phenylethynyl groups at C-1, C-2, and C-4 were synthesized, as were the *trans*-2- and *trans*-4-(3,4-dimethoxystyryl) and β-methyl-2-styryl derivatives. The static absorption and fluorescence spectra of these compounds were measured, as were their redox potentials in acetonitrile. Transient spectra in a range of solvents were obtained on a microsecond time scale. The compounds showed marked solvent-dependent behavior. In solvents of low polarity, the principal photochemical process for the styryl derivatives is cis−trans isomerization via triplet intermediates. In polar solvents, singlet processes become more important, including photoionization from upper excited states. There are also significant regiochemical differences. The triplets from the 2-substituted fluorenones have microsecond lifetimes and λ_{max} values in the 400−500-nm range, indicating that they have a trans configuration. By contrast, 1- and 4-substituted fluorenones give rise to triplets with much smaller lifetimes and λ_{max} values, suggesting that their predominant configuration is perpendicular. There are analogous differences in the spectra of radical ions produced by photoionization. Those from the 2-derivatives have larger λ_{max} values than those from the 1- and 4-derivatives. The photo- and electrochemical data support the thesis that the fluorenone/side-chain interactions are weaker in the 2- than in the 1- and 4-derivatives.

Introduction

The extensive investigations of the photophysics and photochemistry of stilbenes and their analogues[1−3] have spawned a parallel interest in the excited-state behavior of the aromatic and heteroaromatic analogues and homologues of stilbene. For example, it has been shown that numerous styrylarenes undergo rapid intersystem crossing and isomerize in the triplet manifold via a quantum chain process.[4] Others, such as styrylnaphthalene and styrylanthracene, isomerize through the excited singlet state.[5,6] The trans isomer of the latter also participates in a quantum chain cis−trans isomerization via the triplet manifold. Attachment of strongly polarizing (“push−pull”) groups to the arene rings can substantially modify the photochemistry. Singlet pathways involving polar intermediates now become important as evidenced by, inter alia, sizable solvent effects.[1,7,8] Furthermore, when arenes of lower symmetry than benzene are involved, different behavior may be observed among the members of a set of positional isomers.[1,9] If basic sites are present in the molecule, as in styrylpyridines and styrylquinoxalines,[10] then charge and positional effects are both observable. These compounds may also undergo photoelectron transfer, further complicating the task of unraveling their photochemistry.

For all these reasons, the styrylfluorenones (Chart 1) seemed to us interesting molecules in which a variety of photochemical behaviors might be observed. These compounds possess the aromatic carbonyl functionality conducive to rapid intersystem crossing to the triplet manifold; the known large Φ_{ISC} value for fluorenone in nonpolar solvents (>0.99) testifies to this relationship.[11] Also, photoexcited fluorenone is a fairly good electron acceptor,[12] and its carbonyl group is a possible site for protonation. These characteristics might be expected to promote radical ion and/or singlet photochemistry. In fact, we recently reported the photoionization of several styrylfluorenones in acetonitrile solvent.[13] Our evidence, which includes the observation of cation radical transients with microsecond lifetimes, points to an upper excited singlet state as the photoionization precursor. Finally, our data suggest the coexistence of singlet and triplet pathways for cis/trans isomerization in these stilbene-like molecules, a topic of current interest.[14]

We report here a photochemical study of the styryl- and (phenylethynyl)fluorenones shown in Chart 1. (**5** and **6** are synthetic intermediates and are referred to in the Supporting Information.)

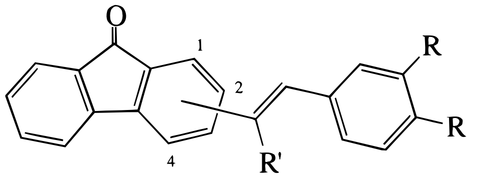
Results

Static Absorption and Fluorescence Spectra. The absorption spectra of the derivatives of **1**, **2**, and **4** (these numbers refer to the position of substitution on the fluorenone ring) exhibit only modest solvent sensitivity, but they do show substantial differences due to regioisomerism (see Table 1). The spectra of the **2** and **4** derivatives resemble the spectrum of fluorenone in the long-wavelength region in that they possess broad, weak bands with maxima between 400 and 500 nm. However, the absorption intensities are considerably greater than in fluorenone itself. There appear to be new bands at shorter wavelengths, with isomer-sensitive positions and intensities, arising from the interaction between the fluorenone and styryl (or phenylethynyl) chromophores. Figure 1 shows the ground-state absorption spectra of fluorenone as well as *trans*-**2** and *cis*-**2** in acetonitrile (MeCN). The spectra in cyclohexane (CH) were similar, although the long-wavelength absorption band exhibited some weak vibrational structure in this solvent.

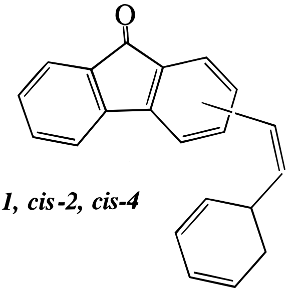
The fluorescence spectra of these compounds in nitrogen-saturated solution are structureless except for those obtained in CH (and methylcyclohexane at 77 K). Each of the isomers exhibits fluorescence with similar spectral band shape, and for the cis and trans isomers of individual regioisomers, the

10.1021/jp990181v CCC: $18.00

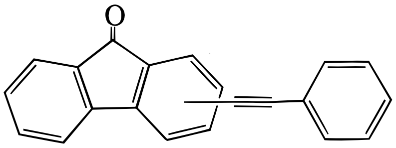
CHART 1



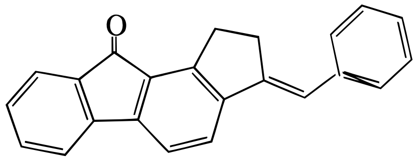
trans-1, trans-2, trans-4 **(R=H; R'=H)**
MeO-2 MeO-4 **(R=OMe; R'=H)**
β-Me-2 **(R=H; R'=Me)**



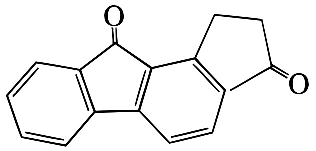
cis-1, cis-2, cis-4



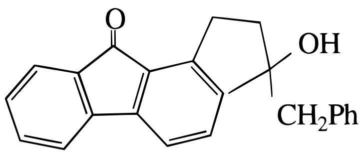
yne-1, yne-2, yne-4



cyclo-2



5



6

TABLE 1: Absorption and Fluorescence Spectral Data and Fluorescence Quantum Yields for Fluorenone Derivatives in Polar and Nonpolar Solvents

