Di(9-anthryl)carbene Revisited. Product Analysis and Spectroscopic Studies

Ken-ichi Yoshida, Eiji Iiba, Yoshinori Nozaki, Katsuyuki Hirai, Yasutake Takahashi, Hideo Tomioka,* Cheng-Tung Lin,[1,†] and Peter P. Gaspar[1]

Chemistry Department for Materials, Faculty of Engineering, Mie University, Tsu, Mie 514-8507

[1]Department of Chemistry, Washington University, St. Louis, MO 63130-4899, USA

Received January 21, 2004; E-mail: tomioka@chem.mie-u.ac.jp

Irradiation ($\lambda > 300$ nm) of di(9-anthryl)diazomethane (**1**) in degassed benzene gave the trimer (**3**) of dianthrylcarbene (**2**) as the main product along with a small amount of a tetramer (**4**). The structures of those oligomers were characterized as caged compounds produced as a result of three- and four-fold coupling at the 10 and 10′ positions of **2**. Photolysis of **1** in the presence of oxygen with short wavelength UV light resulted in the formation of di(9-anthryl) ketone (**5**) and anthraquinone (**6**), while similar irradiation with a longer wavelength light gave **5** and 9-anthryl 9-anthracenecarboxylate (**9**), which was found to give **6** upon irradiation with a short wavelength light in the presence of oxygen. On the other hand, the photolysis of **4** gave **3** as the main product, while **3** was almost completely photostable under similar conditions. However, irradiation of both **3** and **4** in the presence of oxygen gave **6**. In order to elucidate the reactions observed, we carried out spectroscopic studies (matrix EPR and UV/vis spectroscopies as well as laser flash photolysis) with **1**, **3**, and **4**. These studies revealed that **3** generated a trimer diradical (**10**) formed as a result of C–C bond cleavage upon irradiation and that **10** reformed **3** almost exclusively, while similar photolysis of **1** and **4** generated the same two transient species, **10** and a dimer diradical. It is proposed that triplet carbene **2** equilibrates with the dimer diradical **2-2** and that the main decay pathway of this mixture is to generate the trimer diradical **10** while dimer diradical **2-2** undergoes coupling to produce the tetramer **4**. The structure of the triplet carbene in equilibrium with diradicals is also discussed.

Triplet carbenes are usually characterized by electron paramagnetic resonance (EPR) spectroscopy.[1,2] The EPR signals can be analyzed in terms of zero-field splitting (ZFS) parameters, D and E values, which provide information on the molecular and electronic structure of triplet carbenes. The D value is related to the average separation between the unpaired electrons, and the E value is a measure of the difference of the magnitude of the dipolar interaction along the x and y axes. More plainly, the more the two electrons are delocalized in conjugated π systems, the smaller the D value will be. On the other hand, increasing the bond angle at the carbene center leads to a smaller value for E.

Among the many triplet arylcarbenes, triplet di(9-anthryl)carbene (**2**)[3–5] is unique in that it shows the smallest D and E values ever reported for a triplet diarylcarbene. This indicates that it has an almost linear geometry at the carbene center, with extensive delocalization of the unpaired electrons onto the attached anthryl groups, whose planes are perpendicular to each other. The extensive delocalization is expected to stabilize this carbene thermodynamically, while the perpendicular geometry of the anthryl groups stabilizes the carbene center kinetically through steric shielding by the four *peri*-hydrogens. That is, both the electronic structure and sterics of the molecule seem ideal for the formation of a stable triplet carbene.

In spite of these highly interesting findings, only two papers have been published concerning this carbene, and extensive characterization of this species and its chemistry still is not available.

Triplet di(9-anthryl)carbene (^{3}**2**) was first generated in 1971 by photolysis of the corresponding diazo precursor (**1**) and characterized by EPR spectroscopy in a dianthryl ketone matrix, which revealed relatively small values for both E and D, i.e., 0.0011 and 0.113 $\mathrm{cm^{-1}}$, respectively, at 4 K (Scheme 1).[3] Annealing the matrix allows the carbene to adopt its minimum energy structure, which is almost completely linear, i.e., the value of E drops to zero (Scheme 1). It has been reported that the half-life of ^{3}**2** in the matrix was 7 min at 200 °C; however, it was also concluded that the stability was due to the rigidity of the environment and not to an intrinsic lack of reactivity. A solid solution of ^{3}**2** in viscous glass matrices such as 2-methyltetrahydrofuran was stable at 77 K, but, upon warming with a consequent thawing of the matrix, ^{3}**2** disappeared irreversibly.[3]

The reactivity of ^{3}**2** in solution at ambient temperatures was then studied in 1988 in more detail, and it was found that ^{3}**2** underwent a bimolecular self-reaction at the diffusion-controlled limit. Singlet carbene **2** was not quenched by a typical trapping reagent for a singlet carbene, i.e., methanol, but the triplet was quenched by oxygen with a rate constant of $1 \times 10^6\ \mathrm{M^{-1}\,s^{-1}}$, nearly 5 orders of magnitude smaller than the rate constants for many other triplet carbenes. Product studies showed that ^{3}**2** reacted with O_2 to form dianthryl ketone and anthraquinone but formed the *carbene dimer* in the absence of O_2, thus supporting the interpretation of the reaction kinetics.[4] As part of

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[†] Current address: Department of Chemistry, Box 864, Tunghai University, Taichung 400, Taiwan

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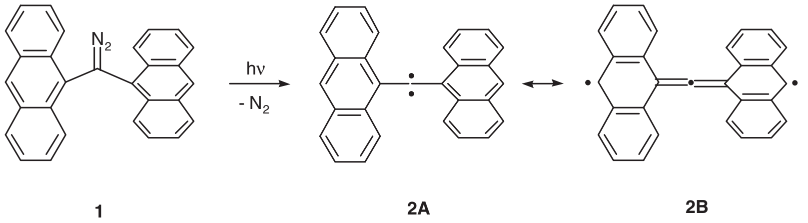
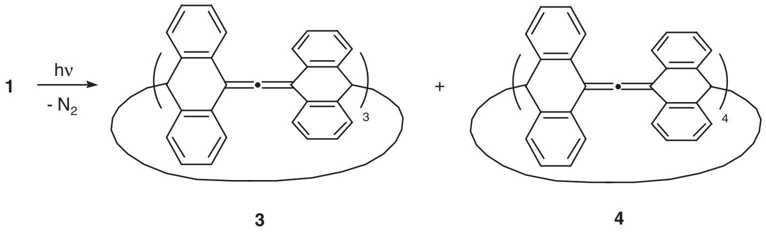


Scheme 1.



Scheme 2.

our continued attempts to isolate a triplet carbene,[6] the chemistry of dianthrylcarbene was investigated by product analysis and spectroscopy.

Results

Product Analysis Studies. Photolysis of Dianthryldiazomethane: Irradiation ($\lambda > 300$ nm) of di(9-anthryl)diazomethane (**1**, 5×10^{-3} M) in degassed benzene caused rapid fading of the orange diazo color with copious evolution of nitrogen gas to give a pale-yellow solution. Gel permeation chromatography of the photomixture resulted in the isolation of white crystals (mp 332–333 °C) in 55% yield. The spectroscopic data suggested that the trimer of dianthrylcarbene (**2**), formed as a result of 10–10′ coupling, is the most likely structure. The mass spectrum (FAB MS) showed a peak at m/z 1099.1 (19.1%), which corresponds to the $M + 1$ ion calculated for three di(9-anthryl)carbene units. Additional peaks were observed at m/z 732.1 (19.6%) and 366 (100%), corresponding to the fragments formed as a result of the successive loss of a carbene unit from the trimer. Thus, the data clearly suggest that the main product is the trimer of di(9-anthryl)carbene rather than a dimer, as suspected earlier.[4] The structure of the trimer which explains the NMR data best is the one (**3**) formed as a result of three-fold coupling at the 10 and 10′ positions of di(9-anthryl)carbenes (Scheme 2). ^{1}H NMR (500 MHz) showed the presence of eight aromatic proton signals ranging from 5.91 to 7.79 ppm, plus one signal of a proton at a benzylic carbon atom at 4.82 ppm. The ^{13}C NMR (126 MHz) displayed a total of 12 sp^2 signals between 136.42 and 125.46 ppm. In addition, two signals were observed at 208.34 and 111.10 ppm, most probably assignable to the central and terminal carbons on an allenic subunit, respectively, and to one sp^3 carbon at 55.06 ppm.

