

Photochemistry and Photoinitiation Activity of Radical Polymerization of 2-Substituted Anthraquinone Derivatives. III. Nanosecond Laser Flash Photolysis Study

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SYNOPSIS

A nanosecond laser flash photolysis study was undertaken on a selected range of 2-substituted anthraquinone derivatives and the data are discussed in relation to the photoactivities in industrial photopolymerization. All the compounds give rise to a triplet-triplet absorption that is quenched by ground-state molecular oxygen. The transient half-lives range from 0.64 to 11.3 μs of which the 2-(1,1-dibromomethyl)anthraquinone exhibits the longest lifetime. In a reductive solvent, 2-propanol, hydrogen atom abstraction takes place with the compounds having the lowest-lying triplet $^3n\pi^*$ state, whereas those with a low-lying triplet $^3\pi\pi^*$ state show mixed kinetics. In the latter case, a disproportionation reaction involving the semianthraquinone radical may be taking place, competing with the direct hydrogen atom abstraction reaction. In addition, investigation of the halogenated derivatives has indicated the possibility of the corresponding halo radicals being formed. In the presence of a tertiary amine, triethylamine, all anthraquinone derivatives show the formation of stable species related to either the exciplex or the radical ion pair. The extent of exciplex formation is more effective with compounds possessing a lowest-lying triplet $^3\pi\pi^*$ excited state than those with a triplet $^3n\pi^*$ excited state. The results from the nanosecond laser flash photolysis study show the differences in behavior toward hydrogen atom abstraction and electron transfer processes that is dependent on the nature of the low-lying triplet state and the type of substituent present, i.e., electron-donating or electron-withdrawing.

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INTRODUCTION

The photochemistry of anthraquinone (AQ) and its derivatives has been extensively studied in relation to their applications in the dye industry.¹⁻⁴ Their roles are widespread and include the following possibilities of application: as photosensitizers, that is, they phototenderize cellulose materials and photosensitize the oxidation of large number of substrates; as photocatalysts for solar energy processor; and as photoinitiators²⁻⁵ for the photopolymerization of

various monomers and prepolymers. This latter role is gaining more importance in the field of radiation curing since the 2-substituted derivatives of anthraquinone are capable of undergoing photochemical reactions from their lowest excited triplet state through the use of visible light.⁶ The mechanisms by which photopolymerization on photocrosslinking occurs are not completely clear at present, although they are believed to undergo photoreduction by either electron or hydrogen atom abstraction to produce radicals that take part in the crosslinking of a prepolymer or a polymer system.

In parts I and II,^{1,2} the photochemical and photoinitiation properties of the fifteen 2-substituted anthraquinone derivatives have been established

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through luminescence and real-time IR spectroscopy, conventional microsecond flash photolysis, and differential scanning photocalorimetric studies. The investigations indicate the photoactivity of the 15 derivatives to be dependent on the nature of the lowest excited triplet state, vis., triplet ${}^3n\pi^*$ or ${}^3\pi\pi^*$ excited state, and the conditions used for photopolymerization.²

In part III, we have undertaken a detailed nanosecond laser flash photolysis study of a selected number of the 15 anthraquinone derivatives (refer to Scheme 1). The transient species produced are characterized and their behavior examined in the presence of a reductive solvent, 2-propanol or a tertiary amine, triethylamine. The mechanism by which the radicals are produced for the photopolymerization reaction is discussed in terms of the particular nature of these transient species that the derivative produces, which in turn is influenced by the type of substituent present at the 2-position depending on their electron-donating or electron-withdrawing effect. Steady-state photolysis studies have also been undertaken on 2-substituted halo-derivatives, and the products were identified by mass spectrometry to ascertain the possible role of the halogen radical in our photoinduced polymerization work.

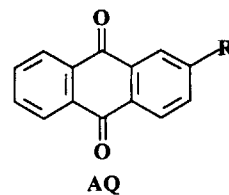
EXPERIMENTAL

Materials

A full list of the derivatives are cited elsewhere,^{1,2} although for this study the selected range of the 2-substituted anthraquinone derivatives are listed in Scheme 1: 2-(1,1-dibromomethyl) (AQ2), 2-(1,1,1-trichloromethyl) (AQ3), 2-chloroamido (AQ6), 2-(2-ethyl)hexylamido (AQ7), 2-(octadecyl-8-ene)amido (AQ8), 2-ethoxyamido (AQ9), 2-(*N-n*-hexyl)methylamido (AQ11), 2-methylcarboxy (AQ12), and 2-(*N,N*-diethyl)amidooxyanthraquinone (AQ15) were all supplied by the Fine Chemicals Service of Zeneca Specialties (Blackley, Manchester, U.K.) and used as received. All solvents were of HPLC grade along with triethylamine were obtained from Aldrich Chemical Co. Ltd., U.K. and were distilled before use.

Nanosecond Laser Flash Photolysis

Nanosecond laser flash photolysis experiments were carried out using frequency-tripled neodymium laser (J.K. Laser Ltd.) that delivered 15-ns pulse at 355-nm irradiation of <10-mJ energy. Transient ab-



- AQ2. R= -CHBr₂
 AQ3. R= -CCl₃
 AQ6. R= -NH-C(O)Cl
 AQ7. R= -NH-C(O)-CH(CH₂CH₃)(CH₂CH₂CH₂)CH₃
 AQ8. R= -NH-C(O)-(CH₂)₇CH=CH(CH₂)₇CH₃
 AQ9. R= -NH-C(O)-O-CH₂CH₃
 AQ11. R= -N(C(O)-CH₃)((CH₂)₅CH₃)
 AQ12. R= -C(O)OCH₃
 AQ15. R= -O-C(O)-N(C₂H₅)₂

Scheme 1

sorption changes were measured by illuminating the quartz cell (1 cm path length) with light from a pulsed xenon lamp. Wavelength selection was achieved with a diffraction grating high irradiance monochromator with a 10-nm bandwidth. Kinetic changes in the light signal at preselected wavelengths were detected and amplified using a Hamamatsu R1477 photomultiplier before collection by a Hewlett Packard 250-MHz digital storage oscilloscope (HP54510A). Data acquisition and processing were carried out using a Hewlett Packard 9000 series 3.0 computer. Time-resolved spectra were obtained by repeating the above procedure at successive wavelengths.⁷ Solutions ($A_{355\text{ nm}} = 0.5$ or $1.0, 10^{-4}M$) were degassed under white spot nitrogen or oxygen for triplet quenching studies for 40 min before use.

Preparative Irradiation

Direct UV irradiation were conducted in a Pyrex immersion reaction well (500 mL) fitted with a water cooling jacket at $20 \pm 2^\circ\text{C}$ and a nitrogen gas inlet. The derivative, 2-(1,1-dibromomethyl)anthraquinone (AQ2), was irradiated in methanol solution (30 mg in 300 mL) with a medium pressure UV lamp (Hanau TQ 150W) that was placed at the bottom of the cooling jacket. The solution was degassed for 20 min before irradiation to ensure total absence of oxygen. Samples were taken from the reaction well at different times for analysis by HPLC.

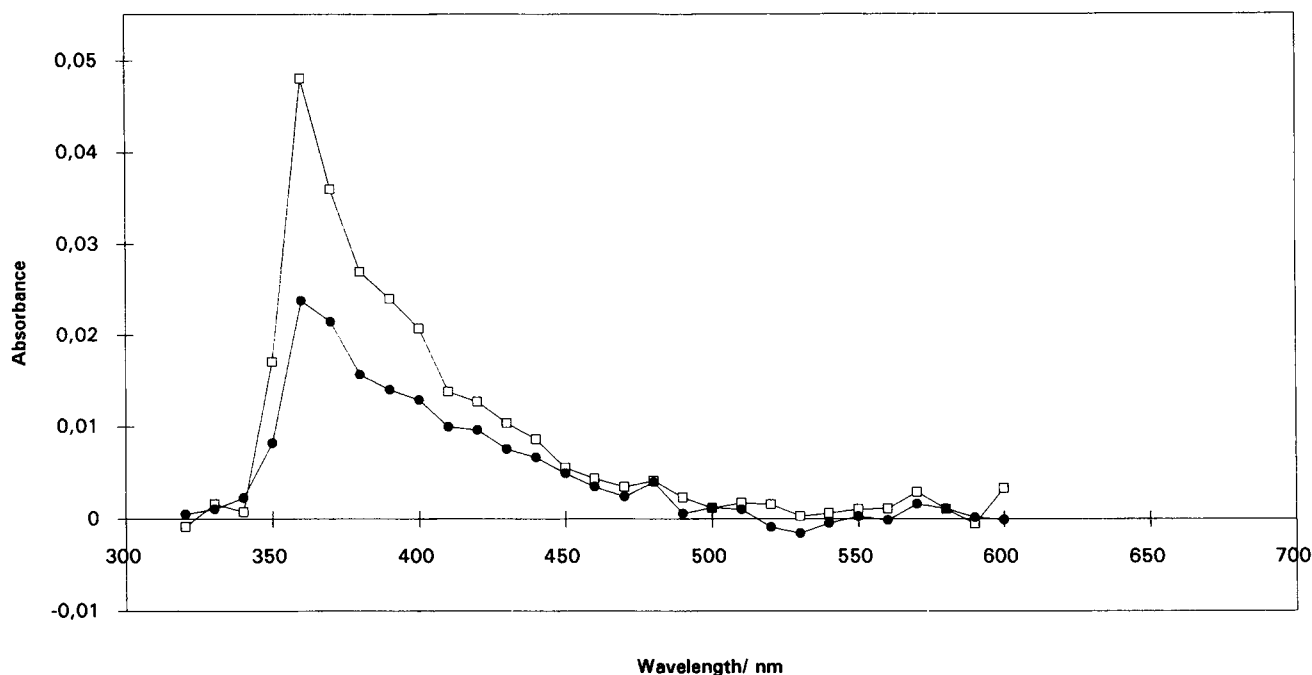


Figure 1 End-of-pulse transient absorption spectra produced on nanosecond laser flash photolysis of 2-(1,1-dibromo)anthraquinone (AQ2, $10^{-4}M$) at (□) 0.9–1.0 μs and (●) 36 μs delay in nitrogen-saturated acetonitrile.

High-Performance Liquid Chromatography Analysis

Qualitative analysis of the photoproducts by HPLC were performed on a model M-45 Waters High Pressure Pump with a Rheodine injector and UV-vis Detector Spectra-Physics model 100, using 254 nm as the detection wavelength. The data were collected and analyzed using DBase software from Waters. A reverse-phase column 15 cm long (5 μm , Lichrosorb, Merck RT-125-4) was selected for this particular study, and elution was achieved with methanol/water, 70 : 30 v/v as the mobile phase. The retention time of 2-(1,1-dibromomethyl)-anthraquinone (AQ2) was 16 min using a constant flowrate of 1.0 mL/min.

RESULTS AND DISCUSSION

The selected range of 2-substituted anthraquinone derivatives (Scheme 1) have been separated into three groups^{1,2} according to the characteristic triplet emission observed through phosphorescence studies. Hence, those of the triplet ${}^3n\pi^*$ excited state are AQ 2, 3, 11, 12, and 15, whereas those with triplet ${}^3\pi\pi^*$ excited states are represented by AQ 7–9. Derivative AQ 6 has shown mixed low-lying triplet states of both ${}^3n\pi^*$ and ${}^3\pi\pi^*$ configurations. The

remainder of this article refers to the collective group of compounds as mentioned above.

Transient absorption spectra of the selected range of 2-substituted anthraquinone derivatives in acetonitrile under anaerobic conditions are shown in Figures 1–9 and are grouped according to the nature of their triplet excited state. Hence, Figures 1–5 represent spectra of triplet ${}^3n\pi^*$ excited state of AQ 2, 3, 11, 12, and 15, respectively, and Figures 6–8 are those of the triplet ${}^3\pi\pi^*$ excited state of AQ 7, 8, and 9, respectively. Finally, Figure 9 is that of the mixed triplet state ${}^3n\pi^*/{}^3\pi\pi^*$ of AQ 6. The transient absorptions are observed in the ranges 320–500 nm and 460–700 nm and are averaged over time periods of 120–900 ns and 0.8–36 μs . The absorption maxima, corresponding half-lives, and both first- and second-order decay rate constants are listed in Table I for the compounds possessing ${}^3n\pi^*$ and ${}^3\pi\pi^*$ excited states, whereas Table II collectively lists data for the mixed ${}^3n\pi^*/{}^3\pi\pi^*$ state of 2-chloroamidoanthraquinone (AQ6). The transients are compared at equivalent absorbances of 0.5 or 1.0 at the laser excitation wavelength of 355 nm. The compounds with a triplet ${}^3n\pi^*$ excited state (Figs. 1–5), with the exception of AQ 11 and 15, exhibit a single triplet absorption with the maximum appearing in the lower end of the visible spectrum. In contrast, the compounds with the triplet ${}^3\pi\pi^*$ excited state (Figs.