	λ_a[a]			λ_f[b]			$10^2\Phi_F$[c]		
compd	CH	PhH	MeCN	CH	PhH	MeCN	CH	PhH	MeCN
trans-**1**	424	425	425	442, 469	466	481	0.14	0.61	1.40
cis-**1**	426	425	425	444, 467	470	482	0.05	0.71	0.91
yne-**1**	420		422	445	470	483	*d*	*d*	0.24
trans-**2**	425		460	482, 506	512	546	7.70	1.60	0.19
cis-**2**	460	459	460	482, 504	511	543	4.80	1.50	0.24
yne-**2**	460	460	459	487	506	516	6.20	5.60	2.10
MeO-**2**	459	461	450	503, 531	542	weak	4.80	0.68	*d*
β-Me-**2**	458	460		477, 504	514	544	6.50	1.80	0.28
cyclo-**2**	462	462	460	503, 533	537	556	3.30	1.70	0.25
trans-**4**	442		460	472	494	512	0.10	0.74	0.77
cis-**4**	421	423	460	475	489	506	0.13	0.63	1.00
yne-**4**	420	423	420	477	488	503	0.09	0.66	1.20
MeO-**4**	432	440	435	492	511	weak	0.44	0.73	*d*

[a] λ_{max} (nm) of the longest wavelength absorption band. [b] λ_{max} (nm) of fluorescence at $\lambda_{ex} = 340$ nm. [c] Fluorescence actinometer was 9,10-diphenylanthracene, $\Phi_F = 0.91$ in CH, $\lambda_{ex} = 340$ nm. [d] $\Phi_F < 10^{-4}$.

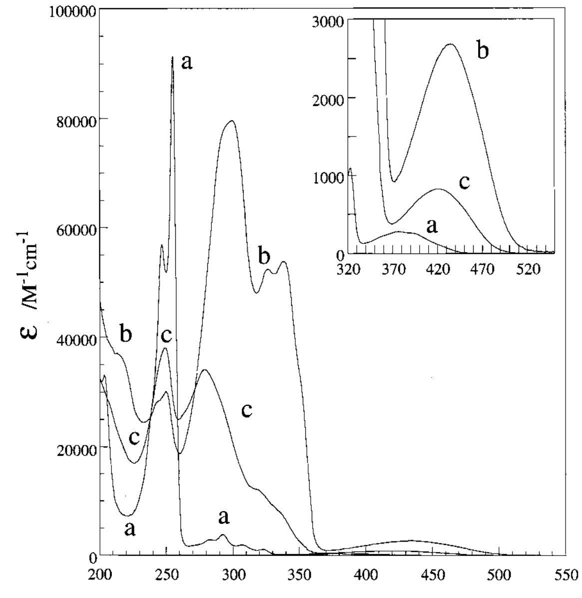


Figure 1. Molar ground-state absorption spectra of fluorenone (curve a), *trans*-**2** (curve b), and *cis*-**2** (curve c) in MeCN. Inset: Detail of the long-wavelength absorption bands.

similarity is even closer. As expected, the fluorescence quantum yields (Φ_F) are low.[15] However, the solvent effect on Φ_F is very much dependent on the regioisomer. For derivatives of **2**, Φ_F *declines* as the solvent polarity rises; for *trans*-**2**, Φ_F decreases from 0.07 in CH to 0.002 in MeCN (Table 1). MeO-**2** and MeO-**4** fluoresce only very weakly in CH_2Cl_2 or MeCN ($\Phi_F < 10^{-4}$). Derivatives of **1** and **4** show the opposite behavior, exhibiting *increasing* Φ_F with increasing solvent polarity.

It is well-known that the solvatochromic shifts of the fluoresence spectra are directly related to the difference in dipole moments between the ground and excited states.[16] The fluorescence shifts we observed on going from CH to MeCN are generally larger for the 2-substituted derivatives than for their 1- or 4-substituted counterparts (Table 2; the glaring exception is yne-**1**). Figure 2 shows the fluorescence emission spectra for *trans*-**2** and *cis*-**2** in CH and MeCN.

TABLE 2: Fluorescence Maxima and Solvatochromic Shifts of Fluorescence Derivatives in CH and MeCN[a]

compd	fluorescence max CH[b]	fluorescence max MeCN	solvatochromic shift
trans-**1**	22,700	20,800	1,900
cis-**1**	22,400	20,500	1,900
yne-**1**	24,700	20,800	3,900
trans-**2**	20,600	18,200	2,400
cis-**2**	20,500	18,400	2,100
yne-**2**	21,300	19,400	1,900
cyclo-**2**	19,900	18,000	1,900
β-Me-**2**	20,600	18,300	2,300
trans-**4**	20,900	19,300	1,600
cis-**4**	21,300	19,900	1,400
yne-**4**	21,300	19,900	1,400

[a] In cm^{-1}. [b] Some spectra exhibit two maxima in CH; in those cases, the longest wavelength maximum is listed and was used to calculate the solvatochromic shift.

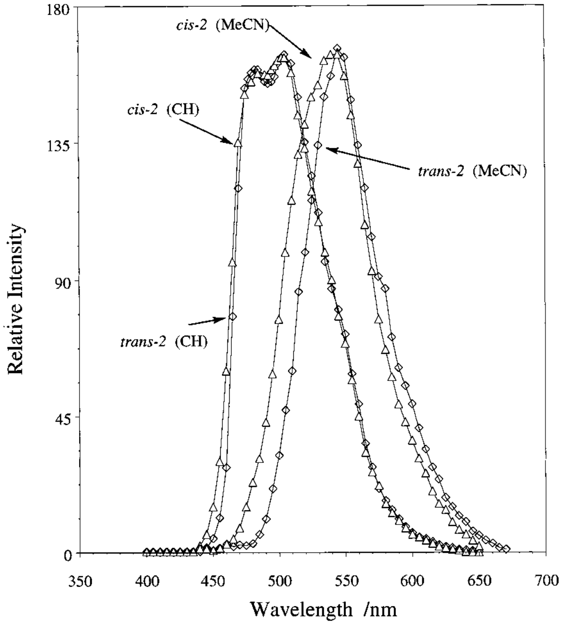


Figure 2. Fluorescence spectra for *trans*-**2** and *cis*-**2** in MeCN and CH.

Different conformational states that are in equilibrium in the ground state could potentially give rise to changes in fluorescence spectra if the equilibrium is not reestablished in the excited state. The existence of such conformers is often reflected in substantial shifts in the absorption spectra and, as a result, in wavelength-dependent fluorescence spectra.[17] However, in all of the compounds studied, excitation at different wavelengths in the region of the onset of the absorption bands did not alter the fluorescence spectra or yields, giving indirect support for the conclusion that the contributions of more than one conformer are not important.

Cyclic Voltammetry. All derivatives of **1**, **2**, and **4** undergo reversible one-electron reduction in MeCN within a narrow range of potentials (Table 3). Thus, *trans*-**2** gives $E_{red} = -1.26$ V in MeCN vs SCE. This is very close to the value obtained for fluorenone itself under similar conditions ($E_{red} = -1.245$ vs SCE in DMF).[18] The values change relatively little with structure, E_{red} varying between -1.26 and -1.36 V, and reduction is always reversible at a sweep rate of 250 mV s^{-1}.