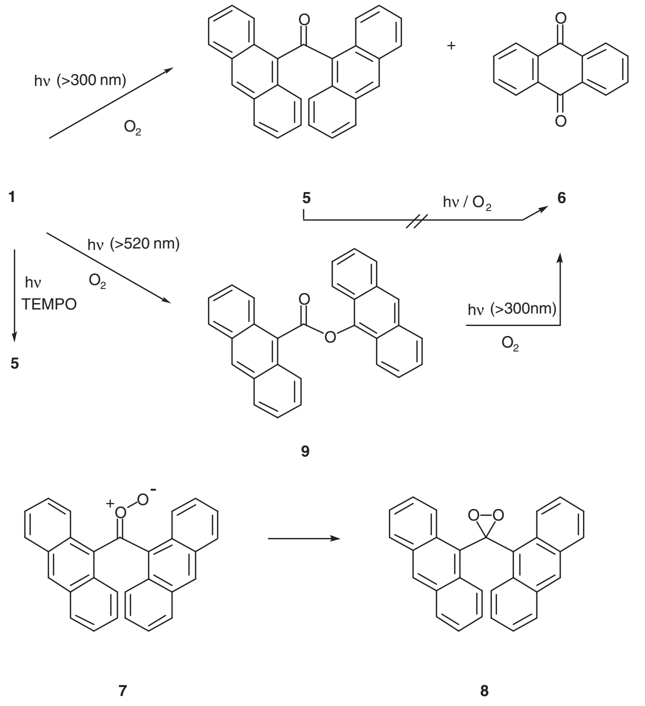
The X-ray crystallographic analysis of **3** revealed that the compound has a complicated structure and a flattened hexagonal bipyramidal shape.[5c]

A minor product was isolated from a higher-molecular-weight fraction as white crystals (mp 222–223 °C) in 12% yield. The ^{1}H and ^{13}C NMR spectra of the minor product were very similar to those observed for the trimer **3**, but the mass spectrum showed a peak at m/z 1466.2 (10.5%), corresponding to the $M + 1$ ion calculated for the tetramer, along with 1098.5 (12.2%) and 732.2 (63.2%) corresponding to the fragments formed as a result of the loss of one and two carbene units, respectively. The structure of the tetramer which fits those data best is that of (**4**), formed as a result of four-fold coupling at the 10 and 10′ positions of **2** (Scheme 2).

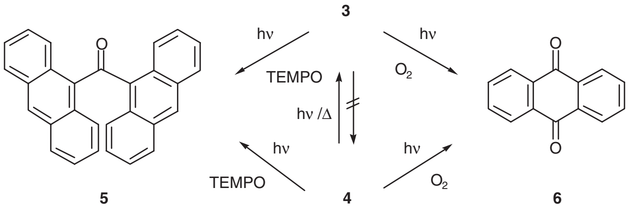
The formation of the oligomers (**3** and **4**) is not quenched even in the presence of typical carbene trapping agents.[8] Thus, similar irradiations in the presence of methanol, 1,4-cyclohexadiene, 2-methyltetrahydrofuran, and phenylsilane again produced the oligomers in similar corresponding yields. No evidence was found for any reaction with these trapping agents at either the divalent carbon atom or the 10 and 10′ positions. Neither the methyl ether, which is expected to be formed as a result of insertion of the carbene into an O–H bond of the alcohol,[7] nor a reduction product such as di(9-anthryl)methane or 9,9′-di(9-anthrylidene)allene, which might have been formed as a result of H atom abstraction at the divalent carbon or at the 10,10′-positions, respectively, was detected. However, dianthrylcarbene reacted with thiophenol in a dark at room temperature to give di(9-anthryl)methyl phenyl sulfide.

The ratio of the oligomers appears to be sensitive to the reaction conditions. When a frozen glass containing 2.5×10^{-3} M **1** dissolved in 2-methyltetrahydrofuran was irradiated at 77 K until no **1** remained and then thawed, **3** was still the major product, but chromatographic and spectroscopic analysis indicated the presence of an increased amount of a higher oligomer of **2**.

However, when the irradiation was carried out in a non-degassed benzene solution, two oxidation products, i.e., dianthryl ketone (**5**) and anthraquinone (**6**), were formed at the almost complete expense of oligomer formation (Scheme 3). Although the formation of the ketones in the photolysis of diaryldiazomethanes in the presence of oxygen via the intermediacy of the related carbonyl oxides (e.g., **7**) followed by the self-reaction has been demonstrated,[9] the formation of anthraquinone (**6**) cannot be explained easily. The possibility that **6** is pro-



Scheme 3.



Scheme 4.

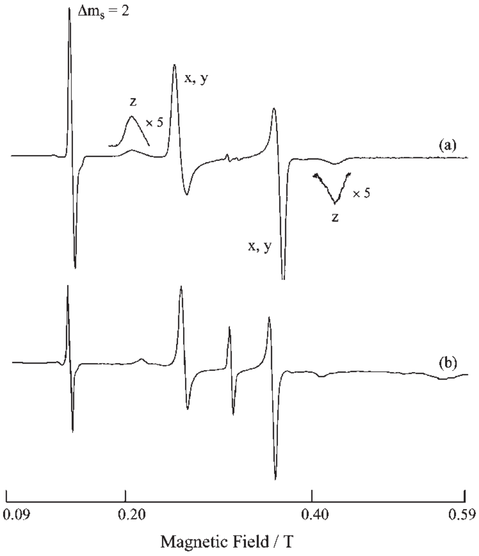


Fig. 1. ESR spectra of di(9-anthryl)carbene (^{3}**2**) in 2-methyltetrahydrofuran (2-MTHF) matrix (a) at 77 K and (b) at 110 K.

duced by the photo-oxidation of **5** is precluded by the finding that **5** is almost completely stable under the photolysis conditions. It is unlikely, however, that the quinone is formed by a completely different pathway from that producing the ketone. It has been shown that carbonyl oxides undergo rearrangement, either thermally or photochemically, to give dioxiranes (e.g., **8**) and then esters (e.g., **9**) in competition with the oxygen transfer to form ketones.[9] Thus, the ester, i.e., 9-anthryl 9-anthracenecarboxylate (**9**), is proposed to be the most likely precursor for quinone **6**. Indeed irradiation of ester (**9**) under essentially the same conditions as employed for the photolysis of **1** gave the quinone (**6**) almost exclusively. Moreover, the ester (**9**) was detected when the irradiation of **1** was carried out with longer wavelength light (λ > 520 nm) and decomposed to give **6** upon further irradiation with shorter wavelength light (λ > 300 nm) (Scheme 3).

Another reagent which can trap **2** with moderate efficiency was a persistent nitroxide radical. Thus, irradiation of **1** in degassed benzene containing 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) gave dianthryl ketone (**5**) and tetramethylpiperidine in equimolar amounts (Scheme 3).[10] It has been pointed out that the reaction of triplet diphenylcarbene with a persistent nitroxide is spin-allowed and over 100 kcal/mol exothermic. Indeed, the reaction proceeds smoothly to give benzophenone and piperidine. The absolute rate constant was determined to be 2.7×10^8 M^{-1} s^{-1} in acetonitrile, which is well below the diffusion limit and much slower than the corresponding reaction with molecular oxygen ($k_{O_2} = 5 \times 10^9$ M^{-1} s^{-1}).[9,11]

Photolysis of a Trimer and a Tetramer: In spite of its sterically highly congested structure, the trimer **3** exhibited surprising stability. It remained unchanged both upon heating in degassed C_6D_6 at 140 °C for 2 h and upon irradiation in degassed benzene with light (λ > 300 nm) for 2 h. However, it decomposed in air either thermally or photochemically to give anthraquinone (**6**) as the main product. More interestingly, it reacted with TEMPO under irradiation (λ > 300 nm) to form dianthryl ketone (**5**) exclusively (Scheme 4).

The tetramer **4** showed completely different reactivity upon heating and irradiation. Thus, irradiation of **4** in degassed C_6D_6 produced the trimer **3** almost exclusively. The tetramer **4** was also thermally labile; it started to decompose already at 50 °C in degassed C_6D_6, then rapidly and completely decomposed at 100 °C to form the trimer **3** as the only identifiable product among a large amount of tarry compounds. However, the tetramer exhibited essentially the same reactivity as that of the trimer toward O_2 and TEMPO; it gave, upon irradiation in the presence of TEMPO or O_2, **5** or **6**, respectively (Scheme 4).

Spectroscopic Studies in Frozen Media at Low Temperature. In order to gain more direct information about the structure and reactivity of **2**, the following spectroscopic studies were carried out.

Matrix Photolysis of 1: Irradiation of **1** (2.5×10^{-3} M) in 2-methyltetrahydrofuran (2-MTHF) at 77 K gave EPR signals with typical fine structure patterns for unoriented triplet species (Fig. 1a). The spectrum showing unresolved x and y lines and a rather intense line at 152 mT corresponding to $\Delta m_s = 2$ is very similar to that recorded for triplet dianthrylcarbene in a dianthryl ketone matrix[3] and, hence, can be safely assigned to ^{3}**2**. Very small D and E values ($D = 0.1038$ cm^{-1} and $E = 0.0000$ cm^{-1}) calculated from the spectra are also in good agreement with those reported for ^{3}**2**. The EPR signals not only were stable at this temperature for hours but also survived warming up to 130 K. However, when the samples were gradually warmed, the signals became sharp at around 90 K, a small shift in the *z* lines was observed, and a small but distinct decrease in the *D* value is noted ($D = 0.089$ cm^{-1} and $E = 0.0000$ cm^{-1}) (Fig. 1b).

A decrease in the *D* and *E* values upon annealing the matrix has often been observed for sterically congested triplet diarylcarbenes and is usually interpreted in terms of geometrical changes.[2c,12] Thus, when a carbene is generated in rigid matrices at very low temperature, it should have the geometry dictated by that of a precursor. Even if the thermodynamically most stable geometry of the carbene is different from that at birth, the rigidity of the matrices prevents the carbene from achieving its minimum-energy geometry. In the present case, this state is now termed ^{3}**2**(nascent) or ^{3}**2**n. When matrices are softened by annealing, the carbene undergoes (e.g., ^{3}**2**n) relaxation to the preferred geometry probably to gain relief from steric compression. It has been shown that the ZFS parameters of sterically unperturbed diphenylcarbenes show little sensitivity toward the temperature of the matrix.[13] The rather small *D* values coupled with the essentially zero *E* value observed for ^{3}**2** indicate that there is extensive delocalization of the unpaired electrons into the anthryl portions and that the carbene has a substantial degree of allenic character. A small but distinct decrease in the *D* value upon annealing the matrix can thus be interpreted as indicating that the triplet carbene relaxed to a nearly linear geometry, in which the unpaired electrons are further delocalized into anthryl portions. This state is now termed ^{3}**2**(relaxed) or ^{3}**2**r. Although the *E* values must accordingly have changed in this case, their small magnitudes did not allow us to observe these changes.