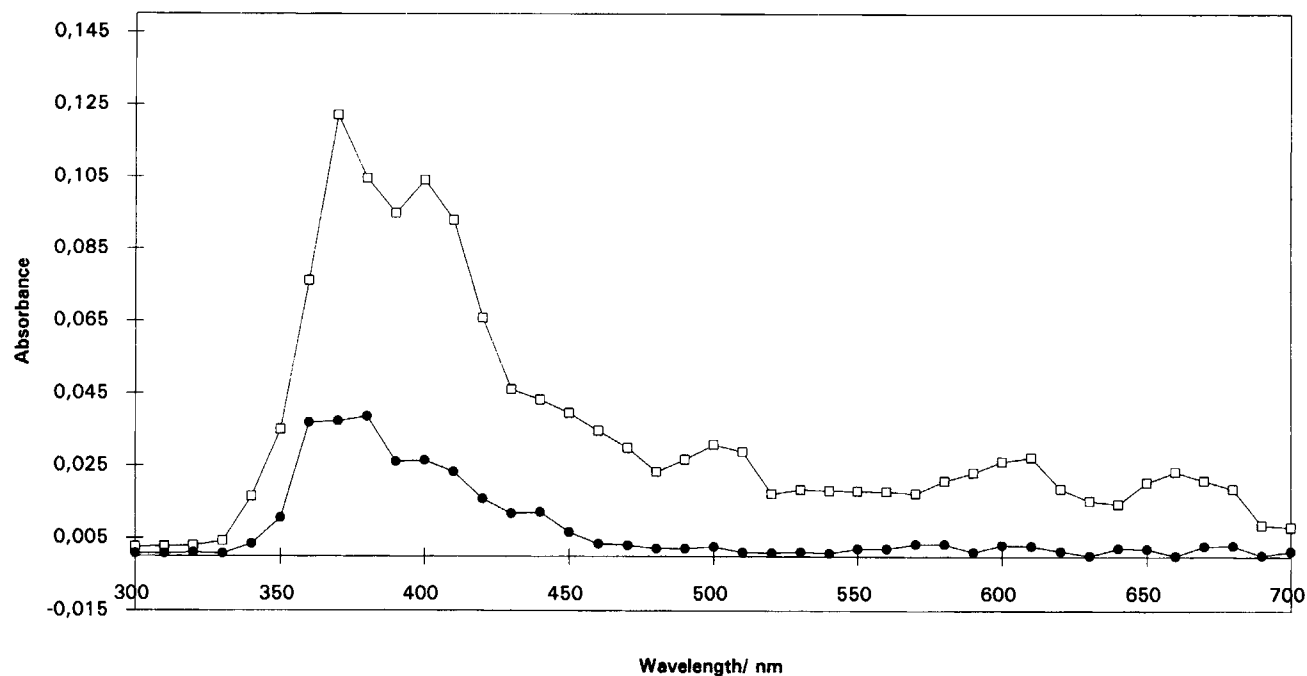


Figure 2 End-of-pulse transient absorption spectra produced on nanosecond laser flash photolysis of 2-(1,1,1-trichloromethyl)anthraquinone (AQ3, $10^{-4}M$) at (□) 120–140 ns and (●) 8.12–8.16 μs delay in nitrogen-saturated acetonitrile.

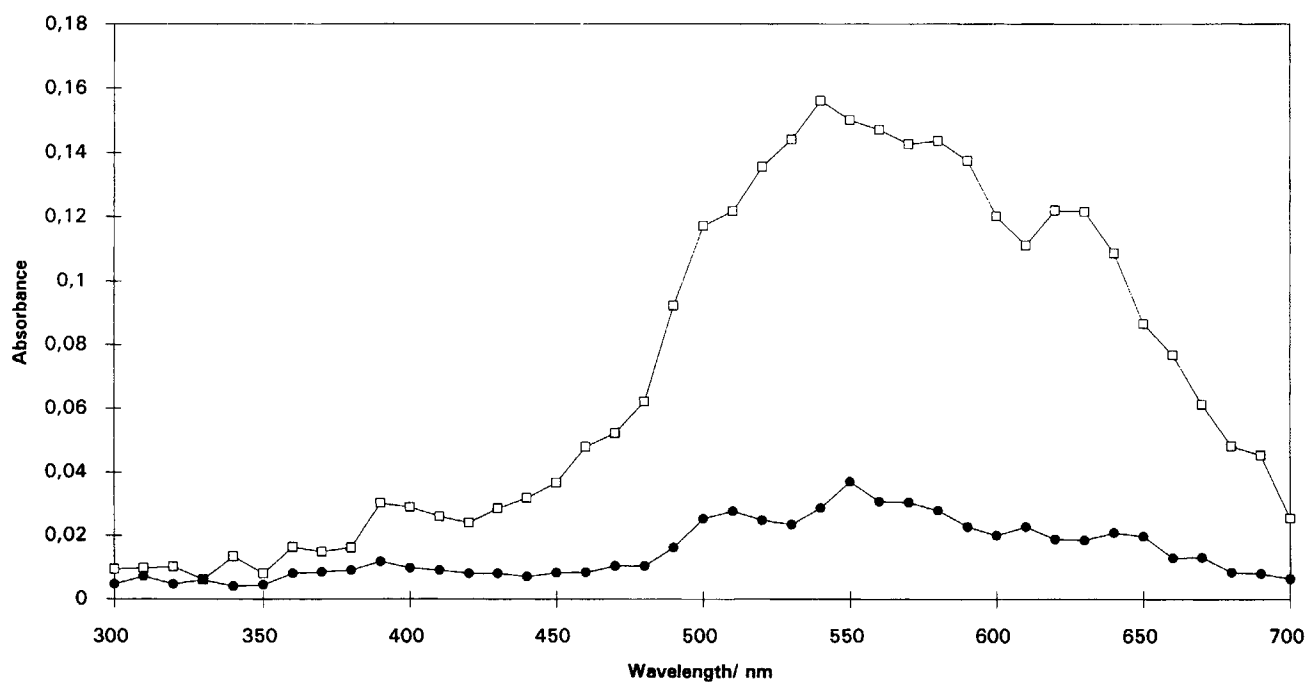


Figure 3 End-of-pulse transient absorption spectra produced on nanosecond laser flash photolysis of 2-(*N-n*-hexyl)methylamidoanthraquinone (AQ11, $10^{-4}M$) at (□) 240–280 ns and (●) 16.0 μs delay in nitrogen-saturated acetonitrile.

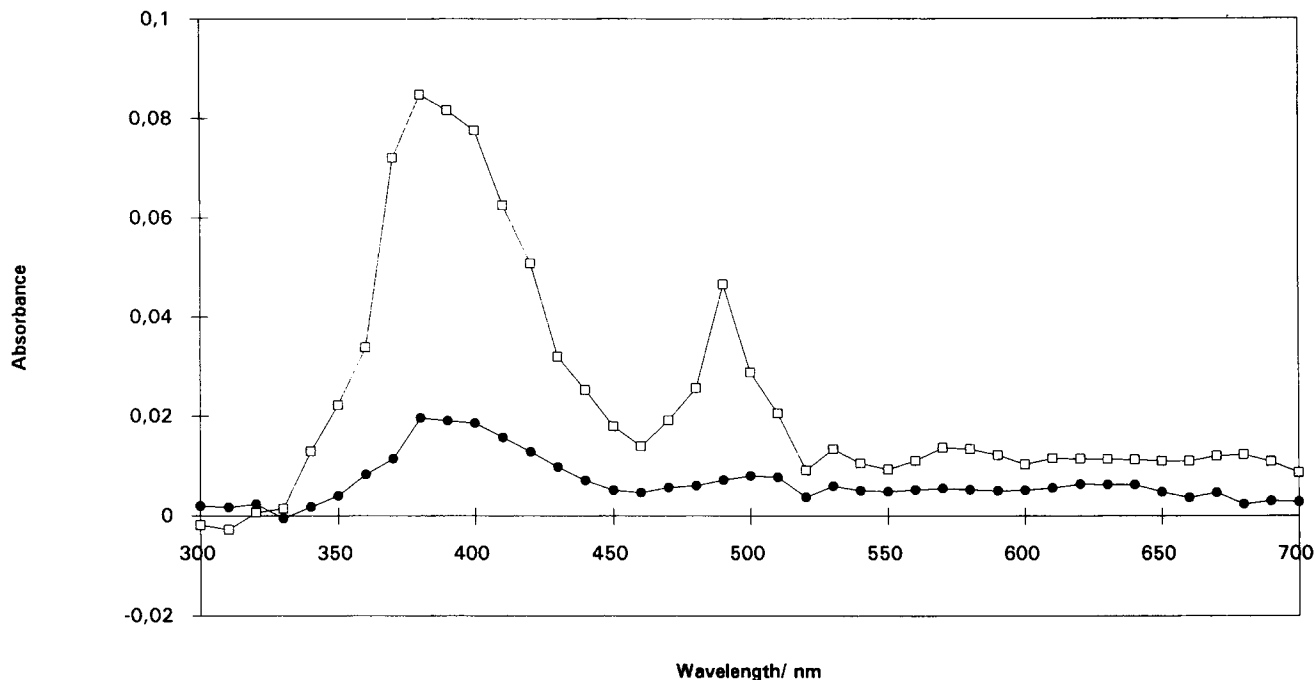


Figure 4 End-of-pulse transient absorption spectra produced on nanosecond laser flash photolysis of 2-methylcarboxyanthraquinone (AQ12, $10^{-4} M$) at (□) 400-440 ns and (●) 8.4-8.44 μs delay in nitrogen-saturated acetonitrile.

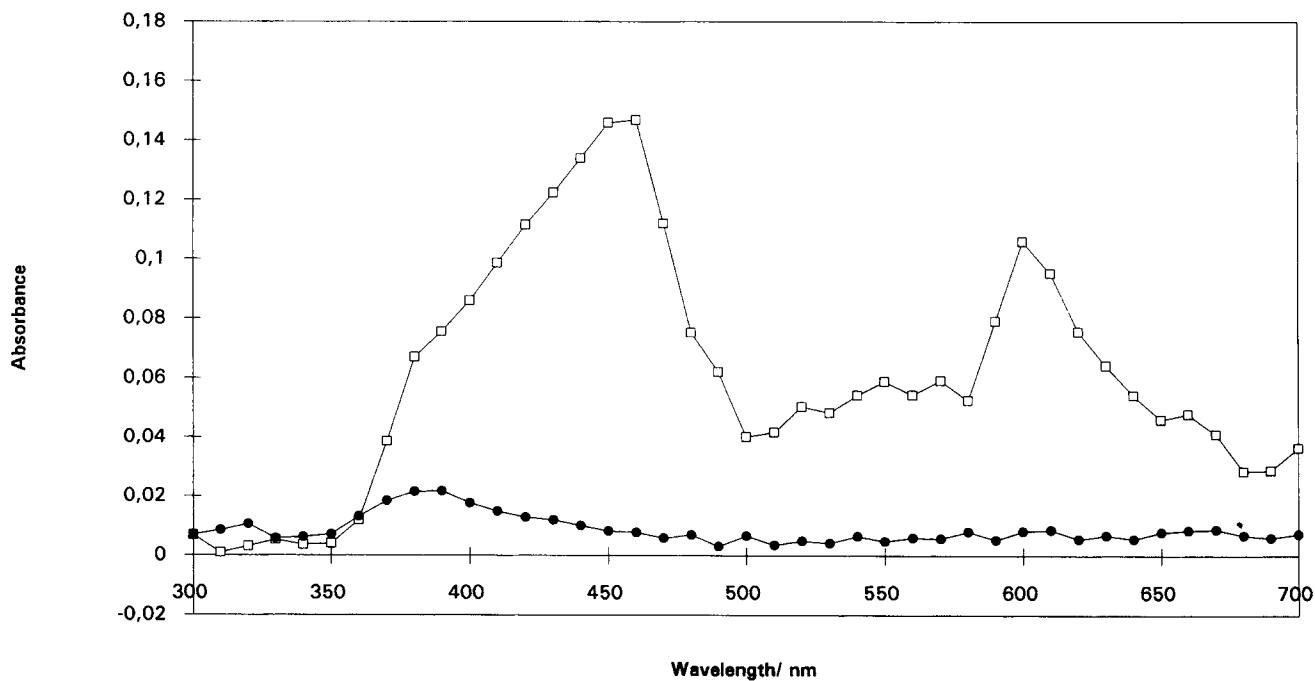


Figure 5 End-of-pulse transient absorption spectra produced on nanosecond laser flash photolysis of 2-(N,N-diethyl)amidoxyanthraquinone (AQ15, $10^{-4} M$) at (□) 200-240 ns and (●) 17 μs delay in nitrogen-saturated acetonitrile.