Oxidation, rather, gives more varied behavior. Under conditions that lead to reversible reduction, none of the oxidations is reversible. No reduction peak for the radical cation is obtained[19] even when the solvent is changed to the less nucleophilic CH_2Cl_2 and the sweep rate increased to 1000 mV s^{-1}; only the anodic wave is visible. The oxidation potential is influenced by substituents on the side chain and by the nature of the multiple bond.

TABLE 3: Redox Potentials of Styryl and Phenylethynyl Fluorenones[a]

compd	$-E_{red}{}^{b,c}$	$-E_{1/2}{}^{d}$(red)	$E_{ox}{}^{b}$
trans-**1**	1.30, 1.40	1.35	1.57
cis-**1**	1.30, 1.40	1.35	1.58
yne-**1**	1.25, 1.32	1.29	
trans-**2**	1.24, 1.28	1.26	1.41
5% TFE			1.38
50% TFE			1.28
100% TFE			1.22
cis-**2**	1.29, 1.35	1.32	1.47
yne-**2**	1.24, 1.34	1.29	
MeO-**2**	1.27, 1.39	1.33	1.06
β-Me-**2**	1.30, 1.36	1.33	1.39
trans-**4**	1.32, 1.37	1.34	1.55
cis-**4**	1.32, 1.40	1.36	1.71
yne-**4**	1.18, 1.36	1.27	
MeO-**4**	1.30, 1.41	1.35	1.40

[a] Ca. 1×10^{-3} M. [b] Measured in MeCN vs Ag/Ag^+ with ferrocene as the internal standard, expressed vs SCE. Electrolyte: 0.1 M TBAP. [c] Values are for reduction and oxidation waves, respectively. [d] Approximate.

The E_{ox} value for *trans*-**2**, +1.41 V, is reduced to +1.06 V by the methoxy groups of MeO-**2**. It rises to +1.47 for *cis*-**2** and cannot be detected for yne-**2** even at potentials up to +2.2 V in CH_2Cl_2. The E_{ox} values for *trans*-**2** and MeO-**2** are close to those for the corresponding styrene[20] and 1-(3,4-dimethoxyphenyl)propene,[21] respectively. E_{ox} values could not be obtained for any of the alkynyl derivatives; no oxidation wave is detectable.

We observe a marked solvent effect on the position and intensity of E_{ox} for derivatives of **2**. As Table 3 shows, addition of 5 vol % of 2,2,2-trifluoroethanol (TFE) to an MeCN solution of *trans*-**2** resulted in a lowering of the oxidation potential and a marked decrease in the peak intensity. In 100% TFE, E_{ox} was 0.19 V less positive and the peak intensity only one-quarter of its value in MeCN. Switching from MeCN to TFE also lowered the intensity of the oxidation wave of a ferrocene standard, but less markedly than for *trans*-**2**. TFE also had a pronounced influence on the transient spectrum of *trans*-**2** (vide infra).

Substantial effects on the magnitude of E_{ox} also resulted from changes in the position of attachment of the side chain to the fluorenone ring. The differences between corresponding isomers (cis or trans) of the **2** and **4** series ranged from 0.14 to 0.34 V (Table 3). Oxidation potentials were always higher for the **1** and **4** isomers than for their **2** analogues, paralleling regioisomer differences with respect to the changes of Φ_F with a change in solvent (vide supra).

Thermal Equilibrium and Photostationary Cis/Trans Isomer Distributions. As expected, the trans diastereomer predominates at equilibrium in the ground state of each regioisomer of the unsubstituted styryl derivatives (Table 4). However, it is noteworthy that appreciable quantities of both *cis*-**1** and *cis*-**4** are detected and that *cis*-**1** accounts for one-third of the equilibrium mixture. Thermal equilibrium was established by heating a pure isomer or an isomer mixture in either KSCN/MeCN or KI/DMF until no further change in the isomer ratio could be detected by TLC and NMR (accurate to ±10%).

The pure stereoisomers undergo facile photoisomerization in CH, benzene (PhH), $CDCl_3$, or MeCN when irradiated in a Rayonet reactor with 300-nm lamps under N_2. At 3.5×10^{-4}

TABLE 4: Proportions of the Trans and Cis Isomers of Styrylfluorenones in the Ground and Photostationary States[a]

		photostationary state[b]					
		3.5×10^{-4} M			4×10^{-2} M		
stereoisomer	ground state	CH	PhH	MeCN	$CDCl_3$	PhH	MeCN
trans-**1**	67	40	33	30	29		
cis-**1**	33	60	67	70	71		
trans-**2**	100	65	74	90	100	100	100
cis-**2**	0	35	26	10	0	0	0
trans-**4**	85	32	30	25	30		40
cis-**4**	15	68	70	75	70		60

[a] Relative proportions determined by NMR with $CHCl_2CHCl_2$ as the internal standard. [b] Samples irradiated at 300 nm under N_2 in a Rayonet reactor.

M, mixtures of cis- and *trans*-**2** are found in all solvents, while at 4×10^{-2} M only *trans*-**2** is observed. (As little as 2% *cis*-**2** is potentially detectable.) Furthermore, at 3.5×10^{-4} M, the proportion of *trans*-**2** increases with increasing solvent polarity despite the fact that the extinction coefficient at 308 nm, ϵ^{308}, decreases more rapidly for the cis than for the trans isomer on going from CH to MeCN.

If we had carried out the irradiations with a monochromatic light source, then the ratio of isomerization quantum yields ($\Phi_{c\rightarrow t}/\Phi_{t\rightarrow c}$) would be described by eq 1 for the specific

$$\Phi_{c\rightarrow t}/\Phi_{t\rightarrow c} = (\%_{trans}\epsilon_{trans})/(\%_{cis}\epsilon_{cis}) \qquad (1)$$

wavelength and solvent. We have substituted ϵ^{308} in eq 1 since the maximum output of the lamps used in this study is close to 308 nm. By using the isomer proportions found for the **2** isomer at 3.5×10^{-4} M, we obtain a ratio of 5.6 in CH and 22 in MeCN.

The **1** and **4** isomers exhibit noticeably different behavior. Under photoisomerization conditions, mixtures of the cis and trans isomers are always obtained over the entire concentration range used. In addition, increasing the solvent polarity generally results in small increases in the proportion of cis isomer. When the appropriate photostationary isomer proportions and ϵ^{308} value for the **4** regioisomer are substituted into eq 1, the values obtained are close to unity and show little solvent sensitivity: the ratios were 1.0 and 1.2 in CH and MeCN, respectively.

Transient Absorption Measurements. The fluorescence, CV, and photoisomerization data all indicate strong behavioral differences between the derivatives of regioisomers **1** and **4**, on one hand, and derivatives of **2**, on the other. Differences are also observable in the spectra of the transients generated from these derivatives by laser flash photolysis (LFP).