Another interesting feature of the EPR spectra is the fact that peaks at around 333.7 mT became stronger at the expense of the signals attributable to ^{3}**2**r as the matrix temperature increased (Fig. 1b). Usually, these peaks are observed in the photolysis of diazo compounds in organic matrices at low temperatures and are assigned to "radical impurities" formed under the photochemical conditions.[2] In the present case, however, the new signals increased at the expense of the signals due to ^{3}**2**r; hence, they are ascribable to a doublet species produced as a result of a thermal reaction of ^{3}**2**r.

When the irradiation of **1** (1.2×10^{-4} M) in a 2-MTHF glass at 77 K was monitored by UV/vis spectroscopy, a new absorption band at 359 nm and a rather broad band at 450 nm appeared at the expense of the original absorption due to **1** (Fig. 2b).[14] The glassy solution did not exhibit any spectral change for several hours when kept at this temperature. However, when it was allowed to warm to room temperature and then cooled to 77 K, the characteristic bands disappeared (Fig. 2e). On the basis of these observations coupled with EPR data (vide supra), the absorption spectrum can be attributed to the nascent triplet dianthrylcarbene (^{3}**2**n).

When the spectral changes of the matrix were more carefully monitored as a function of temperature, an interesting feature appeared. For example, when the matrix was warmed gradually to 85 K, a broad absorption band at 450 nm changed rather dramatically to a sharp and strong band with its maximum shifting to a shorter wavelength at 448 nm, while the band at 359 nm shifted very little with a slight increase in the intensity (Fig. 2c). At 115 K, the band at 448 nm shifted further to a shorter wavelength, 433 nm, with a significant decrease in intensity, while the band at 359 nm again shifted very little with a decrease in intensity (Fig. 2d). Upon further thawing, all of those bands disappeared to form a featureless band with an apparent maximum at 294 nm (Fig. 2e), which is essentially the same as the spectrum of the final product, e.g., **3**. These observations suggest that at least three transient species including ^{3}**2** were involved, i.e., nascent triplet carbene ^{3}**2**n (359, 450 nm), species A (359, 448 nm), and B (361, 433 nm). These changes were not reversed even when the samples were recooled.

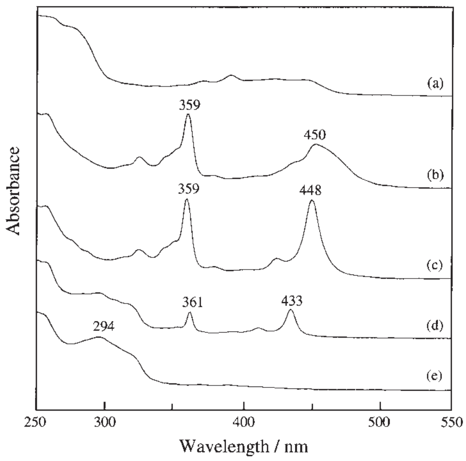


Fig. 2. UV/vis spectra obtained by irradiation of **1** in MTHF. (a) Spectra of **1** in 2-MTHF at 77 K; (b) same sample after 5 min irradiation ($\lambda > 350$ nm); (c) same sample after warming to 85 K; (d) same sample after warming to 115 K; (e) same sample after warming the matrix to room temperature and refreezing to 77 K.

The EPR studies clearly showed that the signals changed from the nascent, less linear geometries to the relaxed, almost linear ones ^{3}**2**r as the temperature was increased from 77 to 110 K in 2-MTHF. Therefore, the initial changes (from ^{3}**2**n to A) are interpreted in terms of the geometrical changes leading to relaxed triplet carbene ^{3}**2**r, associated with viscosity changes rather than intermolecular reactions, e.g., hydrogen abstraction, with matrices. These spectral changes associated with geometrical changes have often been observed in similar spectroscopic studies of sterically congested diarylcarbenes.[15] The successive changes (from A = ^{3}**2**r to B) are explained in terms of the chemical reactions of ^{3}**2**r rather than the geometrical changes since the EPR signals due to a doublet species dominated under these conditions at almost the complete expense of the original signals due to ^{3}**2**r.

Support for the assignment was obtained when the spectral changes were monitored using other organic glasses of different viscosity. For instance, in a viscous matrix, i.e., triacetin matrices ($\eta/\eta_{\text{3-MP}} = 1.2 \times 10^{45}$),[16] the initial, second, and final spectral changes were observed at 190, 220, and 230 K, respectively (Fig. 3). In marked contrast, when soft matrices were used, the initial photoproduct at 77 K was very similar to the secondary product formed upon annealing the initial product in the hard matrix, i.e., 2-MTHF ($\eta/\eta_{\text{3-MP}} = 6.9 \times 10^{5}$).[16] Thus, irradiation of **1** in 3-methylpentane–isopentane (3-MP–

IP, 1:1, $\eta/\eta_{\text{3-MP}} = 6.3 \times 10^{-4}$)[16] matrices at 77 K resulted in the appearance of two sharp bands at 357 and 445 nm without showing a broad band centered at around 450 nm. The spectra started to change already at 85 K to form the 432 nm species (Fig. 4).

Matrix Photolysis of Oligomers 3 and 4: In order to gain more insights into the nature of the other transient species detected in the photolysis of **1** in a matrix at low temperature, we also irradiated the final stable products, i.e., **3** and **4**, and studied them spectroscopically under identical conditions. Irradiation of **3** in a 2-MTHF matrix at 77 K gave EPR signals centered at 333 mT ascribable to a doublet species, but no triplet signals were observed (Fig. 5a). When the irradiation was monitored by UV/vis spectroscopy, new absorption bands with maxima at 361 and 433 nm were detected (Fig. 5b). The EPR signals and the absorption disappeared upon thawing the matrix, but reappeared upon irradiation at 77 K. Those spectral changes could be repeated several times. Moreover, analysis of the spent solution indicated that no new product was detected. These observations suggest that the transient species is likely to be diradical (**10**) produced as a result of cleavage of a C–C singlet bond connecting the dihydroanthracene unit in **3** (Scheme 5). Essentially the same spectroscopic changes were observed in the photolysis of the tetramer **4** under identical conditions. However, in this case, the formation of a trimer was confirmed in the spent solution (Schemes 4 and 5). Taking into account the fact that **3** and **4** are composed of the same unit, i.e., two dihydroanthracene units connected by an allene bond, it is

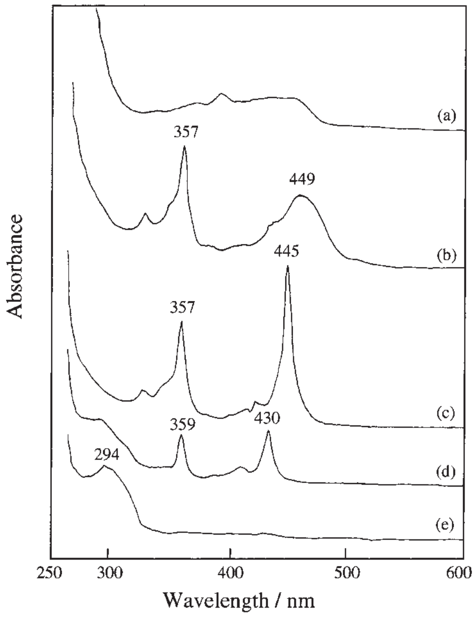


Fig. 3. UV/vis spectra obtained by irradiation of **1** in triacetin matrices. (a) Spectra of **1** in triacetine at 77 K; (b) same sample after 5 min irradiation; (c) same sample after thawing at 190 K; (d) same sample after thawing at 220 K; (e) same sample after thawing at 230 K.

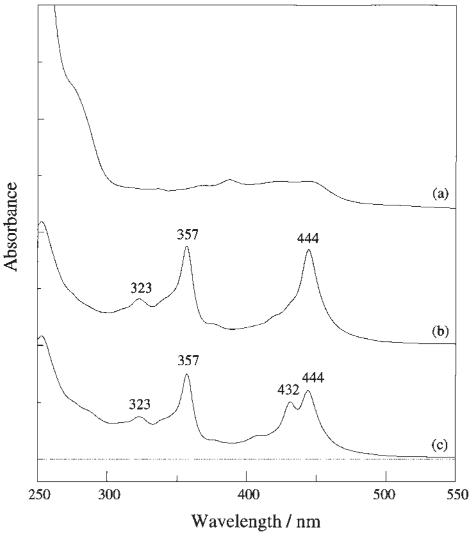


Fig. 4. UV/vis spectra obtained by irradiation of **1** in 3-methylpentane–isopentane matrices. (a) Spectra of **1** in 3-methylpentane–isopentane at 77 K; (b) same sample after 5 min irradiation; (c) same sample after thawing at 85 K.