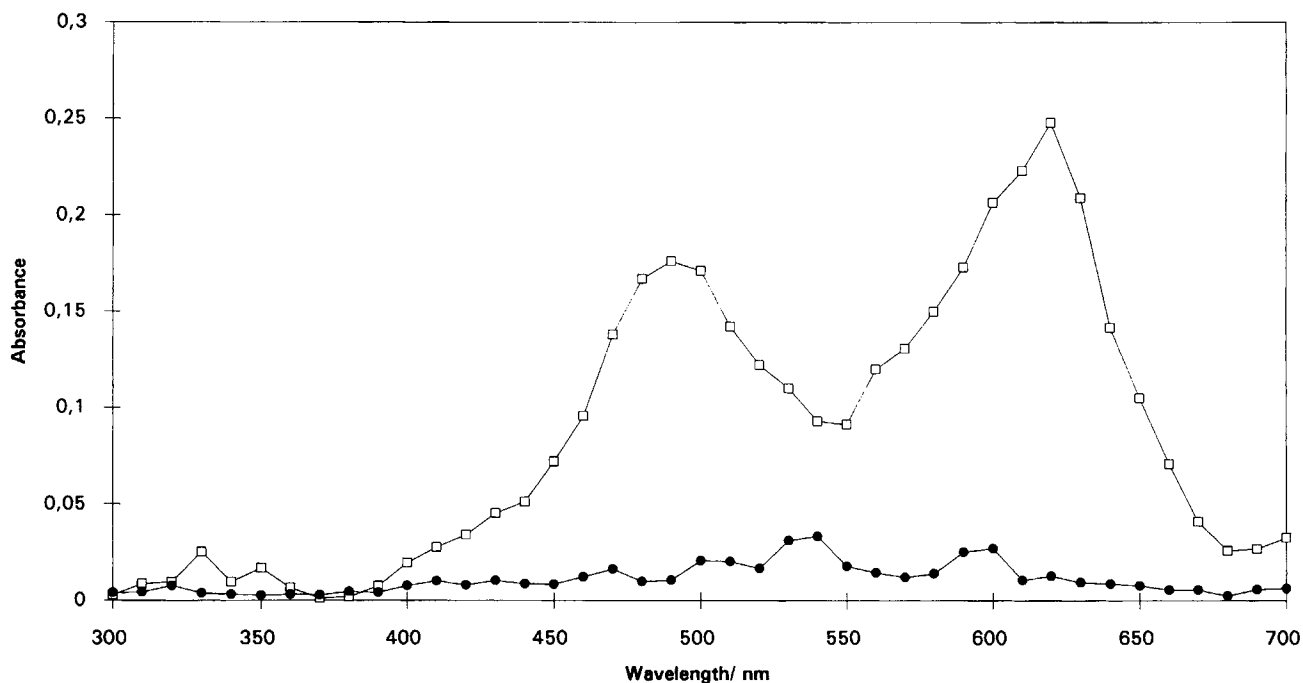


Figure 6 End-of-pulse transient absorption spectra produced on nanosecond laser flash photolysis of 2-(2-ethyl)hexylamidoanthraquinone (AQ7, $10^{-4}M$) at (□) 280–320 ns and (●) 16.0 μs delay in nitrogen-saturated acetonitrile.

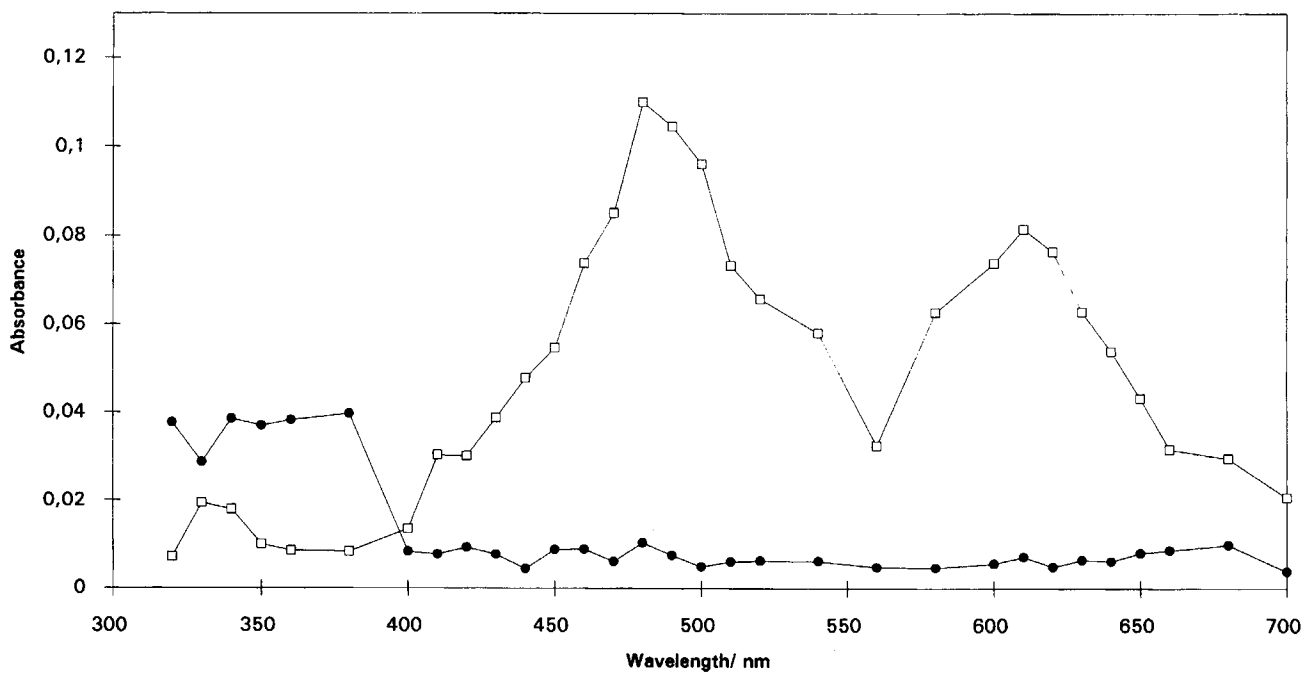


Figure 7 End-of-pulse transient absorption spectra produced on nanosecond laser flash photolysis of 2-(octadecyl-8-ene)amidoanthraquinone (AQ8, $10^{-4}M$) at (□) 280–320 ns and (●) 17.0 μs delay in nitrogen-saturated acetonitrile.

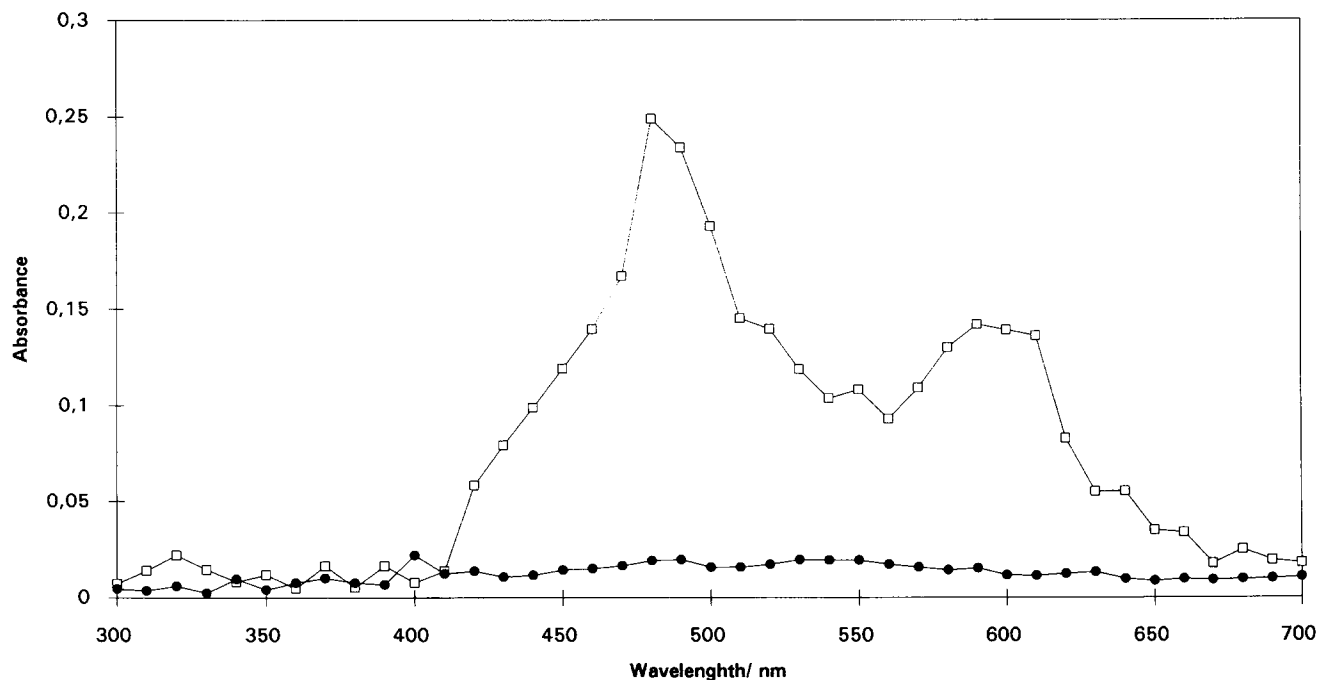


Figure 8 End-of-pulse transient absorption spectra produced on nanosecond laser flash photolysis of 2-ethoxyamidoanthraquinone (AQ9, $10^{-4}M$) at (□) 160–200 ns and (●) 17.0 μs delay in nitrogen-saturated acetonitrile.

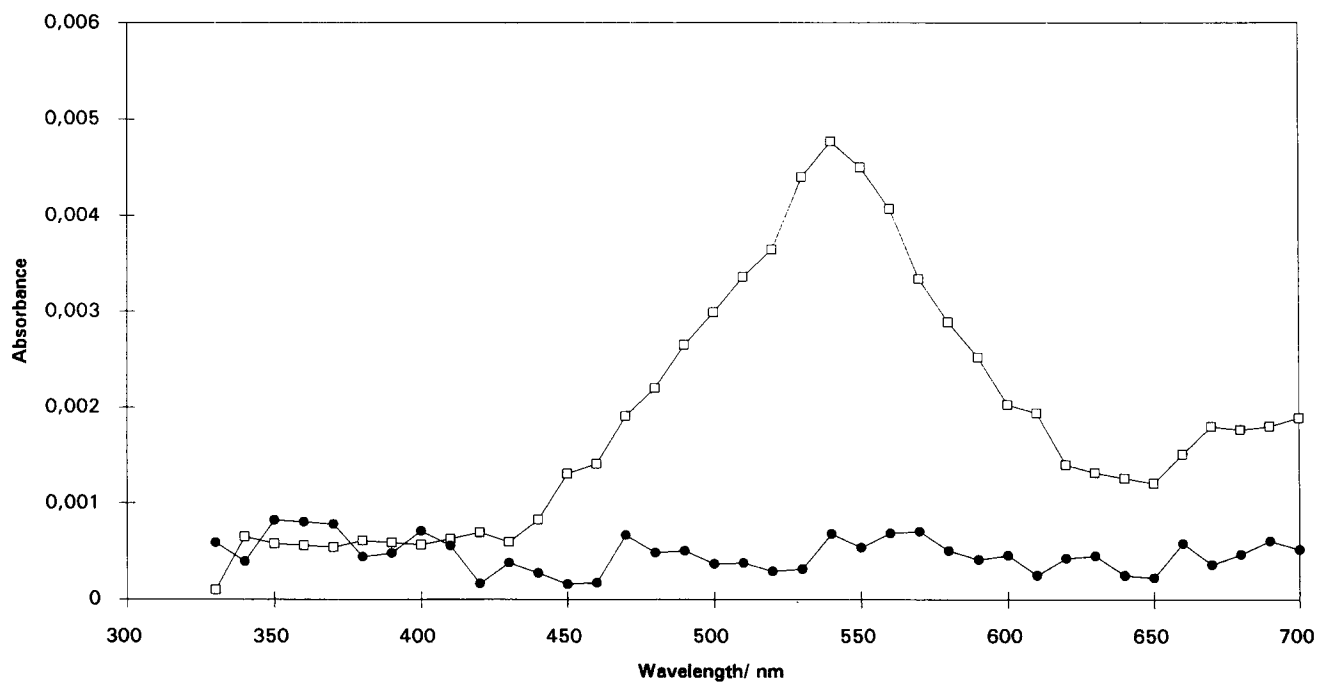


Figure 9 End-of-pulse transient absorption spectra produced on nanosecond laser flash photolysis of 2-chloroamidoanthraquinone (AQ6, $10^{-4}M$) at (□) 400–500 ns and (●) 8.3–8.4 μs delay in nitrogen-saturated acetonitrile.