(a) LFP in Low-Polarity Solvents. LFP of *trans*-**2** in CH at 3×10^{-5} M under N_2 (308 nm, 8-ns pulse, 40 mJ) produces a transient with λ_{max} at 460 nm that is strongly quenched by air (Figure 3, triangles). Essentially the same transient is seen in $PhCH_3$ and CH_2Cl_2 under N_2, and it is again absent in the presence of air. On the basis of its lifetime (several microseconds), air quenchability, and absorption characteristics, we conclude that it is the triplet of *trans*-**2** (^{3}*trans*-**2***).[4] It is significant that these spectra do not vary with the excitation wavelength, since irradiation at 308 nm (excitation to S_n) and at 445 nm (S_1) produces the same transients.

Analogously, irradiation of *cis*-**2** at 445 nm in $PhCH_3$ under N_2 yields a spectrum much like that of ^{3}*trans*-**2*** under the same conditions, with λ_{max} 470 nm. We likewise generated ^{3}MeO-**2*** (λ_{max} 490 nm) and ^{3}yne-**2*** (λ_{max} 430 nm). However, irradiation of β-Me-**2** in CH under N_2 yields a weak absorption with no peak in the 400−500-nm region and only a tail in the UV. The lifetime monitored at 360 nm was 170 ns. Analogous behavior is found for *cyclo*-**2**. There was evidence in both cases of a much longer-lived species that also absorbed at 360 nm.

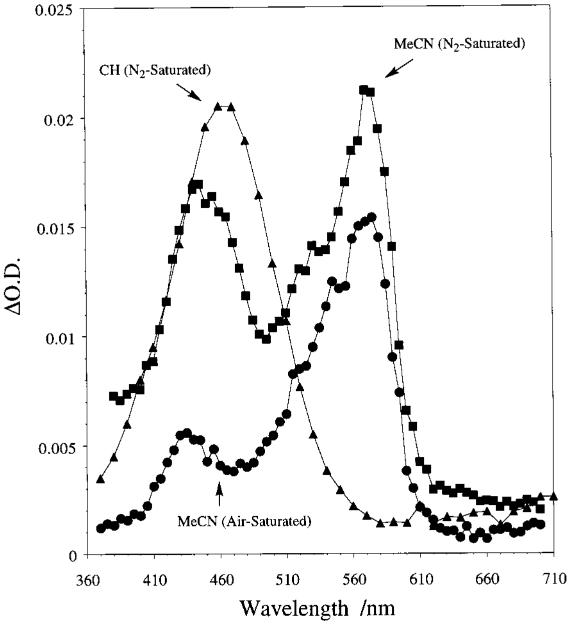


Figure 3. Transient absorption spectra obtained 1 μs following 355-nm LFP of *trans*-**2** in nitrogen-saturated CH (triangles) and MeCN (squares) and air-saturated MeCN (circles).

The alkynes yne-**1** and yne-**4** resemble yne-**2** in giving rise to triplet excited states with microsecond lifetimes. However, the behavior of the styryl-**1** and styryl-**4** compounds is more complex. For example, irradiation of *trans*-**1** at 308 nm in CH under N_2 yields an air-quenchable absorption tail in the UV but no absorption in the 400−500-nm region. By contrast, irradiation of *cis*-**1** under similar conditions yields two air-sensitive transients in the UV, characterized by a long-lived (5-μs) absorption with λ_{max} 370 nm and a much shorter-lived absorption tailing into the 300−400-nm region with $\lambda_{max} < 320$ nm.

Irradiation of *trans*-**4** at 308 nm in CH under N_2 produces a very short-lived transient ($\tau < 100$ ns) with a peak at 370 nm. (There is also an air-insensitive transient absorption in this wavelength region.) Under the same conditions, *cis*-**4** shows only a short-lived UV tail ($\lambda_{max} < 320$ nm; $\tau < 100$ ns).

(b) LFP of *cis*- and *trans*-2 in Polar Solvents. Irradiation of *trans*-**2** at 308 nm in MeCN under N_2 results in production of both ^{3}*trans*-**2*** and a second transient characterized by major and minor absorption bands with λ_{max} 575 and 445 nm, respectively. Figure 3 shows clear evidence for the two transient species. The absorption due to ^{3}*trans*-**2***, which contributes to the intense peak at 460 nm under degassed conditions, is absent when the solution is saturated with air. The residual absorption under air is due to a new transient whose lifetime is unaffected by oxygen. If the transient absorption is monitored at 440 nm, under air-saturated conditions, it is possible to observe both the rapid decay of the quenched triplet ($\tau \ll 1$ μs) and the slower decay of a new transient that has the same lifetime as the 575-nm band ($\tau \sim 3.5$ μs).

A comparison of the transient spectra of *cis*-**2** in air- and N_2-saturated MeCN also clearly shows the presence and differing character of the two transients. The peak in the 575-nm region (565 nm for *cis*-**2**) is present in both spectra, while the 440−450-nm band in the N_2 spectrum is slightly red-shifted relative to the air-saturated spectrum (λ_{max} 430 nm). Once again, the decay lifetimes measured at 430 and 565 nm under air are identical. (Under N_2, the absorption of ^{3}*cis*-**2*** (λ_{max} 470 nm) overlaps the 430-nm peak and causes the observed red shift.)

The following observations establish the radical cation structure of the air-insensitive transient from *trans*-**2**:

(i) The transient can be generated in MeCN but not in less polar solvents.

(ii) Addition of $Bu_4N^+Br^-$ to the MeCN efficiently quenches the transient ($k_q = 3.3 \times 10^9$ M^{-1} s^{-1}), while addition of $Bu_4N^+ClO_4^-$ increases its lifetime, as does addition of ~1% CF_3COOH.

(iii) The transient is not observable in MeOH solvent.

(iv) Irradiation of *trans*-**2** at either 308 nm (excimer laser) or 355 nm (Nd:YAG laser) produces the transient, although with optically matched samples and equal laser pulse energies, the yield is greater at 308 nm. The intensity of the 575-nm absorption is linearly dependent on laser energy. However, irradiation at 445 nm (dye laser; excitation to S_1) yields no transient in air-saturated MeCN, even when the pulse energy exceeds that of the excimer or Nd:YAG lasers.

(v) Addition of 0.1 M 1,4-dicyanobenzene (DCNB) does not increase the transient yield, nor does the irradiation of ^{3}*trans*-**2*** in MeCN in the presence or absence of added DCNB. (Excitation of ^{3}*trans*-**2*** is achieved by sequential two-laser excitation of *trans*-**2** under N_2 using a UV laser to produce ^{3}*trans*-**2*** and a dye laser pulse, tuned to the T−T absorption band, firing 1 μs later to re-excite ^{3}*trans*-**2***.)