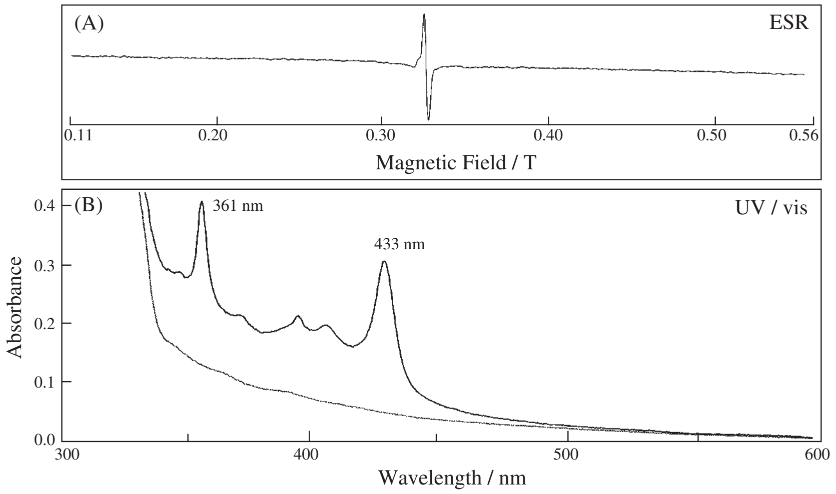
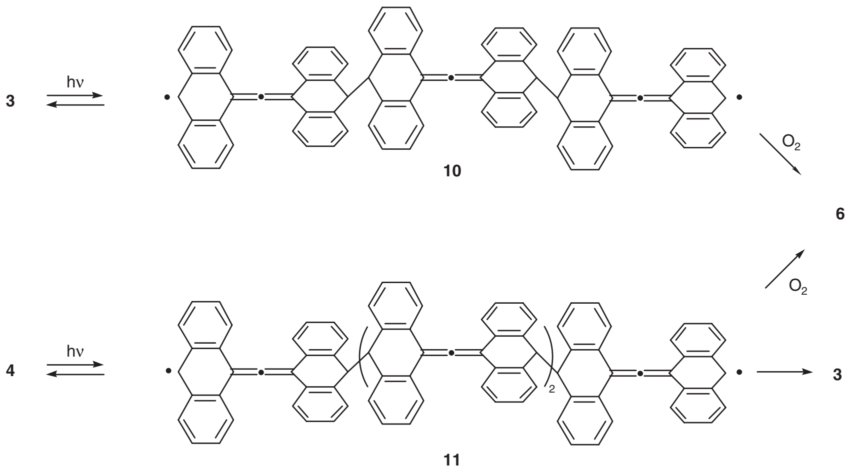


Fig. 5. (a) ESR spectra obtained by irradiation of **3** in 2-MTHF at 77 K. (b) UV/vis spectra obtained by irradiation of **3** in 2-MTHF at 77 K.



Scheme 5.

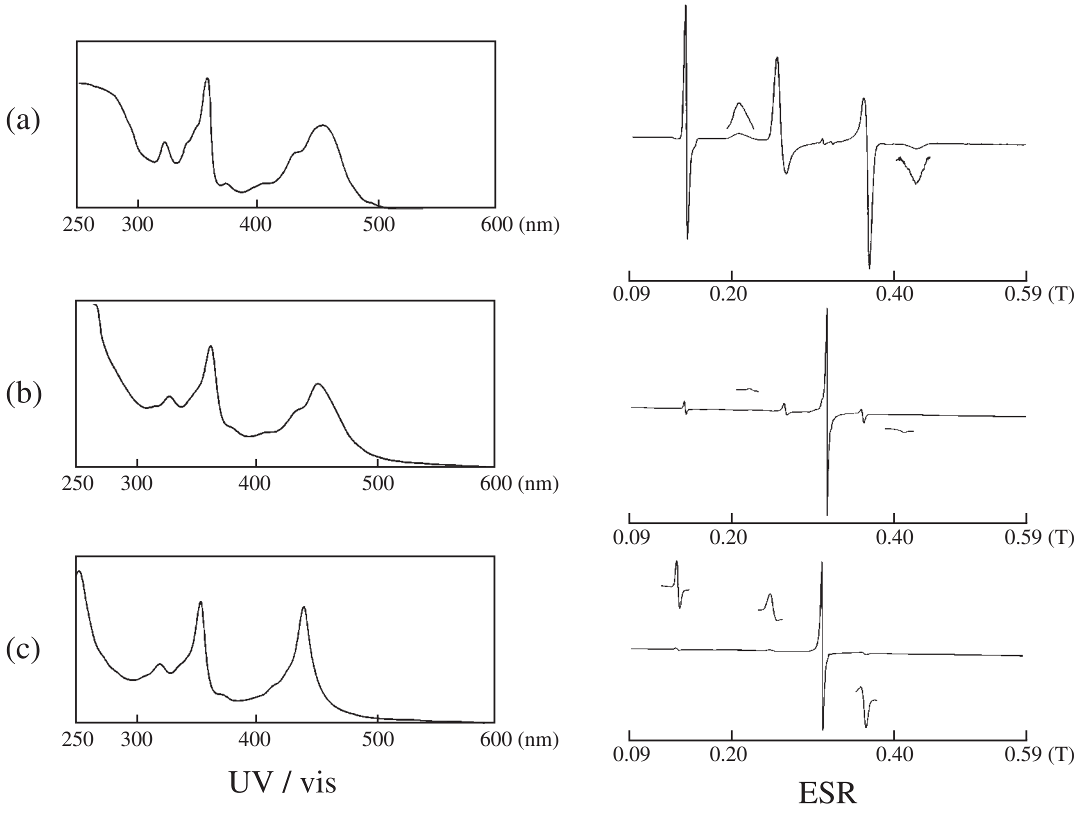


Fig. 6. UV/vis and ESR spectra obtained by irradiation of **1** in (a) 2-methyltetrahydrofuran, (b) 3-methylpentane, and (c) 3-methylpentane–isopentane matrices at 77 K.

reasonable to expect that the diradicals (**10**, **11**) formed as a result of C–C bond cleavage should have a very similar spectroscopic feature.

A comparison of the spectra observed in the photolysis of **3** and **4** with those obtained in the irradiation of **1** suggests that the spectroscopic features of the diradicals formed upon photolysis of **3** and **4** are very similar to those of the species B produced from the relaxed triplet carbene ^{3}**2**r upon annealing the matrix. Careful comparison of the results from both techniques, UV/vis and EPR, suggests that the ratio of the triplet carbene signals to the "radical" doublet signals roughly corresponds to the ratio of the 457-nm broad bands to the 448-nm sharp bands in the UV/vis spectra. Thus, in triacetin and 2-MTHF matrices, where the doublet radical signals were essentially not observed at 77 K, only broad 457-nm bands appeared at 77 K; in the 3-MP–IP (1:1) matrix, on the contrary, where the sharp 445-nm band formed initially even at 77 K, no carbene signals were observed in EPR. The 3-MP matrix probably lies between the two extremes; the 457 and 448-nm bands were apparent in the UV/vis spectra as were the radical and carbene signals, which were observed in EPR (Fig. 6). Detailed analysis of the thermal changes of triplet carbene **2** using EPR spectroscopy also supports this assignment. Thus, when the triacetine matrix containing triplet **2** was gradually thawed, the characteristic triplet signals started to decrease with a concomitant increase in the intensity of the diradical signals at around 200 K, the same temperature at which the broad 455-nm bands started to decay to form the sharp 445-nm bands in the UV/vis spectrum. These observations suggest that the broad 457-nm bands that initially formed at 77 K in hard matrices are assignable to the triplet carbene **2**, while the sharp 445-nm bands formed either in the soft matrices at 77 K or upon thawing of the hard matrices are obviously not attributable to the geometrical isomers of the triplet carbene.

Laser Flash Photolysis (LFP) Studies in Solution at Room Temperature. The LFP of Diazomethane 1: Laser flash photolysis (LFP) of **1** (1.6×10^{-4} M) in a degassed benzene solution at room temperature with a 10 ns, 10 mJ, and 308-nm pulse from a XeCl laser produced a transient species showing strong, rather sharp bands at 362 and 435 nm, which appeared coincidently with the pulse and disappeared within 1 ms (Fig. 7). Due to overlap with the absorption maxima of the diazo precursor **1**, the samples are not sufficiently transparent for adequate monitoring in the 300–330-nm region. However, the two bands decayed in a similar manner, in which two decay modes were involved. The first 80% of the decay was fit to a first-order decay ($k = 4.3 \times 10^5$ s^{-1}, $\tau = 2.3$ μs), while the residual slower decay was found to be of the second order ($2k/\varepsilon l = 6.5 \times 10^4$ s^{-1}). This observation indicates that two transients with considerably different reactivities but very similar absorption bands are actually involved.

The transient spectra were compared with those observed in the photolysis of **1** in a matrix at low temperature. The transient band observed by LFP is obviously different from the broad band centered at 450 nm (Fig. 2b) that is ascribable to the nascent triplet carbene ^{3}**2**n observed in a rigid matrix at low temperature. The former band is, however, very similar to those assigned as either a relaxed, more linear triplet carbene ^{3}**2**r (Fig. 2c) or as a diradical (**10** and **11**) species (Fig. 3b) generated as a result of the C–C bond cleavage of the oligomers **3** and **4**. The rather poor resolution of the spectra obtained by LFP as opposed to that in the matrix, along with the similarity of the spectroscopic shapes of the two species, did not allow us to make a definite assignment of the species simply on the basis of the shape of the spectra.