Table I Transient Absorption Properties of 2-Substituted Anthraquinone Derivatives on Laser Flash Photolysis for Compounds With Lowest Triplet $^3n\pi^*$ and $^3\pi\pi^*$ Excited State

AQ	Solvent/ Concentration	λ_{\max} (nm)	Half-Life (μs)	First-Order Decay Rate $k \cdot 10^5$ (s^{-1})	Second-Order Decay Rate $2k/E \cdot 10^6$ ($M^{-1} \text{s}^{-1}$)
2	$5.00 \times 10^{-4}M$ in MeCN (N_2)	360	11.3	0.61 (360 nm)	0.20 (370 nm)
$^3n\pi^*$	$5.00 \times 10^{-4}M$ in MeCN (Air)		2.74	2.52 (360 nm)	—
	$5.00 \times 10^{-4}M$ in MeCN (O_2)		0.13	54.3 (360 nm)	0.24 (370 nm)
	$2.50 \times 10^{-4}M$ in IPA (N_2)	320	69.3	0.10 (360 nm)	—
	$2.50 \times 10^{-4}M$ in IPA (O_2)	370	63.0	0.11 (380 nm)	—
3	$6.65 \times 10^{-4}M$ in MeCN (N_2)	370	0.64	10.8 (370 nm)	8.15 (370 nm)
$^3n\pi^*$	$6.65 \times 10^{-4}M$ in MeCN (Air)		0.57	12.1 (370 nm)	—
	$6.65 \times 10^{-4}M$ in MeCN (O_2)	360	0.32	21.4 (370 nm)	—
7	$1.19 \times 10^{-4}M$ in MeCN (N_2)	490	1.14	6.05 (490 nm)	2.41 (490 nm)
$^3\pi\pi^*$	$1.19 \times 10^{-4}M$ in MeCN (N_2)	620	1.37	5.03 (620 nm)	1.62 (620 nm)
	$1.19 \times 10^{-4}M$ in MeCN (Air)		0.46	14.9 (490 nm)	—
	$1.19 \times 10^{-4}M$ in MeCN (Air)		0.21	32.9 (620 nm)	—
	$1.19 \times 10^{-4}M$ in MeCN (O_2)		0.06	107.2 (490 nm)	—
	$1.19 \times 10^{-4}M$ in MeCN (O_2)		0.06	119.0 (620 nm)	—
	$1.19 \times 10^{-4}M$ in IPA (N_2)	510	1.88	3.67 (510 nm)	—
	$1.19 \times 10^{-4}M$ in IPA (Air)		0.32	21.5 (510 nm)	—
	$1.19 \times 10^{-4}M$ in IPA (Air)	590	0.48	14.3 (590 nm)	—
8	$4.44 \times 10^{-4}M$ in MeCN (N_2)	480	2.55	2.71 (480 nm)	—
$^3\pi\pi^*$	$4.44 \times 10^{-4}M$ in MeCN (N_2)	610	2.07	3.33 (610 nm)	—
	$4.44 \times 10^{-4}M$ in MeCN (Air)		0.20	33.9 (480 nm)	—
	$4.44 \times 10^{-4}M$ in MeCN (Air)		0.19	35.5 (610 nm)	—
	$4.44 \times 10^{-4}M$ in MeCN (O_2)		0.04	147.0 (480 nm)	—
	$4.44 \times 10^{-4}M$ in MeCN (O_2)		0.05	138.0 (610 nm)	—
9	$2.80 \times 10^{-4}M$ in MeCN (N_2)	480	2.64	2.61 (480 nm)	—

Table I Continued

AQ	Solvent/ Concentration	λ_{\max} (nm)	Half-Life (μs)	First-Order Decay Rate $k \cdot 10^5$ (s^{-1})	Second-Order Decay Rate $2k/E \cdot 10^6$ ($M^{-1} \text{s}^{-1}$)
$^3\pi\pi^*$	$2.80 \times 10^{-4}M$ in MeCN (Air)		0.17	40.17 (480 nm)	—
	$2.80 \times 10^{-4}M$ in MeCN (O_2)		0.10	65.5 (480 nm)	—
11	$2.71 \times 10^{-4}M$ in MeCN (N_2)	540	2.07	3.34 (540 nm)	2.12 (540 nm)
$^3n\pi^*$	$2.71 \times 10^{-4}M$ in MeCN (Air)		0.18	37.5 (540 nm)	—
	$2.71 \times 10^{-4}M$ in MeCN (O_2)		0.05	132.0 (540 nm)	—
12	$7.70 \times 10^{-4}M$ in MeCN (N_2)	480	1.76	3.91 (380 nm)	3.11 (380 nm)
$^3n\pi^*$	$7.70 \times 10^{-4}M$ in MeCN (Air)		1.25	5.52 (380 nm)	6.41 (380 nm)
	$7.70 \times 10^{-4}M$ in MeCN (O_2)		0.55	12.9 (380 nm)	—
	$7.70 \times 10^{-4}M$ in IPA (N_2)	410	0.10	68.2 (410 nm)	—
	$7.70 \times 10^{-4}M$ in IPA (Air)		26.0	26.5 (410 nm)	—
15	$6.71 \times 10^{-4}M$ in MeCN (N_2)	460	1.05	6.55 (460 nm)	10.7 (460 nm)
$^3n\pi^*$	$6.71 \times 10^{-4}M$ in MeCN (Air)		0.33	20.7 (460 nm)	—
	$6.71 \times 10^{-4}M$ in MeCN (O_2)		0.11	62.6 (460 nm)	—

MeCN, acetonitrile; IPA, isopropyl alcohol (2-propanol).

6–8) show two major absorption bands with maxima around 600 nm. Derivative AQ11, 2-(*N-n*-hexyl)-methylamidoanthraquinone, has a broad absorption centered around 550 nm with shoulder bands at 390, 580, and 640 nm, whereas 2-(*N,N*-diethyl)-amidooxyanthraquinone (AQ15) has a more well-defined spectrum with absorption maxima at 470 and 600 nm with shoulder bands at 380 and 660 nm. In both cases, the transient species may be assigned to the triplet-triplet absorption since they were effectively quenched by ground-state molecular oxygen. It is apparent from the range of anthraquinone derivatives used in this study that generally those with an amide link in the 2-position possess a triplet $^3\pi\pi^*$ excited state, whereas those with an ester link have a triplet $^3n\pi^*$ excited state. Hence, in the case of derivative AQ15, the substituent at the 2-position has both ester and amide group that is consequently reflected in the triplet-triplet absorption spectrum

by showing both types of excited state configurations. The 2-chloroamidoanthraquinone (AQ6) has been established from previous studies¹ as having mixed state of both triplet $^3n\pi^*$ and $^3\pi\pi^*$ excited states and an absorption maximum at 540 nm (Fig. 9).

Transient absorption spectra of the selected anthraquinone derivatives (AQ 2, 7, and 12) were measured in a hydrogen atom donating solvent 2-propanol to determine the reactivity of the triplet-triplet transient. Each derivative chosen for this particular study represents the two major group of compounds mentioned above, and the spectra are shown in Figures 10–12 with averaged time periods of 80–120 ns and 0.8–17 μs . For the triplet $^3n\pi^*$ group of compounds, i.e., AQ 2 and 12, a bathochromic shift of at least 10 nm is observed on changing solvents from acetonitrile to 2-propanol (refer to Figs. 1, 4, 10, and 12), whereas the group of com-

Table II Transient Absorption Properties of 2-Substituted Anthraquinone Derivatives on Laser Flash Photolysis for Compounds With Lowest Triplet ${}^3n\pi^*/{}^3\pi\pi^*$ Mixed Excited State

AQ	Solvent/ Concentration	λ_{\max} (nm)	Half-Life (μs)	First-Order Decay Rate $k \cdot 10^5$ (s^{-1})	First-Order Growth Rate $k \cdot 10^5$ (s^{-1})	Second-Order Decay Rate $2k/E \cdot 10^6$ ($M^{-1} \text{s}^{-1}$)
6	$3.38 \times 10^{-4}M$ in MeCN (N_2)	450–540	2.90	2.38 (540 nm)	—	—
	$3.38 \times 10^{-4}M$ in MeCN (Air)		0.15	44.6 (540 nm)	—	—
	$3.38 \times 10^{-4}M$ in MeCN (O_2)		—	◆	—	—
	$3.38 \times 10^{-4}M$ in MeCN (N_2) + 0.26M IPA		3.29	2.10 (540 nm)	—	—
	$3.38 \times 10^{-4}M$ in MeCN (N_2) + 5.40M IPA		2.61	2.64 (540 nm)	—	—

MeCN, acetonitrile; IPA, isopropyl alcohol (2-propanol).

◆, Beyond the detection limit of the instrument.

pounds representing triplet ${}^3\pi\pi^*$ excited state (AQ7) undergoes a hypsochromic shift (Figs. 6 and 11) of 30 nm with a less-defined absorption spectrum. For the former group of compounds in 2-propanol, their spectra exhibit long-lived transient species with perhaps side-chain photolysis taking place and that

seems to confirm our previous results² on the photopolymerization of the 2-substituted anthraquinone derivatives. It is interesting to note that the derivative 2-methylcarboxyanthraquinone (AQ12), which has an ester link, exhibits a long-lived residual transient similar to the halo derivatives (AQ 2 and

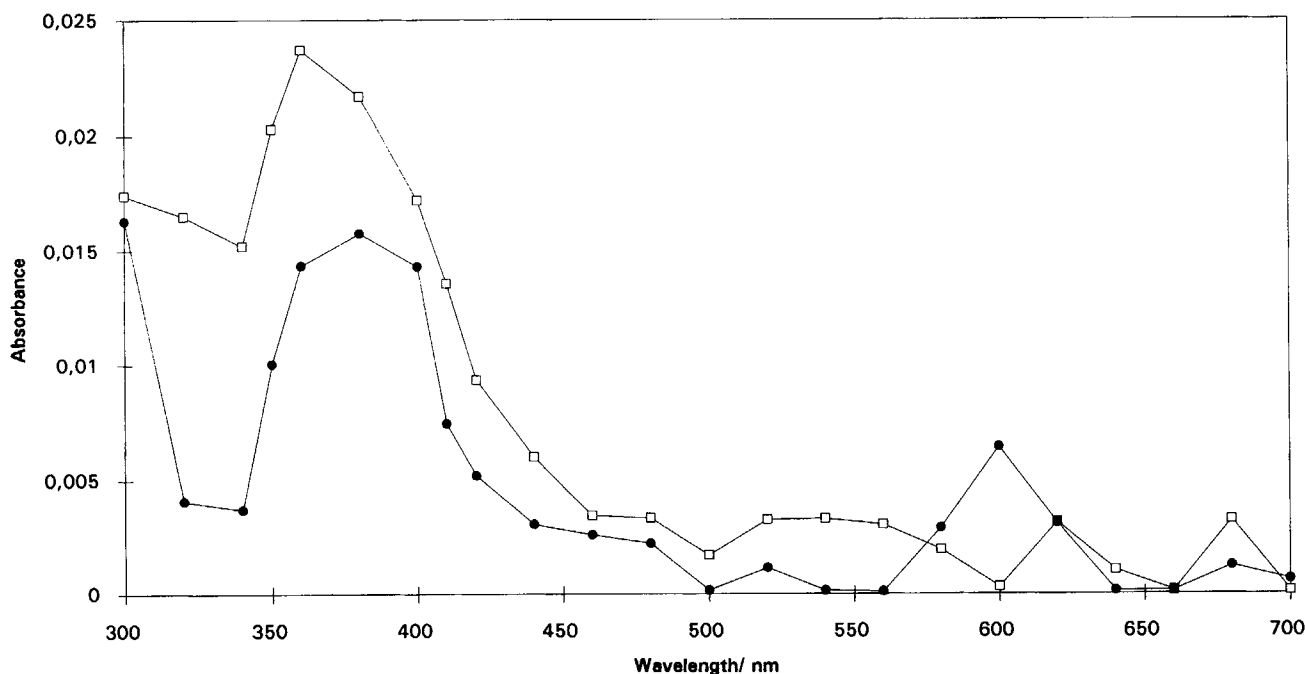


Figure 10 End-of-pulse transient absorption spectra produced on nanosecond laser flash photolysis of 2-(1,1-dibromo)anthraquinone (AQ2, $10^{-4}M$) at (□) 0.8–1.2 μs and (●) 17 μs delay in nitrogen-saturated 2-propanol.