(vi) Irradiation of the *trans*-2-styryl-9-fluorenol (a reduction product of *trans*-**2**) in MeCN gave a transient spectrum with a peak at λ_{max} 545 nm. This observation rules out the possibility that our transient is a fluorenol cation radical or a fluorenyl cation derived from the alcohol present as an impurity in *trans*-**2**.[22] (It should also be noted that the alcohol could not be detected in either ^1H or ^{13}C NMR spectra of *trans*-**2**.)

(c) LFP of Other Styryl and Phenylethynyl Derivatives of 1, 2, and 4 in Polar Solvents. All styryl derivatives of **2** give similar transient spectra when photolyzed in air-saturated MeCN. (See table in ref 13.) The similarity of the spectra suggests that the transients have similar conformations, close to those of their precursors. Only MeO-**2** among these compounds is capable of giving rise to a cation radical in CH_2Cl_2 as well.

Due to their high polarity and nonnucleophilicity, fluorinated alcohols are known to be favorable media for generating and studying cationic species.[23] However, excitation of *trans*-**2** in 2,2,2-trifluoroethanol (TFE) at 308 nm under N_2 gives only the spectrum of ^{3}*trans*-**2***; in air, no transient was detectable.

Excitation of the styryl derivatives of **1** and **4** at 308 nm in MeCN also results in generation of air-insensitive transients. The long-wavelength absorption bands of these species are blue-shifted by approximately 60−70 nm relative to the corresponding peaks in the transient spectra of the **2** regioisomers (see ref 13).

No air-insensitive transient could be generated reproducibly in MeCN by irradiation of yne-**2**. However, photolyzed solutions of yne-**2** containing ~1% CF_3COOH in MeCN exhibited a weak transient spectrum, λ_{max} 530 nm, which we tentatively assign to yne-$\mathbf{2}^{\bullet+}$. No air-insensitive transients could be detected in the spectra of yne-**1** or yne-**4** in MeCN with or without added CF_3COOH.

Discussion

Singlet States. The CV data strongly suggest that in the 2-substituted fluorenones, the LUMO is mainly localized in the fluorenone ring. E_{red} varies little with the change in substituent, and the values are only slightly more negative than that for fluorenone itself. Similar reasoning with respect to the E_{ox} values leads to the conclusion that the HOMO is principally localized in the styryl side chain. It follows that the $S_0 \rightarrow S_1$ (HOMO → LUMO) transition should produce a fairly polar excited state, a conclusion supported by the solvatochromic shift data (Table 2). Recent work has placed the dipole moment for S_1 of fluorenone in the range 5.5−6 D.[24] Solvatochromic shifts observed in the fluorescence spectra of *trans*-**2** when combined with this value for the ground-state dipole moment allow the calculation of the S_1 dipole moment, ~15−16 D. The proposed polar S_1 states for these fluorenones are also in accord with the diminution of Φ_F with increasing solvent polarity.

Bérces and co-workers have thoroughly dissected the rates of photophysical processes in fluorenone and 2-substituted fluorenones.[15] The behavior of our 2-substituted fluorenones parallels that of their 2-methoxyfluorenone, in which the substituent is also a good electron donor. Φ_F for the methoxy derivative drops by a factor of 10 as the solvent changes from methylcyclohexane to MeCN. The value of k_{ISC} grows only slightly as the solvent polarity rises, but there is a substantial increase in k_{IC}. The Budapest group theorized that in polar solvents, a polar S_1 state having considerable charge-transfer character is produced and that this charge-transfer state is strongly coupled to upper vibrational levels of the ground state, giving rise to high rates of internal conversion and thus lowering Φ_F. This interpretation gains further support from our observation that the derivative with the most easily oxidized side chain, MeO-**2**, exhibits the most dramatic diminution in Φ_F. Conversely, the derivative with the least oxidizable side chain, yne-**2**, shows the smallest solvatochromic shift and the least diminution of Φ_F.

The CV data also imply that the HOMOs and LUMOs of the 1- and 4-substituted fluorenones are much less localized than those of the 2-derivatives. The E_{red} values are more negative and the E_{ox} are more positive in the 1- and 4-substituted fluorenones. Extending the reasoning just given leads to the conclusion that the excited states of these compounds will be less polar than those of the 2-isomers. A comparison of the relevant solvatochromic shifts supports this conclusion. It is also noteworthy that the values of Φ_F now *increase* with increasing solvent polarity. Bérces and Biczók have found the same trend in fluorenone itself; the principal factor driving this trend is the 35-fold decrease in k_{ISC} as the solvent changes from methylcyclohexane to MeCN, while k_{IC} remains essentially constant.[11] It seems plausible that similar relationships hold for 1- and 4-substituted fluorenones and, by extension, that their S_1 states are not particularly polar.

The inferences drawn about the electron densities in the HOMOs and LUMOs of the various positional isomers will be shown to be consistent with the observations on their triplet transients and on their cis/trans interconversion processes.

While isomerization takes place in the excited triplet state, as outlined below, the similarity of the fluorescence emission band shapes and quantum yields for the cis and trans forms of the regioisomers suggests that isomerization may also occur adiabatically on the excited singlet surface.[6,25] Hence, the spectra measured for the cis and trans isomers may actually be due only to the trans isomer (cis isomers of some stilbene derivatives may have weak emission or are nonemissive[26]). To investigate this possibility, low-temperature (77 K) fluorescence spectra were obtained in methylcyclohexane for *cis*-**2** and *trans*-**2** on the assumption that if the low-temperature matrix is sufficiently rigid, it could prevent isomerization and lead to differences between the isomers. In fact, the spectra obtained were nearly identical to the room-temperature spectra of the corresponding isomers, and there were minor but reproducible differences between isomers. These results suggest that adiabatic isomerization on the excited singlet surface is not a major process. However, it remains a possibility. See Figure 4 in Supporting Information.

Triplet States and Photoisomerization. Most measurements of triplet-state energies rely on "vertical" processes such as energy transfer or phosphorescence. The triplet states involved (spectroscopic triplets) generally resemble the ground states from which they originate or to which they decay, respectively. In the case of alkenes, these states usually have an approximately planar geometry around the double bond. However, it has long been known that the planar configuration does not necessarily represent the energy minimum. In many cases, the planar state is in equilibrium with a twisted or perpendicular state that is comparable or lower in energy.[1]

Previous work has shown that planar triplets, which rapidly attain the more stable trans configuration (^{3}t*), have longer lifetimes (typically $10^1 < \tau_t < 10^3$ μs) and longer wavelength absorption maxima than their perpendicular counterparts (^{3}p*; $10^1 < \tau_p < 10^2$ ns).[4,27] Supporting this generalization is our finding that upon LFP under N_2, the alkyne derivatives yne-**1**, yne-**2**, and yne-**4** generate triplets with microsecond lifetimes and $\lambda_{max} > 400$ nm. These triplets are almost certainly planar and likely have *linear* configurations, by analogy with T_1 of diphenylacetylene.[28]

The styryl derivatives of **2** without double-bond substituents give triplet transients with lifetimes of several microseconds and λ_{max} values between 400 and 500 nm, indicating the presence of ^{3}t*. However, substitution at the β-position of the styryl group (β-Me-**2**, *cyclo*-**2**) results in the disappearance of absorptions attributable to ^{3}t*. Since the now favored ^{3}p* species have short lifetimes and absorb at short wavelengths, they cannot be observed spectroscopically under our experimental conditions.