The LFP of **1** in the presence of oxygen gave somewhat different results (Fig. 8). Thus, the LFP of a non-degassed solution of **1** again produced essentially the same transient species as observed in the LFP of the degassed solution of **1**. However, there are two observations that should be noted. First, the decay rate of the transients was found to increase as a function of the oxygen concentration, indicating that the transient species are quenched by oxygen. The plot of the decay rate as a function of the oxygen concentration in the range of 0.1 to 10 mM is linear. The slope of this plot yields a quenching rate constant by oxygen, $k_{O_2} = 4.0 \times 10^8$ M^{-1} s^{-1}, and the intercept yields $k_0 = 4.1 \times 10^5$ s^{-1} (inset in Fig. 8). Second, the optical yields of the species were notably decreased as the concentration of oxygen in the solution increased. This suggests that a precursor leading to the observed species is also trapped by oxygen. The product studies in Scheme 3 indicated that the photolysis of **1** in the presence of oxygen produced di(9-anthryl) ketone and 9-anthryl 9-anthracenecarboxylate, which are most probably derived from the reaction of triplet dianthrylcarbene with oxygen, most probably by way of the oxides **7**. Therefore, it is likely that the precursor to the observed species is triplet carbene ^{3}**2**. It is well documented that diarylcarbenes with triplet ground states are readily trapped by oxygen to give the corresponding diaryl ketone oxides, which exhibit rather broad bands in the visible region and, hence, are relatively easily detected by LFP.[9,11] However, all attempts to detect the oxides **7** were unsuccessful. It may be that the oxide is not long-lived enough to be observed, at least to the limit of the time resolution (~50 ns) of our LFP system or that the absorption bands are too broadened and/or too red-shifted to be detected to the limit of detection of our system.

The transient species were not trapped at all by 1,4-cyclohexadiene, which is also known as an equally efficient trapping

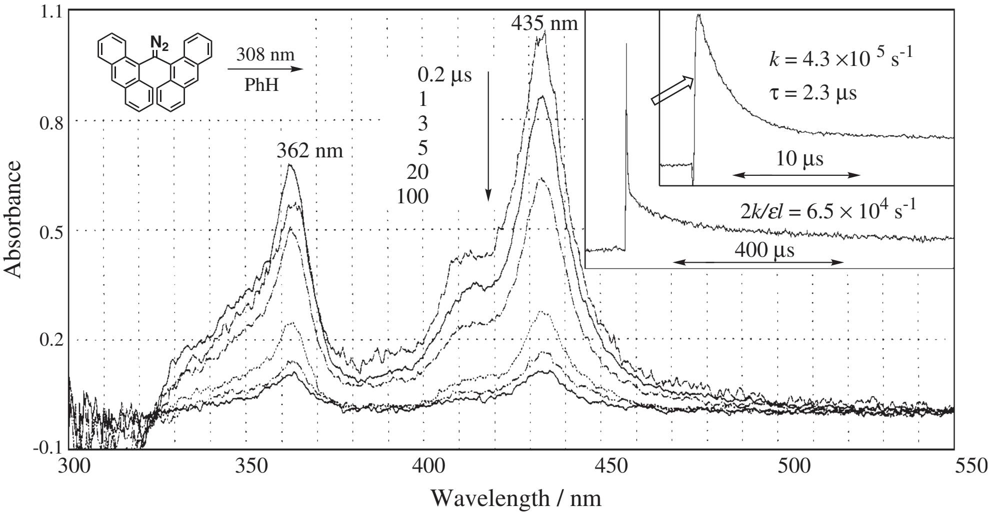


Fig. 7. Absorption spectra of the transient products obtained upon 308-nm excitation of **1** in degassed benzene recorded after 0.2, 1, 3, 5, 20, and 100 μs. Inset shows the decay of the transient products monitored at 435 nm.

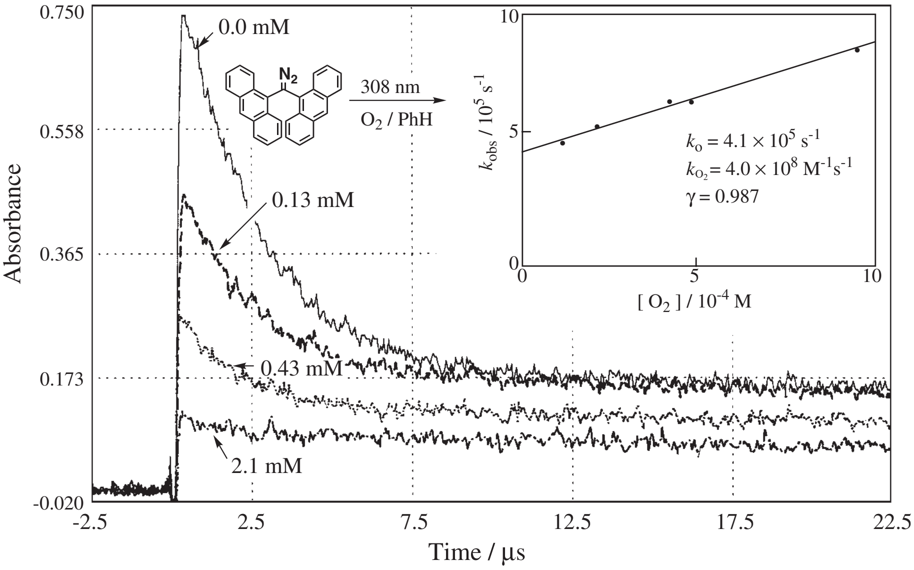


Fig. 8. Effect of increasing oxygen concentration on the decay of transient following pulse irradiation in benzene at 20 °C, monitored at 435 nm. Inset shows plot of decay rate as a function of oxygen concentration.

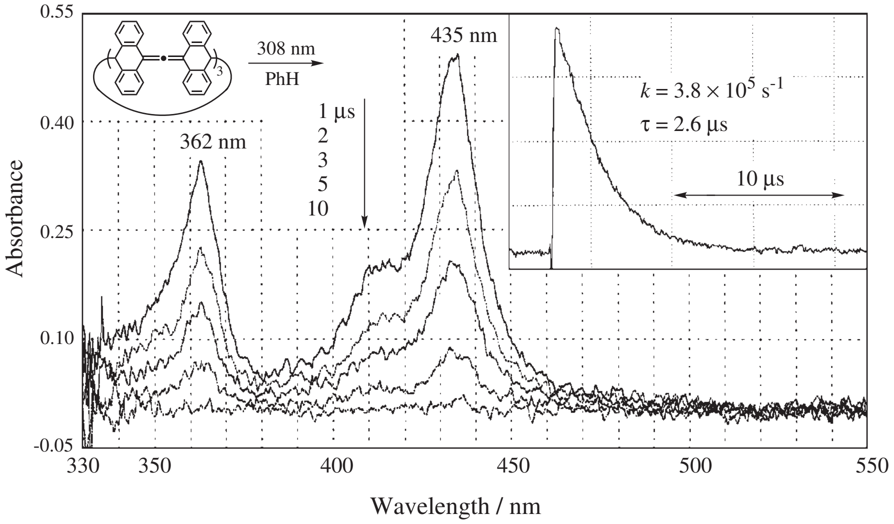


Fig. 9. Absorption spectra of the transient products obtained upon 308-nm excitation of **3** in degassed benzene recorded after 1, 2, 3, 5, and 10 μs. Inset shows the decay of the transient products monitored at 435 nm.

reagent for triplet carbene.[17] Thus, the LFP of **1** in the presence of 1,4-cyclohexadiene gave the same transient absorption bands, which decayed in a similar manner as in degassed benzene. It is also well known that diarylcarbenes generated in good hydrogen donors, such as the diene, undergo H-abstraction leading to the corresponding diarylmethyl radicals, which usually show transient absorption at longer wavelengths than that of the precursor carbene and are, hence, easily detected.[18] The LFP of **1** in methanol also gave the same results. Those spectroscopic observations, along with the product analysis studies, which show that the formation of **3** and **4** is not quenched at all either by methanol or by the diene, suggest that the transient species is not a triplet carbene but is likely an intermediate leading to the final products, **3** and **4**.