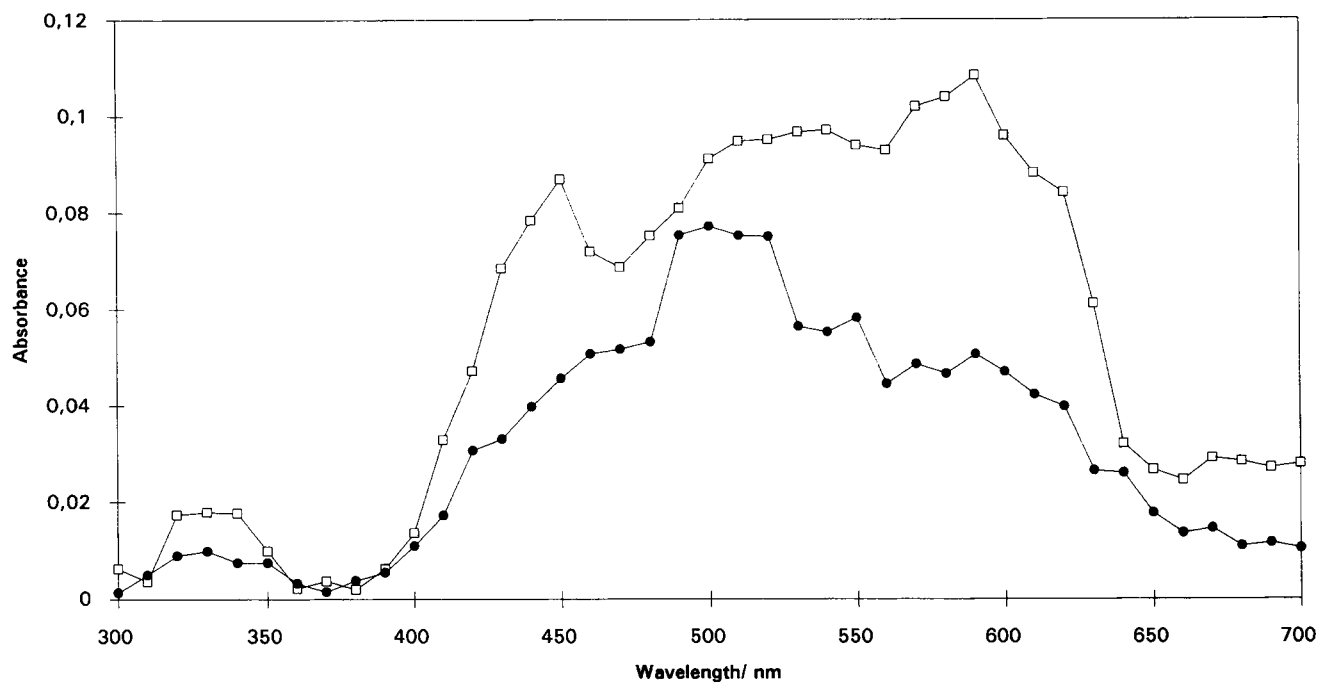


Figure 11 End-of-pulse transient absorption spectra produced on nanosecond laser flash photolysis of 2-(2-ethyl)hexylamidoanthraquinone (AQ7, $10^{-4} M$) at (□) 80-120 ns and (●) 920-960 ns delay in nitrogen-saturated 2-propanol.

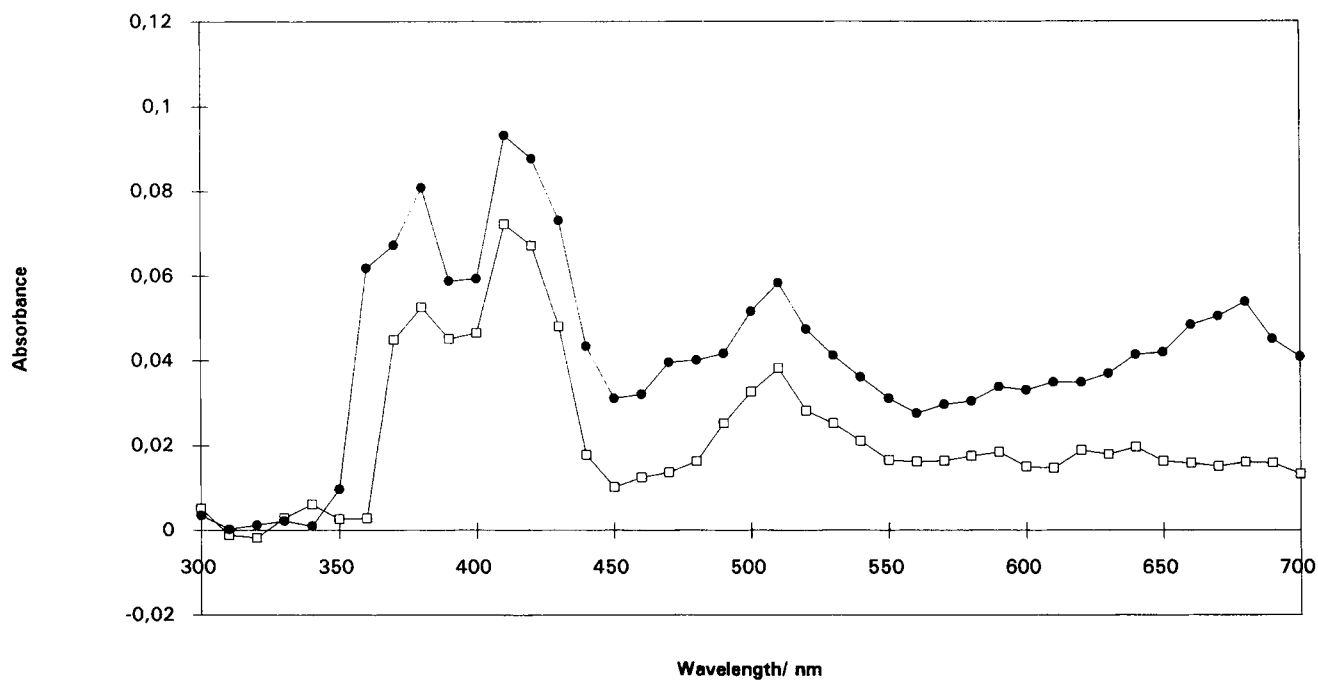


Figure 12 End-of-pulse transient absorption spectra produced on nanosecond laser flash photolysis of 2-methylcarboxyanthraquinone (AQ12, $10^{-4} M$) at (□) 90-120 ns and (●) 880-890 ns delay in nitrogen-saturated 2-propanol.

3). This would possibly suggest de-esterification is taking place at the ring position to give a long-lived, stabilized aromatic radical. The fact that this residual transient is not the triplet state is shown by the data in Table I for 2-methylcarboxyanthraquinone. Here, significantly long-lived transients were observed in 2-propanol compared with acetonitrile, especially in the presence of molecular oxygen. Thus, the primary mechanism of photoreduction appears to be less important for this particular derivative.

The triplet half-life times are also very different depending on the nature of the triplet excited state. Thus, for the compounds with a low-lying triplet ${}^3n\pi^*$ excited state, the triplet-triplet transients are longer lived in the range of 8–36 μs , whereas those with low-lying triplet ${}^3\pi\pi^*$ states, the transients are relatively short-lived to within 17 μs . The triplet lifetimes agree well with our previous results on the photopolymerization activity,² i.e., being greater for the group of compounds with a triplet ${}^3n\pi^*$ than triplet ${}^3\pi\pi^*$ excited states when monochromatic light of 355 nm is used.

Effect of Air/Oxygen

The first-order triplet decay constants and half-lives in the absence and presence of air/oxygen are summarized in Tables I and II. It is clear from the results that all the derivatives are effectively quenched by ground-state molecular oxygen. From many studies,³⁻⁵ it is well known that anthraquinone and its derivatives sensitize singlet oxygen by quenching the photoexcited triplet state of the former with ground-state molecular oxygen. In this respect, the first-order decay rate constants increase steadily in the presence of air/oxygen and confirm the absorption maximum to be that of the triplet state. The derivatives AQ 7–9, with a low-lying triplet ${}^3\pi\pi^*$ excited state, are efficiently quenched by molecular oxygen, whereas the remaining (triplet ${}^3n\pi^*$ excited state), with the exception of AQ11, exhibit some quenching but with lower bimolecular rate constants (Table III). It is recognized in general⁸ for various anthraquinone derivatives that the triplet state is quenched by molecular oxygen with a bimolecular rate constant $k_q(\text{O}_2)$ of approximately $1.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (in the order of a diffusion controlled process), which is comparable in this study with the rate constants of the compounds possessing triplet ${}^3\pi\pi^*$ excited states (AQ7–9). For the triplet ${}^3n\pi^*$ group of compounds (AQ 2, 3, 12, and 15), with the exception of AQ11, the bimolecular rate constants are lower by at least one order of magnitude. The slight insensitivity toward oxygen quenching by the com-

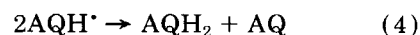
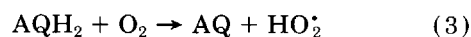
Table III Bimolecular Rate Constants ($K_{3,Q}$) for Oxygen Quenching of the 2-Substituted Anthraquinone Derivatives on Laser Flash Photolysis

AQ	Oxygen Quenching $K_{3,Q}$ ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)
2	5.97×10^8
3	1.21×10^8
6	2.35×10^9
7	1.22×10^9
8	1.55×10^9
9	6.99×10^8
11	1.45×10^9
12	9.20×10^7
15	6.22×10^8

pounds with a lowest triplet ${}^3n\pi^*$ excited state is perhaps due to the lowest excited state possessing a higher degree of charge transfer character and hence would be less susceptible to the effects of molecular oxygen. One interesting result observed is that of 2-chloroamidoanthraquinone (AQ6), which has mixed triplet excited state characteristics, and is quenched very efficiently by molecular oxygen with a bimolecular rate constant of about $2.35 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Table III).

Hydrogen Atom Abstraction

The excited triplet state of the anthraquinone derivatives are known to undergo a photoreduction reaction in the presence of hydrogen atom donors such as 2-propanol or amines. The mechanism of photoreduction by 2-propanol may be summarized as follows:



The triplet excited state of the anthraquinone derivative (${}^3\text{AQ}^*$) abstracts a hydrogen atom [eq. (1)] from 2-propanol to form the semianthraquinone radical (AQH $^{\cdot}$) and the photoinitiating radical (R $^{\cdot}$). The semianthraquinone radical can further abstract a hydrogen atom from the solvent RH [eq. (2)] to produce the hydroanthraquinone type structure (AQH $_2$) and another photoinitiating radical (R $^{\cdot}$). In the presence of air/oxygen, the hydroanthraquinone is unstable and may reoxidize back [eq. (3)]

to the original anthraquinone (AQ). Alternatively, two semianthraquinone radicals may undergo a disproportionation reaction [eq. (4)] to produce the hydroanthraquinone type structure (AQH₂) and the starting anthraquinone (AQ). This is a particular behavior of anthraquinone photoinitiators where the reaction sequence takes up oxygen dissolved in the system and simultaneously recycles the chromophore structure of the photoinitiator.