The substantial localization of the HOMO and LUMO on the side chain and fluorenone ring, respectively, in the 2-styryl derivatives indicates a relatively weak overlap between the p orbitals on C-2 of fluorenone and C-β of the side chain. As the side-chain double bond twists to the perpendicular configuration, the unpaired electron at C-β will depend heavily on the fluorenone ring for conjugative stabilization. If the C-2/C-β overlap is poor, however, there will be little stabilization, driving the equilibrium toward ^{3}t*; this is apparently what happens with ^{3}*cis*- and ^{3}*trans*-**2** and ^{3}MeO-**2**.

K_{pt}, the constant for $^3\text{p}^* \rightleftarrows {}^3\text{t}^*$ equilibration, should also be sensitive to the degree of substitution at C-β. The steric crowding provided by alkyl substituents will destabilize the planar triplets and will thus shift the equilibrium toward ^{3}p*.[27] The absence of signals ascribable to ^{3}t* in the transient spectra of β-Me-**2** and *cyclo*-**2** is in complete accord with this interpretation.

Irradiation of *trans*-**1** and *cis*-**4** generates only air-quenchable end absorption, while *trans*-**4** in CH gives rise to a very short-lived transient (λ_{max} 370 nm; $\tau < 100$ ns). We infer from the absence of long-lived absorption in the 400−500-nm range that the $^3\text{p}^* \rightleftarrows {}^3\text{t}^*$ equilibrium for these transients is shifted heavily toward ^{3}p*. Since the CV measurements indicate a significant degree of interaction between HOMOs and LUMOs of the side chain and those of fluorenone at the 1- and 4-positions, stabilization of the unpaired electrons in ^{3}p* would be significant.

Irradiation of *cis*-**1** at 308 nm in CH is somewhat anomalous; an air-quenchable transient with a relatively long lifetime ($\tau \sim 5$ μs) is observed, but its absorption is strongly blue-shifted (λ_{max} 370 nm) with respect to the triplets of *trans*-**2** and *cis*-**2**. These data may signal that a new photochemical process has occurred, or it may simply be the case that λ_{max} values vary substantially as a function of substituent position, as happens with styrylanthracene triplets.[29]

Because a broad-band light source was used in our photoisomerization studies, conclusions cannot be drawn from the individual trans/cis ratios. However, there are trends that do have significance. The result that for the 2-isomer this ratio increases with increasing concentration (Table 4) points toward a quantum chain process.[4] This process requires the long-lived ^{3}t* intermediate, the presence of which was established by LFP. By contrast, there is no evidence suggesting such a quantum chain process for the 1- and 4-isomers, which according to the LFP data isomerize by way of the short-lived ^{3}p*.

It is likely that in solvents of low polarity, where Φ_{ISC} is high for fluorenones,[15] all styrylfluorenones isomerize mainly, if not exclusively, via a triplet pathway. It is also likely that for the 1- and 4-styrylfluorenones this is the predominant mechanism in polar solvents as well, since the approximate $\Phi_{c\rightarrow t}/\Phi_{t\rightarrow c}$ ratios are solvent-insensitive. Similar suggestions have been made in other systems.[30] By contrast, $\Phi_{c\rightarrow t}/\Phi_{t\rightarrow c}$ for 2-styrylfluorenone is markedly larger in MeCN than in CH. This trend is in accord with the presumption that polar states play a role in isomerization of 2-styrylfluorenone in polar solvents.[31] This hypothesis is supported by a variety of other evidence, indicating that the 2-isomers have the most polar excited states. It thus seems possible that singlet states play a part in the photoisomerization of these isomers in polar solvents.

The Tsukuba group has shown that in styrylarenes the relative energies of the two triplet conformations and of the equilibrium constant, K_{pt}, are a function of the triplet energy of the arene itself.[4] If it is assumed that fluorenone behaves like an arene, its triplet energy (53 kcal/mol[32]) would put it in a "borderline" region in which both intermediates are present in significant amounts. Our results show that the equilibrium is affected not only by the triplet energy of the arene but also by the point of attachment of the styryl group as well; they make an interesting comparison with styrylphenanthrene studies in which different points for the styryl group attachment led to different photoisomerization mechanisms.[33]

Radical Cations. Irradiation of all the styryl derivatives gives rise to the relatively long-lived absorptions consistent with radical cations. The fact that the lifetimes of the transient absorptions are decreased by addition of $Bu_4N^+Br^-$ (nucleophilic quenching) and increased in the presence of $Bu_4N^+ClO_4^-$ (salt effect) and CF_3COOH argues convincingly for the cationic nature of the transients. The formation of radical cations is clearly a result of ionization from an upper excited state since excitation at 445 nm ($S_0 \rightarrow S_1$) produces no transient other than the triplet state. Furthermore, when optically matched samples of *trans*-**2** are irradiated at 308 and 355 nm, greater radical cation absorption is observed for the 308-nm sample, reflecting the greater energy available for ionization. The inability of DCNB to increase the radical ion yield is also consistent with photionization from an upper excited state, S_n, since its lifetime would be too short to allow for bimolecular processes.

The absorbance at $\lambda \sim 570$ nm is directly proportional to the laser intensity, suggesting that ionization is monophotonic. The singlet character of the ionization precursor is confirmed by our failure to detect an increase in the radical cation yield following irradiation of ^{3}*trans*-**2*** by a second laser pulse in the absence or presence of DCNB.

The lack of an air-insensitive transient following excitation of *trans*-**2** in TFE may appear inconsistent with our assignment of a radical cation structure, given the ability of TFE to stabilize radical cations.[23] However, TFE also has a marked effect on the CV of *trans*-**2** (see Table 3), reducing both the oxidation potential and the peak current. Such behavior is characteristic of a radical cation that is becoming less stable.[34] Unlike most radical cations generated in solution, *trans*-$\mathbf{2}^{\bullet +}$ and its precursor are both capable of hydrogen bonding with the solvent. Such hydrogen bonding would increase both the oxidation potential of the starting material and the electrophilic reactivity of the radical cation. Either or both effects could account for our failure to observe the radical cation spectrum in TFE.

Photoionization of the alkynyl derivatives appears more difficult than that of the styryl compounds, only yne-$\mathbf{2}^{\bullet +}$ being detected. However, whether radical cations are produced in low yields or simply have very short lifetimes is not clear. Either explanation is compatible with both the lack of radical cation transient absorption and our inability to detect these species electrochemically.