The LFP of Oligomers: In order to identify the origins of the intermediate, the LFP studies of the trimer (**3**) and the tetramer (**4**) were performed. The LFP of **3** in degassed benzene produced a transient species (Fig. 9) showing essentially the same bands as observed in the matrix photolysis of **3** (Fig. 5). The bands were also similar to those observed in the LFP of **1**. However, all the transient bands exhibited very clean first order kinetic decay, and the decay rate was essentially the same ($k_1 = 3.8 \times 10^5$ s^{-1}, $\tau = 2.6$ μs) as that of the fast-decaying species observed during the LFP of **1**. The product analysis data indicate that the trimer undergoes C–C bond cleavage to form a diradical (Scheme 5), which undergoes recombination almost exclusively in the absence of a trapping reagent but forms oxidation products in the presence of oxygen. This data along with the matrix spectroscopy observations mean that the most likely transient species is the trimer diradical (**10**) formed as a result of fission of the sp^3 C–C bond of the dihydroanthryl portion. This in turn suggests that the major species observed in LFP

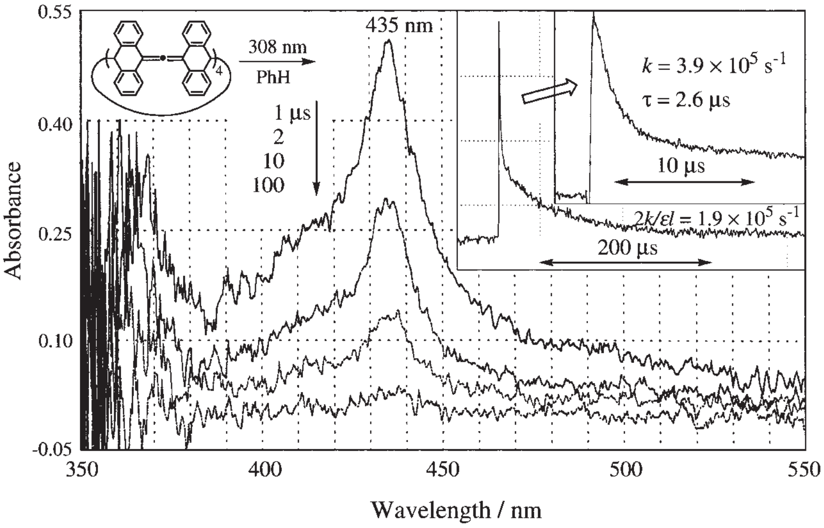
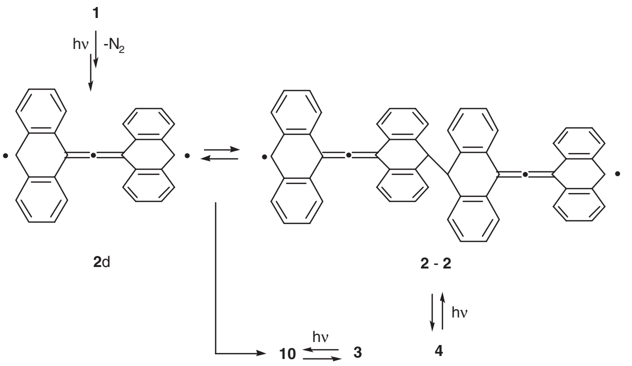


Fig. 10. Absorption spectra of the transient products obtained upon 308-nm excitation of **4** in degassed benzene recorded after 1, 2, 10, and 100 µs. Inset shows the decay of the transient products monitored at 435 nm.

of **1** can be assigned as **10**.

The LFP of **4** gave somewhat different results. Absorption bands obtained in the LFP of **4** were essentially identical to those observed in the LFP of **1** and **3**, but the bands decayed similarly to those from **1** rather than to those from **3** (Fig. 10). Thus, most of the bands decayed by first-order kinetics ($k_1 = 3.9 \times 10^5$ s^{-1}, $\tau = 2.6$ µs), while the remaining minor component decayed very slowly in a second-order fashion ($2k_2/\mathcal{E}l = 1.9 \times 10^5$ s^{-1}). This means that the LFP of **1** and **4** results in the generation of the same two species.

The fast-decaying main species observed in the LFP of both **1** and **3** can be safely assigned to a trimer diradical **10** if one compares its spectroscopic features and decay kinetics with those of the LFP of a trimer **3**. The assignment is in agreement with the results of a product analysis, which showed that the main product obtained in the photolysis of both **1** and a tetramer is a trimer. What is this slow-decaying minor species observed in the LFP of tetramer (and also of **1**), then? Since a tetramer is formed in both cases, the most likely species is a precursor leading to the tetramer. As this species decays by second-order kinetics, a dimer diradical (**2-2**) can be assumed as a possible intermediate (Scheme 6).



Scheme 6.

Discussion

Photolysis of di(9-dianthryl)diazomethane (**1**) resulted in the formation of the trimer (**3**) as a main product along with a small amount of the tetramer (**4**), both of which are most probably formed by way of the corresponding carbene (^{3}**2**). The structures of the products strongly reflect the unique nature of the triplet carbene (^{3}**2**), that is, an almost linear and perpendicular molecular structure with extensive delocalization of the unpaired electrons onto the two anthryl rings (Scheme 1). Due to this unusual structure, the carbene has an unexpectedly short life time, much shorter than that of even diphenylcarbene (see below), although it has an ideal molecular and electronic structure for a stable triplet carbene.

The unusual reactivity of this carbene is also noted in its reaction with typical carbene traps. Thus, the triplet state ^{3}**2** is intercepted with a very efficient trapping reagent, oxygen and TEMPO, but not by a good hydrogen donor, such as 1,4-cyclohexadiene. The singlet state is not trapped even with a very efficient quencher, i.e., methanol. Such observations are completely unprecedented in the chemistry of diarylcarbenes.[1]

We are not able to detect triplet carbene ^{3}**2** itself by LFP in solution at room temperature mainly because of the very similar nature of the absorption bands for the species formed, e.g., ^{3}**2** (nascent and relaxed), diradicals (dimer and trimer), and also because of the rather rapid decay process from ^{3}**2** to diradicals species. There are subtle differences between ^{3}**2**n and the others, which can only be discriminated by UV/vis in a hard matrix at low temperature, in which the resolution is better than in LFP at room temperature. However, one can estimate a rough lifetime of the carbene by the Stern–Volmer treatment of trapping experiments with oxygen (Fig. 8), assuming that the precursor leading to the species observed is a triplet carbene (either ^{3}**2**n or ^{3}**2**r). Thus the ratio of the difference in optical density (ΔOD) as a function of the oxygen concentration is expressed as:

$$\Delta\mathrm{OD}^0/\Delta\mathrm{OD} = 1 + k_{\mathrm{O}_2}\tau[\mathrm{O}_2] \qquad (1)$$

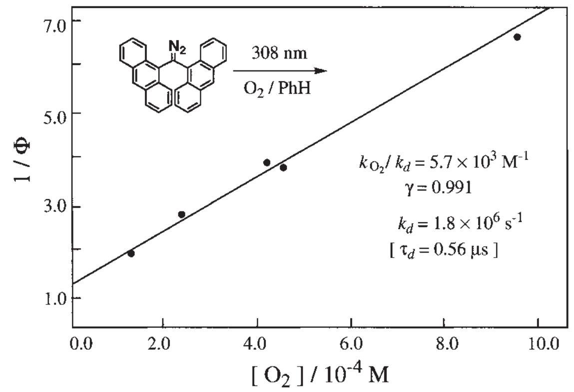


Fig. 11. Stern–Volmer analysis of the yield of transient product as a function of oxygen.

where k_{O_2} is the quenching rate constant of ^{3}**2** by oxygen and τ is the lifetime of ^{3}**2** in the absence of oxygen. A plot of $\Delta OD^0/\Delta OD$ versus the concentration of oxygen is linear (Fig. 11), and the slope is equal to $k_{O_2}\tau$ ($= 5.7 \times 10^3$ M^{-1}). Assuming that k_{O_2} is a diffusion rate constant ($= 10^{10}$ M^{-1} s^{-1} in benzene at 20 °C),[11] one can estimate k_d to be 1.8×10^6 s^{-1}, $\tau = 0.56$ μs.

The mechanism of formation of the trimer **3** and the tetramer **4** from ^{3}**2** is problematic. One possibility was that those oligomers are formed by the reaction of the carbene ^{3}**2** with the precursor diazomethane **1**. For instance, carbene ^{3}**2** may attack the diazomethane **1** at position 10 with subsequent extrusion of nitrogen, resulting in the formation of a dimer diradical, which then may undergo further reaction with **1**. This possibility could be checked by examining the effect of the concentration of **1** on the rate of the light-induced decay of **1**. Thus, two samples containing a considerably different concentration of **1** were irradiated under identical conditions. However, essentially no dependence of the rate on the concentration of **1** was observed.[19] Moreover, the quantum yield of the photodecomposition of **1** was determined to be 0.43.[20] These observations clearly indicate that the photodecomposition of **1** does not involve a chain process at least under these conditions (at 10^{-3} M).

LFP studies indicate that the trimer diradicals (**10**) are generated as a main initial product in the photolysis of diazo precursor **1**. A convenient way to explain the formation of the diradical **10** as a major product is to assume that a monomeric species **2**d (see below) formed from **1** is in equilibrium with the dimer diradical **2-2** and that the mixture decays rapidly to form the trimer diradical **10**, which eventually leads to the trimer **3**. As a trimer diradical was observed as the major transient product at the initial stage of the LFP of **1**, this decay pathway is assumed to be very rapid and efficient.[14,21] The formation of the tetramer **4** from a triplet carbene can then be explained in terms of the dimerization of a dimer diradical, which is in equilibrium with **2**d. As the tetramer diradical (**11**) could not be detected by LFP of either **1** or **4**, and given that the dimer diradical decays by second-order kinetics (to form **4**), it is likely that the dimer diradical undergoes coupling directly to form **4** without recourse to the tetramer diradical **11**. This may explain why this process is much slower than other processes.