In line with other results,² here the addition of increasing amounts of 2-propanol to acetonitrile solutions of anthraquinone derivatives showed that the compounds with triplet ³*nπ** excited states undergo hydrogen atom abstraction,^{9,10} although there is an upper limit of 0.26*M* concentration within which only first-order decay rates are observed (Tables IV and V). It is evident from the data that the mechanism of hydrogen atom abstraction is complex as both first- and second-order decay rate constants are observed in some cases and is perhaps due to interference from further reactions of disproportionation and reoxidation mentioned above. The compounds with a triplet ³*ππ** state do not show any significant increase in the first-order decay rate constant for hydrogen atom abstraction, with the exception of 2-ethoxyamido-anthraquinone (AQ9), where under the condition of very high concentration of 2-propanol, the triplet decay rate increases (Table V).

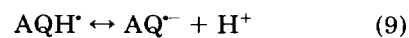
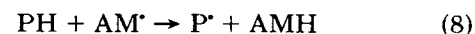
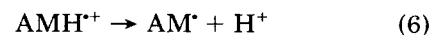
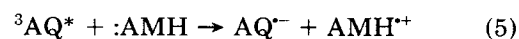
The photochemical reactions are generally initiated by the lowest excited triplet state in which the triplet ³*nπ** state is known to be more active than the ³*ππ** state. The results in the current study agree well in this respect and with our previous work² on the photopolymerization activity and conventional microsecond flash photolysis for the 15 anthraquinone derivatives. It was observed that the group of compounds with a triplet ³*nπ** excited state showed absorption due to the semianthraquinone radical with medium to high photopolymerization activity. The group with a triplet ³*ππ** excited state exhibited weak spectra with less defined absorption and in turn showed low photopolymerization activity. In addition to these results, the bimolecular rate constants for hydrogen atom abstraction (Table VI) indicate that the dependence of the excited state configuration on photopolymerization follows the established order of reactivity *T_{nπ*}* > *T_{ππ*}* > *T_{CT}* for an anaerobic environment without an amine. In the case of compounds with a low-lying triplet ³*ππ** excited state, particularly those with charge transfer characteristics, tend to cause an electronic displacement toward the oxygen atom that loses its affinity for the hydrogen atom^{6,11} and hence is less susceptible to hydrogen atom abstraction. However, in conditions

of extremely high concentrations of 2-propanol (almost to saturation point), it is possible to observe the expected increase in the first-order rate constant (refer to the result of AQ9 in Table V).

The side chain interaction with the triplet carbonyl of the anthraquinone derivative is another important point to consider as this would allow intramolecular hydrogen atom abstraction to take place. This derivative possesses a long alkyl-ene side chain with *n* = 14 methylene groups that would have the potential to interact intramolecularly with the carbonyl group. A study on a range of 2-alkyl anthraquinone carboxylate derivatives¹² has suggested that the relatively long side chain (*n* > 10) shows an increase in the hydrogen atom abstraction reaction rate, in accordance with the collision frequency between the carbonyl and the methylene groups. In addition, it is also possible for either one of two carbonyls at the 9- and 10-positions of anthraquinone, which are not equivalent with respect to the carboxyl group at the 2-position, to also abstract a hydrogen atom by a competitive intermolecular process. The implications of these results in photopolymerization would be difficult to ascertain since the alkyl radicals on the side chain could also be involved.

Exciplex Formation With Amine

It is well known that anthraquinone in the presence of an amine co-initiator enhances the photopolymerization activity of a given monomer or a prepolymer system. The photoexcited state of the anthraquinone (³AQ*) abstracts an electron from the amine (:AMH) to produce an active radical anion species (AQ^{•-}) in eq. (5) and a reactive alkylamino radical (AM[•]) in eq. (6). The former is capable of abstracting a proton to give the semianthraquinone radical (AQH[•]) in eq. (7), whereas the latter will abstract a hydrogen atom from the polymer (PH) in reaction (8). In addition, the radical anion (AQ^{•-}) can exist in equilibrium with the semianthraquinone radical (AQH[•]) as shown in eq. (9):



The initial products formed are either a triplet exciplex, the contact ion pair, the solvent separated ion pair, or the free ions. The spectra of these four

Table IV Transient Absorption Properties of 2-Substituted Anthraquinone Derivatives in Different Environments on Laser Flash Photolysis for Compounds With Lowest Triplet $^3n\pi^*$ Excited State

AQ	Solvent/ Concentration	λ_{\max} (nm)	Half-Life (μ s)	First-Order Decay Rate $k \cdot 10^5$ (s^{-1})	First-Order Growth Rate $k \cdot 10^5$ (s^{-1})	Second-Order Decay Rate $2k/E \cdot 10^6$ ($M^{-1} s^{-1}$)
2	$5.0 \times 10^{-4}M$ in MeCN (N_2) + 0.13M IPA	380	0.19	36.3 (380 nm)	21.6 (380 nm)	—
	$5.0 \times 10^{-4}M$ in MeCN (N_2) + 0.26M IPA		—	—	32.2 (380 nm)	—
	$5.0 \times 10^{-4}M$ in MeCN (O_2) + 0.26M IPA		0.13	55.2 (380 nm)	—	—
	$5.0 \times 10^{-4}M$ in MeCN (N_2) + 0.18M TEA		—	—	94.4 (360 nm)	—
3	$6.65 \times 10^{-4}M$ in MeCN (N_2) + 0.065M IPA	370	0.24	28.6 (500 nm)	22.4 (360 nm)	—
	$6.65 \times 10^{-4}M$ in MeCN (N_2) + 0.13M IPA		0.13	53.2 (500 nm)	26.5 (370 nm)	—
	$6.65 \times 10^{-4}M$ in MeCN (N_2) + 0.14M TEA		2.44	2.83 (370 nm) ^b	111 (370 nm) ^a	—
11	$2.71 \times 10^{-4}M$ in MeCN (N_2) + 0.13M IPA	540	4.11	1.68 (540 nm)	—	2.08 (540 nm)
	$2.71 \times 10^{-4}M$ in MeCN (N_2) + 0.26M IPA		3.58	1.93 (540 nm)	—	2.72 (540 nm)
	$2.71 \times 10^{-4}M$ in MeCN (N_2) + 0.52M IPA		4.86	1.42 (540 nm)	—	1.98 (540 nm)
	$2.71 \times 10^{-4}M$ in MeCN (N_2) + 1.00M IPA		4.42	1.56 (540 nm)	—	2.20 (540 nm)
	$2.71 \times 10^{-4}M$ in MeCN (N_2) + 7.50M IPA		5.52	1.25 (540 nm)	—	1.95 (540 nm)
	$2.71 \times 10^{-4}M$ in MeCN (N_2) + 0.07M TEA		—	—	32.6 (540 nm)	—
	$2.71 \times 10^{-4}M$ in MeCN (N_2) + 0.14M TEA		—	—	44.3 (540 nm)	—

species are predicted to be similar to the sum of the overlapped spectra for the anthraquinone anion radical and the amine cation radical. The kinetic studies are useful for differentiating the free ions from the exciplex or the ion pairs: the former and

the latter species decay according to second-order and first-order kinetics,⁶ respectively.

From Tables IV and V, all the anthraquinone derivatives show the formation of radical ion pairs as described by the mechanism above. The first-order

Table IV Continued

AQ	Solvent/ Concentration	λ_{\max} (nm)	Half-Life (μs)	First-Order Decay Rate $k \cdot 10^5$ (s^{-1})	First-Order Growth Rate $k \cdot 10^5$ (s^{-1})	Second-Order Decay Rate $2k/E \cdot 10^6$ ($M^{-1} \text{s}^{-1}$)		
12	$7.70 \times 10^{-4}M$ in MeCN (N_2) + 0.5M IPA	380	—	—	85.5 (380 nm)	—		
	$7.70 \times 10^{-4}M$ in MeCN (N_2) + 1.0M IPA		—	—	131 (380 nm)	—		
	$7.70 \times 10^{-4}M$ in MeCN (N_2) + 0.24M TEA		—	—	345 (380 nm) ^a	—		
	$7.70 \times 10^{-4}M$ in MeCN (N_2) + 0.24M TEA		43.3	0.16 (420 nm) ^b	220 (420 nm) ^a	—		
	$7.70 \times 10^{-4}M$ in MeCN (N_2) + 0.24M TEA		53.3	0.13 (620 nm) ^b	133 (620 nm) ^a	—		
	$7.70 \times 10^{-4}M$ in MeCN (Air) + 0.24M TEA		4.28	1.62 (620 nm) ^b	—	—		
	$7.70 \times 10^{-4}M$ in MeCN (O_2) + 0.24M TEA		1.84	3.76 (620 nm) ^b	—	—		
	15		$6.71 \times 10^{-4}M$ in MeCN (N_2) + 0.13M IPA	460	0.51	13.4 (460 nm)	—	—
			$6.71 \times 10^{-4}M$ in MeCN (N_2) + 0.26M IPA		0.29	24.0 (460 nm)	—	—
$6.71 \times 10^{-4}M$ in MeCN (N_2) + 1.00M IPA		—	•		—	—		
$6.71 \times 10^{-4}M$ in MeCN (N_2) + 0.18M TEA		—	—		393 (460 nm)	—		

MeCN, acetonitrile; IPA, isopropyl alcohol (2-propanol); TEA, triethylamine; •, mixed kinetics.

^a Over a short time scale (ns).

^b Over a long time scale (ms).

growth rate constants of transients were observed in less than 100 ns, with longer lived residual transients (in some cases >20 ms) being detected, suggesting the formation of a radical ion pair. For the compounds with a $^3n\pi^*$ excited states, the growth rate constants are higher than compounds with a lowest triplet $^3\pi\pi^*$ excited states. The first-order decay rate constant for the same radical ion pairs are very low and are only possible to evaluate over long time scales as the half-lives of these species range from 2 to 53 μs , an indication of the formation of very stable species. Hence, this confirms the high

photopolymerization rates observed for the derivatives in the presence of a tertiary amine and under UV irradiation,² indicating that the transient species are most likely to be that of the radical ion pairs⁶ as described above.

The absorption spectra of the two derivatives AQ7 and 12 representing the triplet $^3\pi\pi^*$ and $^3n\pi^*$ excited states, respectively, were conducted in acetonitrile and in the presence of an amine, triethylamine (Figs. 13 and 14). The absorption spectra are very different from those of the triplet state and for the first time show the presence of long-lived species. For the de-

Table V Transient Absorption Properties of 2-Substituted Anthraquinone Derivatives in Different Environments on Laser Flash Photolysis for Compounds With Lowest Triplet $^3\pi\pi^*$ Excited State

AQ	Solvent/ Concentration	λ_{\max} (nm)	Half-Life (μs)	First-Order Decay Rate $k \cdot 10^5$ (s^{-1})	First-Order Growth Rate $k \cdot 10^5$ (s^{-1})	Second-Order Decay Rate $2k/E \cdot 10^6$ ($M^{-1} \text{s}^{-1}$)
7	$1.19 \times 10^{-4}M$ in MeCN (N_2) + 0.065M IPA	490	1.99	3.45 (490 nm)	—	2.11 (490 nm)
	$1.19 \times 10^{-4}M$ in MeCN (N_2) + 0.065M IPA		1.78	3.87 (620 nm)	—	1.59 (620 nm)
	$1.19 \times 10^{-4}M$ in MeCN (N_2) + 0.43M IPA		1.71	4.04 (490 nm)	—	2.00 (490 nm)
	$1.19 \times 10^{-4}M$ in MeCN (N_2) + 0.43M IPA		0.75	9.22 (620 nm)	—	—
	$1.19 \times 10^{-4}M$ in MeCN (N_2) + 1.3M IPA		1.35	5.10 (620 nm)	—	4.00 (620 nm)
	$1.19 \times 10^{-4}M$ in MeCN (N_2) + >3.0M IPA		2.74	2.52 (620 nm)	—	—
	$1.19 \times 10^{-4}M$ in MeCN (N_2) + 0.004M TEA		—	—	28.5 (420 nm) ^a	—
	$1.19 \times 10^{-4}M$ in MeCN (N_2) + 0.004M TEA		—	•	54.7 (520 nm) ^a	—
	$1.19 \times 10^{-4}M$ in MeCN (N_2) + 0.01M TEA		—	—	55.8 (420 nm) ^a	—
	$1.19 \times 10^{-4}M$ in MeCN (N_2) + 0.01M TEA		—	—	28.0 (520 nm) ^a	—
	$1.19 \times 10^{-4}M$ in MeCN (N_2) + 0.12M TEA		—	—	34.0 (420 nm) ^b	—
	$1.19 \times 10^{-4}M$ in MeCN (N_2) + 0.12M TEA		—	—	40.7 (420 nm) ^a	—
	$1.19 \times 10^{-4}M$ in MeCN (N_2) + 0.12M TEA		40.8	0.17 (520 nm) ^b	66.6 (520 nm) ^a	—
	$1.19 \times 10^{-4}M$ in MeCN (N_2) + 0.24M TEA		—	—	35.7 (420 nm) ^b	—
	$1.19 \times 10^{-4}M$ in MeCN (N_2) + 0.24M TEA		—	—	46.3 (420 nm) ^a	—
	$1.19 \times 10^{-4}M$ in MeCN (N_2) + 0.24M TEA		14.4	0.48 (520 nm) ^b	67.5 (520 nm) ^a	—