The $\lambda_{\max}$ values for the radical cations derived from *trans*-**2**, β-Me-**2**, and *cyclo*-**2** are virtually identical, and those for *cis*-**2** and MeO-**2** are very similar. We conclude that all the cations have the same geometry, presumably planar trans, and/or that the electron deficiency is concentrated in the styryl side chain. The latter explanation is supported by the similarity of the oxidation potentials of *trans*-**2** and *cis*-**2** to those of substituted styrenes[20] and that of MeO-**2** to that of 1-(3,4-dimethoxyphenyl)-propene.[21] AM1 calculations indeed show that the lowest energy conformation of the radical cation of *trans*-**2** is trans-planar. They also indicate that the HOMO from which the electron is removed to form the radical cation has a node at the carbonyl group and a large fraction of its electron density in the styryl side chain. This explains nicely the CV results, particularly the ease of oxidation of the styryl-**2** compounds. Finally, the LUMO has considerable electron density at the carbonyl group so that one would expect a sizable polarity difference between the fluorescing excited state and the ground state. This expectation meshes with the empirical solvatochromic shifts.

Our proposal for radical cation formation is supported by numerous examples of styrylarene photoionization in polar solvents. Styrylnaphthalenes,[35] (pyridylethenyl)naphthalenes,[35] and styrylphenanthrenes[9] all undergo monophotonic ionization when irradiated in MeCN at λ 350 nm, while styrylanthracenes undergo biphotonic ionization under similar conditions.[29] Of particular interest are recent reports of photoionization of benzophenone in aqueous solution and of a variety of aromatic ketones in SDS micelles from upper excited states.[36,37] Due to the difficulty of generating ketone radical cations, it is not surprising that these are biphotonic processes. (Such species are usually produced by photooxidation and tend to be highly reactive.[38]) Given that the photoionization of these aryl ketones is usually biphotonic, the monophotonic ionization of the styrylfluorenones may seem anomalous. However, a general theoretical study of the radical cations of carbonyl compounds concluded that while most would have a Σ ground-state configuration, the exception was cyclopentadienone, for which a Π ground state was predicted.[39] Since fluorenone can be considered a derivative of cyclopentadienone, it is likely that the styrylfluorenones in this study also have Π ground states, especially as these would be further stabilized by the styryl side chains. The relative longevity of the observed transients is in accord with such a conclusion.

It is possible to rule out a twisted intramolecular charge-transfer (TICT) state[40] as the species responsible for these long-lived absorptions. Investigations of “push−pull” stilbenes[41] and our own calculations strongly suggest that a TICT state of the styrylfluorenones would be formed by rotation around the styryl−fluorene single bond. However, long-lived transients similar to that observed for *trans*-**2** were also detected for *cyclo*-**2**, a compound for which the expected bond rotation is not structurally possible. In addition, while calculations based on known redox potentials and excitation energies indicate that the TICT state of *trans*-**2** would lie slightly above S_1, it would have an energy lower than S_1 for MeO-**2**. Yet no long-lived transient was observed following 445-nm excitation into the S_1 state of MeO-**2**.

Experimental Section

Materials. All solvents used in the photochemical experiments were “spectrophotometric” or “HPLC” grade and were used as received.

Absorption and Emission Spectroscopy. Ground-state absorption spectra were obtained with a Shimadzu 2100U absorption spectrometer. Fluorescence emission spectra and quantum yields were measured with a Perkin-Elmer LS-50 spectrofluorimeter. Yields were measured using anthracene ($\Phi_F = 0.27$) and/or 9,10-diphenylanthracene ($\Phi_F = 0.91$) in CH as standards.[42]

Laser Flash Photolysis. The laser flash photolysis system used in this study has been described previously.[43] Briefly, samples were irradiated with the output of a frequency-tripled continuum “Surelite” Nd:YAG laser (355 nm; <50 mJ/pulse; 6 ns), a Lumonics EM 510 excimer laser (308 nm; <40 mJ/pulse; 8 ns), or a Candela SLL 250 flashlamp-pumped dye laser (445 nm; <70 mJ/pulse; 400 ns). In the two-laser experiments performed, the transient species produced by the first UV pulse were excited after a short (ca. 1-μs) delay by the flashlamp-pumped dye laser. Most samples (optical density was less than 0.7) were contained in a specially constructed 7 × 7 mm^2 quartz flow cell. The solution was caused to flow from a reservoir through the cell by the action of a peristaltic pump, thus ensuring that each laser pulse irradiated a fresh volume of sample. Some samples were irradiated under “static” conditions, also in a 7 × 7 mm^2 cell. In those experiments that were run under “nitrogen-saturated” conditions, air was removed by constantly bubbling a stream of dry nitrogen through the reservoir. “Air-saturated” experiments were run without nitrogen bubbling.

Ground- and Excited-State Isomerization. The trans/cis isomer ratio for each regioisomer was determined by ^{1}H NMR. Peaks characteristic of each isomer are as follows (ppm): *cis*-**1**, 6.85 (d); *trans*-**1**, 8.45 (d); *cis*-**2**, 6.59 (br s); *trans*-**2**, 7.09 (d); *cis*-**4**, 6.85 (s); *trans*-**4**, 7.07 (d). The trans/cis ratios were calculated by integrating each peak at least three times and comparing its area to that of the proton signal from an internal standard, $CHCl_2CHCl_2$.

The thermal isomerization studies were carried out by dissolving the styrylfluorenone, either a pure isomer or a mixture of isomers, in MeCN or DMF (3.5×10^{-3} M) containing a small amount of KSCN or KI, respectively. The solutions were heated at reflux until no further change could be detected. The solvent was removed under reduced pressure and the sample dissolved in $CDCl_3$ for isomer ratio determination. Photoisomerizations were conducted at ambient temperature in Pyrex tubes in a Rayonet reactor equipped with 300-nm lamps. Samples of styrylfluorenones, either pure isomers or mixtures, were dissolved in various solvents at the concentrations shown in Table 4. N_2 was bubbled through the solutions prior to irradiation. The irradiation was stopped when no further change in the trans/cis ratio could be detected. Solvents were removed under reduced pressure and the residues dissolved in $CDCl_3$. (Irradiations of $CDCl_3$ solutions were carried out directly in NMR tubes.) The ^{1}H NMR spectra were scanned for evidence of other photochemical processes. TLC analysis was also used. The styryl-**2** compounds were photostable; the styryl-**1** and styryl-**4** isomers underwent a small amount of photodecomposition after 0.5 h of irradiation. Irradiation under air intensified the extent of photodecomposition.

Cyclic Voltammetry. CVs were measured with a Princeton Applied Research Model 273 potentiostat. The fluorenone derivatives were dissolved in N_2-saturated MeCN (Aldrich spectrophotometric grade) containing 0.1 M $Bu_4N^+ClO_4^-$. Potentials were measured vs SCE with working and counter electrodes of Pt wire, at a sweep rate of 250 mV/s. Under these conditions, $E_{1/2}$ for fluorenone is -1.30 V (lit.[18] -1.245 V in DMF).