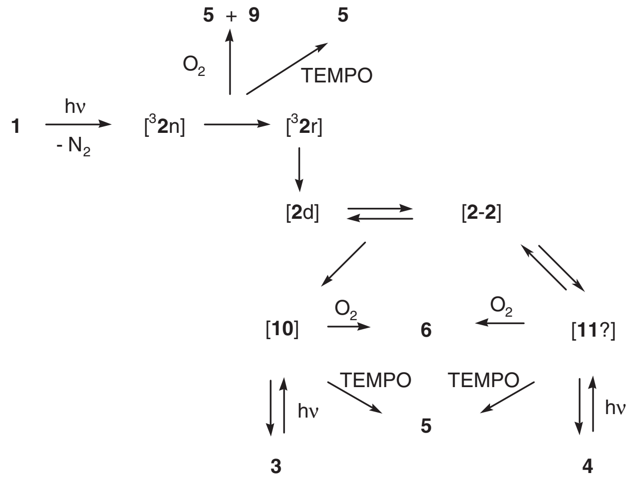
The mechanism outlined in Scheme 6 also explains the LFP and product analysis data on the trimer **3** and the tetramer **4**. Presumably, the tetramer generates, upon photoexcitation, a dimer diradical **2-2**, which is in equilibrium with **2**d. The subsequent events occurring from the equilibrated mixture are essentially the same as those observed in the photolysis of **1**. The lack of formation of the tetramer **4** in the photolysis of **3** and the unimolecular decay of the trimer diradical **10** in the LFP of **3** suggest that **10** undergoes coupling to **3** exclusively, without decaying to a mixture of a carbene and a dimer diradical. This means that the coupling of **2**d and **2-2** leading to **10** is essentially an irreversible pathway.

Thus, the apparently puzzling reactions involved in the photolysis of **1**, **3**, and **4** can be explained by the pathway shown in Scheme 6, at least qualitatively. The exact processes of the coupling to form the trimer diradical **10** from the mixture of **2**d and **2-2** and the tetramer **4** from the dimer diradical **2-2** are not clear yet. Moreover, we do not know the reason why **4** undergoes photolysis to generate the dimer diradical **2-2** (in equilibrium with **2**d) presumably by two C–C bond cleavage, while **3** undergoes one C–C bond cleavage to generate the corresponding diradical **10**.

An interesting issue related to Scheme 6 is the nature of **2**d regenerated by the photolysis of the tetramer **4**. The finding that the irradiation of **4** in the presence of TEMPO produced dianthryl ketone, which is also produced in the photolysis of **1** under similar conditions, suggests that a triplet carbene ^{3}**2** may be generated from **4**. However, the spectroscopic studies do not provide definitive evidence to support this process. For instance, the irradiation of **4** in a matrix indicated EPR signals due to a doublet species without showing those ascribable to the triplet carbene ^{3}**2**. This may simply mean that a dimer diradical **2-2** cannot be in equilibrium with a triplet carbene ^{3}**2** in a matrix.

Dynamic EPR and UV/vis studies indicate that a nascent triplet carbene **2**n with a bent structure is observed but it relaxed to a more linear one **2**r as the matrix is thawed and softened. The EPR spectra upon photolysis of **1** clearly indicate that the latter species still retains the characteristic feature as a triplet carbene. As the matrix temperature is further raised, the triplet EPR signals were found to collapse to a doublet signal. UV/vis spectral changes correlate well with EPR changes. Assuming that the monomer diradical is different from the triplet carbene, the doublet species can be assigned to the monomer diradical **2**d. It may be that there is no spin interaction between the two unpaired electrons on the 10 and 10′ positions in the monomer diradical **2**d, while two unpaired electrons are still interacting with each other in the resonance structure of the triplet carbene (**2A** in Scheme 1). Since these changes are not reversed upon recooling of the matrix, the two species, the relaxed triplet carbene **2**r and the monomer diradical **2**d, can be regarded as different species that are not interconvertible.[22,23] The triplet carbene detected in the matrix photolysis at low temperature is not detected in LFP at ambient temperature. This means that the triplet carbene (**2**n and **2**r) decays to a monomer diradical **2**d very rapidly in solution at room temperature (within 1 μs).

The overall view of the reaction is summarized in Scheme 7 (here, intermediates are indicated in parentheses). There are still unclear issues. For instance, the mechanism of the formation of **4** from **2**, especially the role of **11**, the difference in the reactivity between **10** and **11**, mechanism of the reaction of triplet carbene and diradicals with oxygen and TEMPO and



Scheme 7.

so on. Further studies to solve the remaining issues are in progress.

Experimental

General Methods. IR spectra were measured on a JASCO A-100 recording spectrometer and the mass spectra were recorded on a JEOL MS route JMS-600W.

^{1}H and ^{13}C NMR spectra were determined on either JEOL JNM-EX 270 or JNM-500 spectrometers. UV/vis spectra were recorded on a JASCO CT-560 Grating Monochromator.

Thin-layer chromatography was done on a Merck Kieselgel 60 PF 254. Column chromatography was carried out on silica gel (ICN for dry column chromatography). HPLC and GPC were undertaken with a JASCO 800 chromatograph equipped with a UVIDEC-100-II UV/vis detector using a Fine pack C18-T5 column (4.6 × 25 cm) and a Shodex GPC H-2001 (20 mm × 50 cm) column, respectively. Unless otherwise noted, all the reagents employed in this study are commercial products and were used after standard purification.

Photolysis of Diazomethane (1). A solution of diazomethane (**1**,[3] 40 mg) in anhydrous benzene (15 mL) was placed in a Pyrex tube. The sample was degassed using a minimum of four freeze–degas–thaw cycles at a pressure near 10^{-5} Torr, flame-sealed under reduced pressure and irradiated with a high-pressure, 300-W mercury lamp at room temperature until all the diazo compound was destroyed. The irradiation mixture was then concentrated on a rotary evaporator below 20 °C and individual components were isolated by repeated chromatography on a gel permeation column using CHCl$_3$ as an eluent to afford the following two products:

Trimer (3): 22 mg (55%); white solid; mp 332.4–333.1 °C; FABMS m/z 1099.1 (M + 1, 19.1%), 732.1 ([M − **2**]$^+$, 19.6%), 366 ([M − 2 × **2**]$^+$, 100%); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.79 (d, J = 7.63 Hz, 6H), 7.43 (t, J = 7.02 Hz, 6H), 7.29 (t, J = 7.94 Hz, 6H), 7.21 (d, J = 7.01 Hz, 6H), 7.15 (t, J = 7.02 Hz, 6H), 6.83 (t, J = 7.94 Hz, 6H), 6.34 (d, J = 7.94 Hz, 6H), 5.91 (d, J = 7.02 Hz, 6H), 4.82 (s, 6H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 208.34, 136.42, 131.83, 131.75, 130.73, 129.86, 129.23, 127.60, 127.37, 127.00, 126.44, 125.88, 125.46, 111.10, 55.06; IR (KBr) ν (cm^{-1}) 3056 (m), 3024 (m), 2880 (m), 1598 (m), 1476 (s), 1444 (s), 1291 (m), 1155 (w), 1117 (m), 1046 (w), 768 (vs), 640 (s).

Tetramer (4): 5 mg (12%); white solid; mp 222.4–223.4 °C; FABMS m/z 1466.2 (M + 1, 10.5%), 1098.5 ([M − **2**]$^+$, 12.2%), 732.2 ([M − 2 × **2**]$^+$, 63.2%); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.89 (d, J = 7.35 Hz, 8H), 7.47 (dd, J = 6.61, 6.98 Hz, 8H), 7.28 (overlapping with signals of CDCl$_3$), 7.19 (dd, J = 7.35, 7.53 Hz, 8H), 7.09 (dd, J = 6.79, 7.54 Hz, 8H), 6.96 (d, J = 6.79 Hz, 8H), 6.84 (dd, J = 6.98, 6.99 Hz, 8H), 5.90 (d, J = 7.72 Hz, 8H), 5.00 (s, 8H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 209.82, 137.46, 131.69, 130.39, 129.66, 129.05, 128.89, 128.13, 127.58, 127.20, 126.49, 126.24, 125.90, 111.8, 54.9; IR (KBr) ν (cm^{-1}) 3056 (m), 3024 (m), 2880 (m), 1598 (m), 1476 (s), 1444 (s), 1291 (m), 1155 (w), 1117 (m), 1046 (w), 768 (vs), 640 (s).

When a solution of **1** (5 mg) in nondegassed benzene (5 mL) was irradiated (λ > 300 nm) for 30 min, anthraquinone and di(9-anthryl) ketone were obtained in a roughly 1:1 ratio. When a similar irradiation was carried out with long wavelength light (λ > 520 nm) for 1.5 h, 9-anthryl 9-anthracenecarboxylate (**9**) was isolated along with di(9-anthryl) ketone in a roughly 1:1 ratio, no anthraquinone being formed in this case.

9-Anthryl 9-Anthracenecarboxylate (9): ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.74 (s, 1H), 8.71 (d, J = 8.85 Hz, 2H), 8.51 (s, 1H), 8.30 (d, J = 7.93 Hz, 2H), 8.17 (d, J = 7.93 Hz, 2H), 8.12 (d, J = 7.32 Hz, 2H), 7.69 (t, J = 7.01 Hz, 2H), 7.61 (t, J = 8.70 Hz, 2H), 7.54–7.58 (m, 4H); IR (KBr) ν (cm^{-1}) 1161, 1727; UV/vis (CHCl$_3$) 351, 369, 390 nm.

Photolysis of 9-Anthryl 9-Anthracenecarboxylate (9). Irradiation (λ > 300 nm) of the ester (**9**, 1 mg) in non-degassed benzene (2 mL) for 15 min gave anthraquinone (~80%) as the main product.