Table V Continued

AQ	Solvent/ Concentration	λ_{\max} (nm)	Half-Life (μs)	First-Order Decay Rate $k \cdot 10^5$ (s^{-1})	First-Order Growth Rate $k \cdot 10^5$ (s^{-1})	Second-Order Decay Rate $2k/E \cdot 10^6$ ($M^{-1} \text{s}^{-1}$)
8	$4.44 \times 10^{-4}M$ in MeCN (N_2) + 0.08M IPA	480	2.88	2.40 (480 nm)	—	—
	$4.44 \times 10^{-4}M$ in MeCN (N_2) + 0.08M IPA		2.33	2.96 (610 nm)	—	—
	$4.44 \times 10^{-4}M$ in MeCN (N_2) + 0.67M IPA		1.89	3.66 (480 nm)	—	—
	$4.44 \times 10^{-4}M$ in MeCN (N_2) + 0.50M TEA		—	—	17.3 (480 nm)	—
9	$2.80 \times 10^{-4}M$ in MeCN (N_2) + 0.26M IPA	480	1.43	4.82 (480 nm)	—	7.02 (480 nm)
	$2.80 \times 10^{-4}M$ in MeCN (N_2) + 0.65M IPA		1.38	5.00 (480 nm)	—	136.0 (480 nm)
	$2.80 \times 10^{-4}M$ in MeCN (N_2) + 6.50M IPA		0.26	26.6 (480 nm)	—	—
	$2.80 \times 10^{-4}M$ in MeCN (N_2) + 0.14M TEA		53.1	0.13 (480 nm) ^b	49.6 (480 nm) ^a	—

MeCN, acetonitrile; IPA, isopropyl alcohol (2-propanol); TEA, triethylamine; •, mixed kinetics.

^a Over a short time scale (ns).

^b Over a long time scale (ms).

rivative 2-(2-ethylhexyl)amidoanthraquinone (AQ7), the absorption spectrum (Fig. 13) shows a hypsochromic shift of between 70 and 80 nm when the amine is present, indicating the presence of a stable radical ion pair, although there is a small absorption between 550 and 600 nm that shows complete decay after 42 μs and is most likely to be that of the residual triplet state. In addition, there is some indication of the triplet state being quenched at 420 nm by the amine at relatively high concentrations as the first-order rate constants increase upto a limit (Table V).

In the case of 2-methylcarboxyanthraquinone (AQ12) (Fig. 14), the triplet absorption at 490 nm almost disappears upon the addition of triethylamine with the formation of a new absorption band at 620 nm, showing a bathochromic shift and signifying the presence of a triplet exciplex being formed. The main absorption at 370 nm observed

in acetonitrile (Fig. 4) becomes broad and structureless in the presence of an amine with an absorption maximum centered around 390 nm (Fig. 14). There is also a slight air/oxygen quenching taking place with 2-methylcarboxyanthraquinone (AQ12), shown by the small increases in the first-order decay rate constant at 620 nm (Table IV), although this occurs over a long time scale of several microseconds.

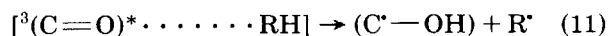
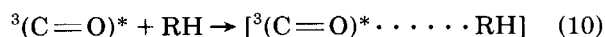
The results of the anthraquinone derivatives from this study has shown that the photopolymerization activity is highly dependent on the type of hydrogen atom donor used for the photoreduction step related to the formation of radicals. In the case of 2-propanol as the hydrogen atom donor, the group of compounds with the triplet ${}^3n\pi^*$ excited state undergo direct hydrogen atom abstraction upto a limit, whereas the group of compounds with a triplet ${}^3\pi\pi^*$ excited state do not show any significant activity as listed in Table

Table VI Bimolecular Rate Constant ($K_{3,Q}$) for the 2-Substituted Anthraquinone Derivatives on Laser Flash Photolysis

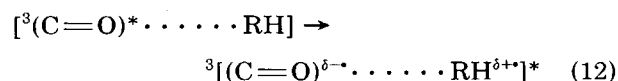
AQ	Hydrogen Atom Abstraction $K_{3,Q}$ (dm ³ mol ⁻¹ s ⁻¹)	Amine Exciplex Formation $K_{3,Q}$ (dm ³ mol ⁻¹ s ⁻¹)
2	1.24×10^7	—
3	4.09×10^7	—
6	No significant change to merit calculation of $K_{3,Q}$	—
7	Mixed kinetics	2.78×10^7
8	No significant change to merit calculation of $K_{3,Q}$	—
9	3.69×10^6	1.54×10^7
11	No significant change to merit calculation of $K_{3,Q}$	3.16×10^7
12	1.50×10^7	—
15	9.23×10^6	—

VI by the low values or in some cases unable to calculate the bimolecular rate constants. Hence, the lowest excited triplet state configuration for the photopolymerization activity is important when 2-propanol is used as the hydrogen atom donor and the order of reactivity may be summarized as $T_{n\pi^*} > T_{\pi\pi^*} > T_{CT}$. However, in the presence of an amine, the photopolymerization activity is far less dependent on the excited triplet state configuration.¹³

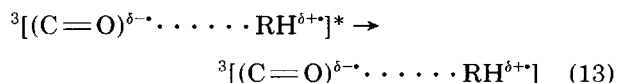
The comparison between the use of two hydrogen donors, i.e., 2-propanol and triethylamine in this study, can be related to their ionization potentials for the particular photoreduction mechanism that they follow.⁶ Many studies have concluded¹³ that the low-lying triplet ${}^3n\pi^*$ state of the carbonyl compound [${}^3(C=O)^*$] is responsible for the hydrogen atom abstraction when a hydrogen atom donor (RH) with high ionization potential, e.g., 2-propanol, is used and it is believed to occur via a nonpolar collision complex [${}^3(C=O)^* \cdots \cdots RH$]:



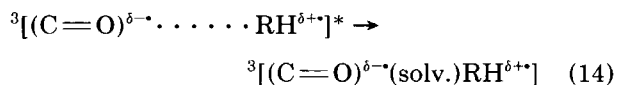
However, when the RH has low ionization potential,¹³ e.g., an amine, the collision complex readily changes to the strong charge-transfer (CT) exciplex, ${}^3[(C=O)^{\delta-\cdot} \cdots \cdots RH^{\delta+\cdot}]^*$, without direct hydrogen atom abstraction taking place (12):



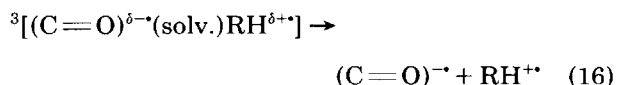
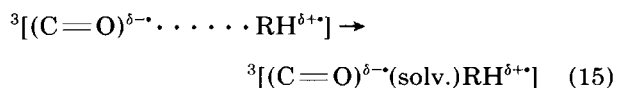
The strong CT complex, ${}^3[(C=O)^{\delta-\cdot} \cdots \cdots RH^{\delta+\cdot}]^*$ is transformed to the contact ion pair ${}^3[(C=O)^{\delta-\cdot} \cdots \cdots RH^{\delta+\cdot}]^*$:



In polar solvents, the strong CT exciplex or ion pair¹⁴ is converted to the solvent-separated ion pair, ${}^3[(C=O)^{\delta-\cdot}(\text{solv.})RH^{\delta+\cdot}]^*$ that collapses to the free ions:



or



The current results show the above trend, that is, only the compounds with a lowest triplet ${}^3n\pi^*$ excited state are capable of overcoming the ionization potential barrier imposed by 2-propanol. The oxygen atom of the carbonyl group in the triplet ${}^3n\pi^*$ excited state is considered to be highly positively charged. Hence, the carbonyl group is accessible by electrostatic interaction to a negatively charged oxygen atom in an alcohol molecule.

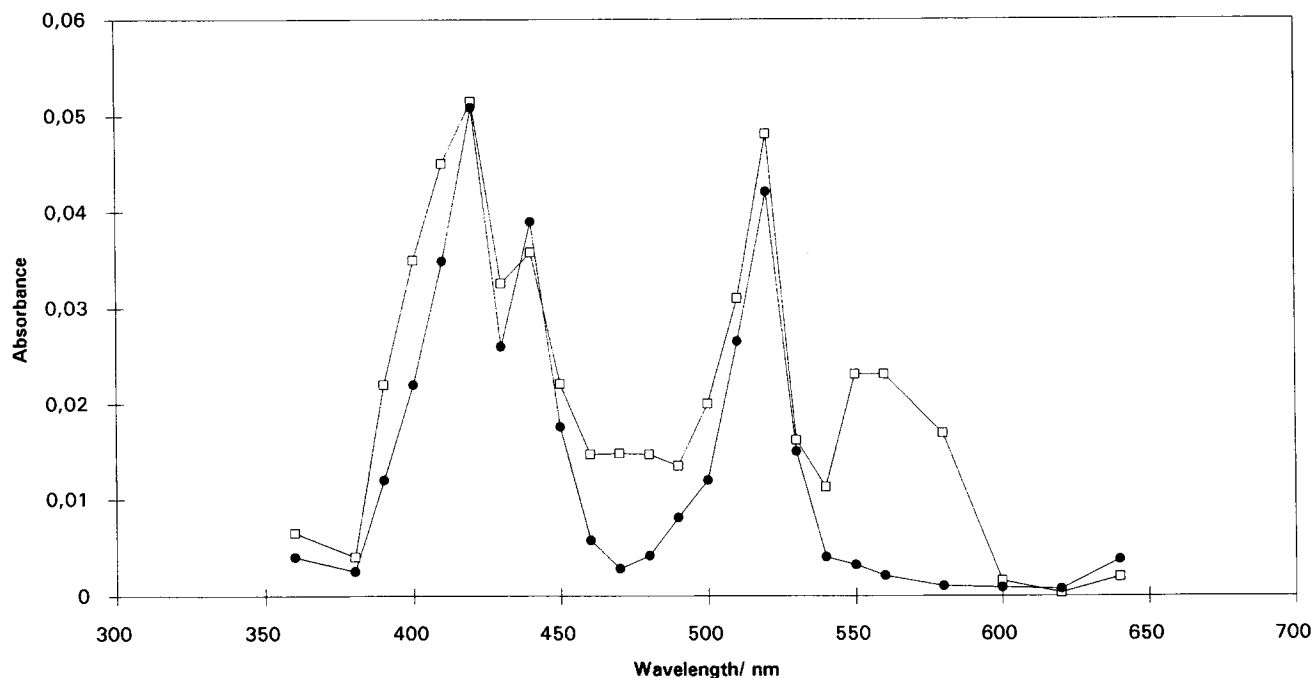
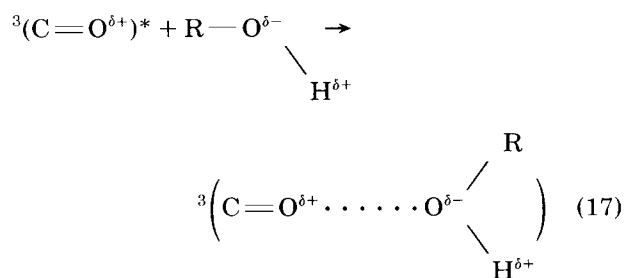
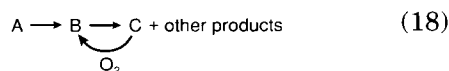


Figure 13 End-of-pulse transient absorption spectra produced on nanosecond laser flash photolysis of 2-(2-ethyl)hexylamidoanthraquinone (AQ7, $10^{-4}M$) at (□) 1.2–1.3 μs and (●) 42 μs delay in nitrogen-saturated acetonitrile with triethylamine (0.01M).