Syntheses. General Methods. ^{1}H NMR spectra were recorded on a Bruker ACE 200 (200-MHz) NMR spectrometer. ^{13}C spectra were recorded on the same instrument at 50.3 MHz. Melting points (mp) are uncorrected. Elemental analyses were performed by Quantitative Technologies, Inc., Whitehouse, NJ. Flash chromatography was performed on SiO_2 (J. T. Baker, 40 μm) under a positive pressure of air. Descriptions of the syntheses are provided in supporting information.

Supporting Information Available: Synthetic details for all of the styryl- and phenylethynylfluorenones. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Görner, H. *J. Photochem. Photobiol. A* **1988**, *43*, 263−289. (b) Görner, H.; Kuhn, H. J. *Adv. Photochem.* **1995**, *19*, 1−117.

(2) (a) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415−436. (b) Meier, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1399−1420.

(3) (a) Saltiel, J.; Chang, D. W. L.; Megarity, E. D.; Russo, A. D.; Shannon, P. T.; Thomas, B.; Uriarte, A. K. *Pure Appl. Chem.* **1975**, *41*, 559−579. (b) Saltiel, J.; Charlton, J. L. In *Rearrangements in Ground and Excited States;* de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 25.

(4) (a) Arai, T.; Tokumaru, K. *Chem. Rev.* **1993**, *93*, 23−39. (b) Arai, T.; Tokumaru, K. *Adv. Photochem.* **1995**, *20*, 1−57.

(5) Saltiel, J.; Eaker, D. W. *Chem. Phys. Lett.* **1980**, *75*, 209.

(6) Saltiel, J.; Zhang, Y.; Sears, D. F., Jr. *J. Am. Chem. Soc.* **1997**, *119*, 11202 and references therein.

(7) (a) Gilabert, E.; Lapouyade, R.; Rullière, C. *Chem. Phys. Lett.* **1988**, *145*, 262−268. (b) Gruen, H.; Görner, H. *J. Phys. Chem.* **1989**, *93*, 7144−7152.

(8) Sun, L.; Görner, H. *Chem. Phys. Lett.* **1993**, *208*, 43−48.

(9) Aloisi, G. G.; Elisei, F.; Görner, H. *J. Phys. Chem.* **1991**, *95*, 4225−4231.

(10) (a) Mazzucato, U. *Pure Appl. Chem.* **1982**, *54*, 1705. (b) Galiazzo, G.; Bortolus, P.; Gennari, G. *Gazz. Chim. Ital.* **1990**, *120*, 581−585.

(11) Biczók, L.; Bérces, T. *J. Phys. Chem.* **1988**, *92*, 3842−3845.

(12) Gersdorf, J.; Mattay, J. *J. Photochem.* **1985**, *28*, 405−411.

(13) Wang, Z.; McGimpsey, W. G.; Ren, Y.; Weininger, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 7925−7926.

(14) Reference 1b, p 91.

(15) Biczók, L.; Bérces, T.; Márta, F. *J. Phys. Chem.* **1993**, *97*, 8895−8899.

(16) For a review, see: Baumann, H.; Bischof, H.; Fröhling, J.-C.; Brittinger, C.; Rettig, W.; Rotkiewicz, K. *J. Photochem. Photobiol. A* **1992**, *64*, 49−72.

(17) For example, see: Mazzucato, U.; Momicchioli, F. *Chem. Rev.* **1991**, *91*, 1679−1719.

(18) Andrieux, C. P.; Gélis, L.; Medebielle, M.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1990**, *112*, 3509−3520.

(19) Arnold, D. R.; Du, X.; Henseleit, K. M. *Can. J. Chem.* **1991**, *69*, 839−852.

(20) Arai, T.; Sakuragi, H.; Tokumaru, K.; Kobayashi, T. *Denki Kag. Kog. But. Kag.* **1982**, *50*, 201−202.

(21) O'Connor, J. J.; Pearl, J. A. *J. Electrochem. Soc.* **1964**, *111*, 335.

(22) McClelland, R. A.; Mathivanan, N.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 4857−4861.

(23) Das, P. K. *Chem. Rev.* **1993**, *93*, 119−144.

(24) Rani, S. A.; Sobhanadri, J.; Prasado Rao, T. A. *Spectrochim. Acta A* **1995**, *51*, 2473−2479.

(25) For example, see: Sandros, K.; Becker, H.-D. *J. Photochem. Photobiol. A* **1988**, *43*, 291.

(26) For example, see: Saltiel, J.; Waller, A.; Sun, Y.-P.; Sears, D. F., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 4580 and references therein.

(27) Lazare, S.; Bonneau, R.; Lapouyade, R. *J. Phys. Chem.* **1984**, *88*, 18−23.

(28) Hiura, H.; Takahashi, H. *J. Phys. Chem.* **1992**, *96*, 8909−8915.

(29) Görner, H.; Elisei, F.; Aloisi, G. G. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 29−34.

(30) For example, see: Görner, H. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 4027−4033.

(31) Reference 1b, pp 16−20.

(32) Gordon, A. J.; Ford, R. A. *The Chemist's Companion;* Wiley-Interscience: New York, 1972; p 350.

(33) Aloisi, G. G.; Elisei, F. *J. Phys. Chem.* **1990**, *94*, 5813−5818.

(34) Bard, A. J.; Ledwith, A.; Shine, H. *Adv. Phys. Org. Chem.* **1976**, *13*, 155−278, 200−201.

(35) Aloisi, G. G.; Elisei, F.; Latterini, L. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2139−2145.

(36) Elisei, F.; Favaro, G.; Görner, H. *J. Photochem. Photobiol. A: Chem.* **1991**, *59*, 243−253.

(37) Ishiwata, N.; Murai, H.; Kuwata, K. *J. Phys. Chem.* **1993**, *97*, 7129−7131.

(38) Akaba, R.; Kamata, M.; Kuriyama, Y.; Sakuragi, H.; Tokumaru, K. *Chem. Lett.* **1993**, 1157−1160 and references therein.

(39) Nakano, T.; Morihashi, K.; Kikichi, O. *THEOCHEM* **1992**, *253*, 161−166.

(40) Rettig, W. *Angew, Chem. Int. Ed. Engl.* **1986**, *25*, 971−988.

(41) Lapouyade, R.; Kuhn, A.; Letard, J.-F.; Rettig, W. *Chem. Phys. Lett.* **1993**, *208*, 48−58.

(42) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993; pp 7, 9.

(43) (a) Smith, G. A.; McGimpsey, W. G. *J. Phys. Chem.* **1994**, *98*, 2923−2929. (b) Wang, Z.; Weininger, S. J.; McGimpsey, W. G. *J. Phys. Chem.* **1993**, *97*, 374−379.