Solution Photolysis

To verify the high photopolymerization activity of the halo derivatives,² further study was undertaken to evaluate the possibility of the formation of halogen radicals and/or hydrogen atom abstraction taking place and/or the complete scission of the substituent at the 2-position of the anthraquinone. The derivative 2-(1,1-dibromomethyl)anthraquinone (AQ2) was selected for this study. The possibility of whether any of the above reactions were taking place were investigated by irradiating with polychromatic light, a nitrogen saturated methanol solution of the selected derivative for different times. The irradiated solutions were monitored by HPLC to detect the presence of photoproduct(s). The reaction sequence may be described as follows:



The analyses showed that the first photoproduct (B) is formed from the original anthraquinone (A) in less than 30 minutes of irradiation time with polychromatic light. Photoproduct B appears at a retention time of 9.5 min via HPLC under the experimental conditions described above. Further irradiation of upto 3.0 h in total showed the gradual depletion of photoproduct B with a simultaneous increase in intensity of a new chromatographic peak at 5 min retention time corresponding to photoproduct C. However, this latter product is not stable and under aerobic conditions reverts back to photoproduct B. Therefore, it was not possible to isolate and characterize photoproduct C. Analysis of photoproduct B by mass spectroscopy showed a molecular ion peak (m/z) of 300.3, indicating the loss of one bromine atom. In addition, an $M + 2$ peak at m/z 302.2 was almost of equal intensity to the former molecular ion peak, confirming the presence of one bromine atom remaining in the substituent. The proton NMR spectrum showed chemical shifts at $\delta = 4.2$ ppm assigned to the bromomethyl substituent and once again indicates the loss of one bromine atom from the derivative on polychromatic

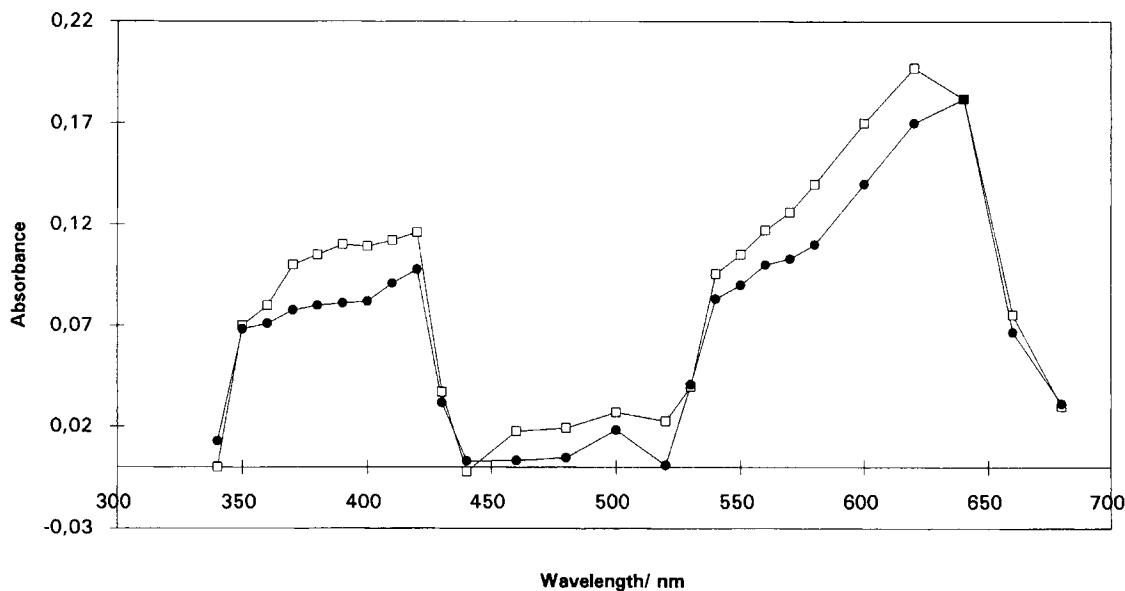
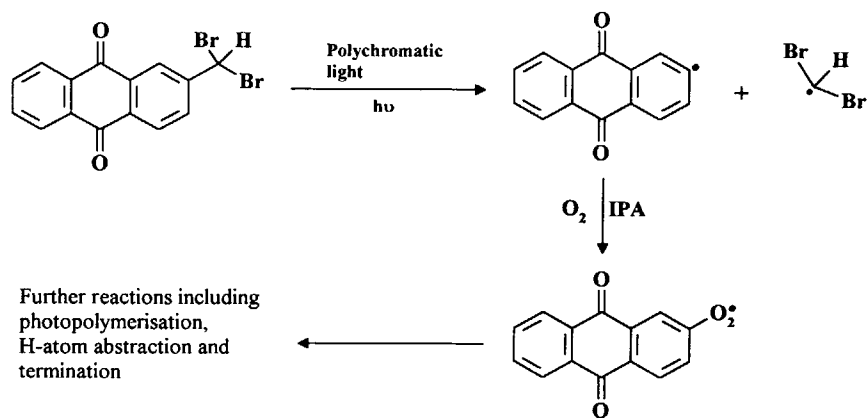


Figure 14 End-of-pulse transient absorption spectra produced on nanosecond laser flash photolysis of 2-methylcarboxyanthraquinone (AQ12, $10^{-4}M$) at (□) 200–300 ns and (●) 35 μ s delay in nitrogen-saturated acetonitrile with triethylamine (0.24M).

irradiation of a methanol solution of AQ2. From the qualitative analysis, it can be concluded that bromo radicals are being formed and that may subsequently take part in the overall photopolymerization process.

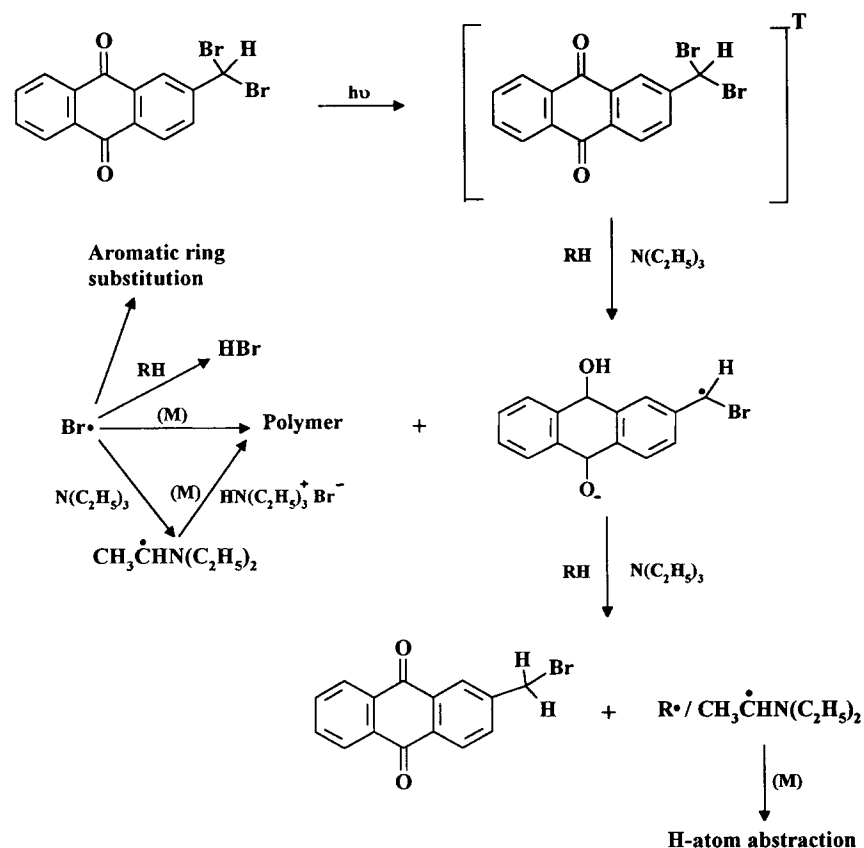
A possible mechanism of the various reactions taking place upon polychromatic irradiation are illustrated in Scheme 2. The first possibility is that of direct photolysis of the anthraquinone and the substituent to give both anthraquinonyl and the 1-dibromomethyl radicals. Both species may react further through polymerization, crosslinking, or hydrogen atom abstraction from the environment

RH or an amine to produce R^{\bullet} or an alkylamino radical. The anthraquinonyl radical may also react in the presence of oxygen and 2-propanol to form the peroxy radical that may undergo a number of reactions, including hydrogen atom abstraction. In this respect, the reactions would be similar to our previous studies on the novel perester derivatives of flourenone¹⁵ that showed the benzoyloxy and *t*-butoxy radicals taking part in reactions involving photopolymerization. The second possibility, in Scheme 3, involves the scission of the C—Br bond from a triplet excited state to produce the bromo and 2-(1-bromomethyl)anthraquinone



IPA = 2-propanol

Scheme 2



Scheme 3

radicals. The fate of the bromo radical (Br^\bullet) may follow a number of reactions. First, hydrogen atom abstraction with the environment RH would result in the formation of HBr and R^\bullet and the latter would initiate polymerization. Second, the bromo radical would directly initiate polymerization in the presence of a monomer (M). Third, the bromo radical may abstract a hydrogen atom from the amine to form the alkyamino radical that itself then initiates polymerization. The 2-(1-bromoethyl)anthraquinone radical would abstract a hydrogen atom from the environment RH or amine, in turn producing R^\bullet or an alkyamino radical, subsequently initiating the polymerization of monomer (M) by hydrogen atom abstraction. Finally, the bromo radical may take part in the aromatic ring substitution at a different position.

It is difficult to ascertain the precise mechanism by which high photopolymerization rates are achieved with the derivative 2-(1,1-dibromomethyl)anthraquinone, although the possibility of bromo radicals taking a contributory part in the overall crosslinking of the monomer should be

considered. The halo derivatives of anthraquinone show a number of advantages as potential photoinitiators. The primary step in forming the excited triplet state is favorable, as efficient intersystem crossing is aided by the heavy atom effect of halogens such as bromine. The formation of bromo radicals is important in terms of its contributory role to the overall photopolymerization process and may have importance in the future as acid generating photoinitiators.

CONCLUSION

The results from the nanosecond laser flash photolysis has given more information on the photochemical behavior of the selected range of anthraquinone derivatives with both electron-donating and electron-withdrawing substituents. In the nonhydrogen atom donating solvent of acetonitrile, the triplet half-lives are relatively long for the group of compounds containing a triplet ${}^3n\pi^*$ lowest excited state compared with those possessing a triplet ${}^3\pi\pi^*$ excited state. The presence of the triplet state in

each case was confirmed by quenching of the former with ground-state molecular oxygen. However, the degree of quenching by molecular oxygen is different for the selected compounds and is dependent on the type of substituent present at the 2-position of the anthraquinone, *vis.* amido or an ester link.

The ability of the photoinitiator to undergo a photoreduction reaction is dependent on the type of hydrogen atom donor used. The group of compounds with a lowest-lying triplet $^3n\pi^*$ excited state are relatively efficient at abstracting a hydrogen atom from 2-propanol, whereas those with lowest-lying triplet $^3\pi\pi^*$ excited state undergo a complicated mechanism in which mixed kinetics have been observed. This latter observation may be related to the side-chain reactions where the semianthraquinone radical undergoes disproportionation reaction to form the hydroanthraquinone and the original anthraquinone. The hydroanthraquinone may also reoxidize back to the original anthraquinone. However, in the presence of amine, the mechanism of electron abstraction (via a triplet exciplex) followed by proton transfer has been generally accepted. In this study, all selected anthraquinone derivatives indicated the formation of stable transients due to the presence of an exciplex or radical ion pair observed through the first-order growth rate constants. All analyses in the presence of an amine have shown the growth of transient to occur in less than 100 ns to form the stable species and the extent of its stability is reflected in the range of observed half-lives being greater than 50 μ s.

For the halo derivatives of anthraquinone (AQ 2 and 3), the results indicate that in addition to hydrogen atom abstraction taking place in the presence of 2-propanol, the possibility of halo radicals also taking part in the overall photopolymerization reaction is indicated by the solution photolysis of 2-(1,1-dibromomethyl)anthraquinone. The photopolymerization results for the halo derivatives are relatively high in the absence of amine² and indicate the mechanism to be different from the conventional hydrogen atom abstraction to form the semianthraquinone radical as shown by Scheme 2. An alternative type of mechanism may involve the complete scission of the dibromomethyl substituent at the 2-position to form the corresponding anthraquinone and the substituent radicals. The possibility of such derivatives behaving as acid-generating photoinitiators would form the basis of future work, in ad-

dition to the effects of electron-donating and electron-withdrawing groups on the photopolymerization process studied through molecular modeling.

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