Photolysis of Oligomers (3 and 4). A solution of tetramer (2 mg) in C$_6$D$_6$ (0.4 mL) was placed in a Pyrex NMR tube and the sample was degassed and flame-sealed under reduced pressure. Irradiation of the sample with a high-pressure, 300-W mercury lamp at room temperature was monitored by ^{1}H NMR, which indicated that characteristic signals due to the trimer appeared at the expense of those due to the tetramer, no other signals being noted. Irradiation of the trimer under essentially the same conditions showed almost no change in the spectrum even after prolonged irradiation. However similar irradiation of either tetramer or trimer in a non-degassed benzene resulted in a rapid disappearance of the starting oligomers with concomitant formation of anthraquinone as the main product (~80% yield). Similar irradiation of oligomer (5 mg) in degassed benzene (5 mL) in the presence of TEMPO (4.7 mg) for 2 h gave dianthryl ketone as a main product (50% yield).

Irradiation of Di(9-anthryl)diazomethane in a Mixture of Tetrahydrofuran and Methanol. A solution of 200 mg (0.50 mmol) di(9-anthryl)diazomethane **1** in 100 mL THF–methanol (2:3) was divided among five 18 mm o.d. Pyrex tubes. The samples were degassed, sealed, and irradiated for 15 min, using a medium-pressure mercury lamp filtered with uranium glass. The product analysis by thin-layer chromatography showed that only two products were formed (R_f = 0.67 and 0.61, elution with benzene). The residue was triturated with acetone giving as an off-white powder 130 mg of **3**, (R_f = 0.67). Pure compound **3** (off-white powder, 106 mg, 53% yield) was obtained by chromatography on silica gel with 3:1 by volume hexane–benzene eluent, mp 330 °C. ^{1}H NMR (100 MHz, C$_6$D$_6$) δ 6.10–7.40 (m, 48H) 4.65 (s, 6H); ^{13}C NMR (25.0 MHz, C$_6$D$_6$, completely decoupled and off-resonance decoupled) δ 208.6, 124.3–136.9, 111.7, 55.26 (d, J = 60 Hz); IR (KBr) ν (cm^{-1}) 3060 (w), 3020 (w), 2890 (w), 1600 (w), 1480 (s), 1450 (s), 1294 (m), 1170 (m), 1050 (m), 920 (m), 770 (s); MW calcd for (C$_{29}$H$_{18}$)$_3$: 1098 g/mol, found: 1109 g/mol; elemental analysis, calcd for (C$_{29}$H$_{18}$)$_3$: C, 95.05, H, 4.95%, found: C, 94.48, H, 5.51%.

Di(9-anthryl) ketone **5** ($R_f = 0.61$) was obtained from the acetone layer and isolated upon chromatography under the same conditions as those employed for **3** (29 mg, 15% yield), mp 264 °C (lit. 264–266 °C).[24] MS (EI, 70 eV) *m/e* (relative intensity) 383 (7.7), 382 (M, 27), 381 (8), 353 (16), 352 (7), 205 (60), 178 (18), 177 (100), 176 (88), 170 (30).

Irradiation of Di(9-anthryl)diazomethane in 2-Methyltetrahydrofuran. A solution of 0.2 g (0.5 mmol) **1** in 32 mL 2-methyltetrahydrofuran was irradiated as previously for 15 min, at which time the reddish solution turned yellow. Evaporation of the solvent gave 180 mg of crude product whose thin-layer chromatographic analysis revealed the same two products as had been formed in the THF–methanol mixture described above. Trituration with acetone gave a 154 mg residue of **3** as a white powder. This was further purified by preparative thin-layer chromatography and chromatography on silica gel as previously (128 mg, 65% yield). The off-resonance decoupled ^{13}C NMR and IR spectra were identical with those of previously isolated **3**. Dianthryl ketone **5** was isolated in 13% yield by chromatography of the residue recovered from the solvent layer in the trituration step.

Irradiation of Di(9-anthryl)diazomethane in a Mixture of Tetrahydrofuran and Phenylsilane. A solution of 0.2 g (0.5 mmol) **1** in 32 mL of tetrahydrofuran-phenylsilane (5:2) was irradiated as previously. The residue, after washing with 3 mL acetone, afforded **3** in 70% isolated yield upon column chromatography. **5** was isolated in 12% yield from the acetone.

Reaction of Di(9-anthryl)diazomethane with Thiophenol. To a solution of 0.2 g (0.5 mmol) **1** in 40 mL THF was added 10 mL thiophenol. The reddish color of the reaction mixture turned to yellow-green as the solution was stirred. An IR spectrum of the residue after evaporation of volatiles indicated the complete depletion of **1**. The product, isolated by column chromatography, was identified as di(9-anthryl)methyl phenyl sulfide (166 mg, 70% yield), mp 97 °C. ^{1}H NMR (60 MHz, $CDCl_3$) δ 5.24 (s, 1H, PhSC*H*An$_2$), 6.2–8.7 (m, 23H, Ar*H*); ^{13}C NMR (25.0 MHz, $CDCl_3$, off-resonance decoupled) δ 124.33–138.56 (19 signals, Ar*C*), 54.83 (d, $J = 79.3$ Hz, PhS*C*HAn$_2$); IR (KBr) ν (cm^{-1}) 3052 (w), 2938 (w, br), 1480 (m), 1475 (m), 882 (m), 840 (m), 770 (s); MS (EI, 70 eV) *m/e* (relative intensity) 476 (M, 4.1), 475 (6.9), 367 (100), 365 (49), 363 (41), 353 (21), 352 (29), 339 (23), 289 (39), 220 (45), 218 (100), 189 (56), 108 (88). **5** (43 mg, 23% yield) was also isolated by column chromatography.

Irradiation of Di(9-anthryl)diazomethane in a 2-Methyltetrahydrofuran Matrix. Five 18 mm o.d. Pyrex tubes were filled with aliquots of a 2.3×10^{-3} M solution of 100 mg (0.25 mmol) **1** in 100 mL 2-MTHF. The samples were irradiated for 15 min with a medium-pressure Hg lamp at 77 K in a 27 cm o.d. Pyrex Dewar flask. The reddish matrix turned to deep green in the course of the irradiation; when allowed to warm slowly to room temperature, it formed a yellow solution. Evaporation of volatiles afforded a brown solid whose IR spectrum indicated that no **1** remained. In contrast to the solution irradiations, the low solubility of the crude product (acetone, THF, benzene, CS_2, $CHCl_3$) made purification difficult. Washing with acetone gave 42 mg of a pale-yellow product that thin-layer chromatography revealed to be **3** ($R_f = 0.67$) contaminated with a long tail of unseparated compounds ($R_f = 0.30$–0.72). ^{1}H and ^{13}C NMR and IR spectra were very similar to those of pure **3**. From the acetone wash solution **5** was isolated in 14% yield.

Quantum Yield Measurement. A sample of 3.33×10^{-4} M solution of the diazomethane **1** in toluene (3 mL) was placed in 1 cm path-length cuvette equipped with a screw cap and a stirrer bar and the whole system was de-aerated by bubbling argon for 15 min. The cuvette was tightly capped and irradiated under stirring with 366 nm light obtained from a Hitachi fluorophotometer (F-4500) for 30 min. The decomposition percentage of **1** was measured at several wavelengths to be 29.6% under these conditions.

The radiant flux was determined by irradiating a toluene solution of *E*-α-[2-(2,5-dimethyl-3-furyl)ethylidene]-α'-(isopropylidene)succinic anhydride (5.0×10^{-3} M) under essentially identical conditions to be 1.06×10^{16} photons/min. The quantum yield was then determined based on those data.[25]

Determination of the Quantum Yield of Di(9-anthryl)diazomethane Photolysis in a 2.15 x 10^{-2} M Solution (1:1 THF–Phenylsilane). An actinometer solution was prepared by mixing 20 mL of an aqueous solution of uranyl acetate (2.09×10^{-2} M) with 20 mL of an aqueous solution of oxalic acid 1.94×10^{-2} M). The solution was irradiated with the medium-pressure Hg lamp for exactly 60 min. The number of Einsteins absorbed by the solution, 3.81×10^{-4}, was calculated from the reported quantum yield for destruction of oxalic acid, 0.57,[26] and the number of moles of oxalic acid decomposed as determined by permanganate titration. The irradiation was repeated using a solution of **1** (340 mg, 0.86 mmol) in 40 mL of a mixture of THF and phenylsilane 1:1 by volume, irradiated in the same photolysis tube until the reddish color of the reaction mixture turned yellow. After concentration of the reaction mixture, an IR spectrum of the residue showed that **1** was entirely consumed. The quantum yield was calculated from the moles of **1** reacted and the number of Einsteins absorbed to be 9.4.

ESR Measurements. The diazo compound was dissolved in 2-methyltetrahydrofuran (10^{-3} M), and the solution was degassed in a quartz cell by three freeze–degas–thaw cycles. The sample was cooled in an optical transmission EPR cavity at 77 K and then irradiated with a Wacom 500-W Xe lamp using a Pyrex filter. ESR spectra were measured on a JEOL JES TE 200 spectrometer (X-band microwave unit, 100 kHz field modulation). The signal positions were read by the use of a gaussmeter.

Low-Temperature UV/Vis Spectra. Low-temperature spectra at 77 K were obtained by using an Oxford variable-temperature liquid-nitrogen cryostat (DN 1704) equipped with a quartz outer window and a sapphire inner window. The sample was dissolved in dry 2-MTHF, placed in a long-necked quartz cuvette of 1-mm path length, and degassed thoroughly by repeated freeze–degas–thaw cycles at a pressure near 10^{-5} Torr. The cuvette was flame-sealed under reduced pressure, placed in the cryostat, and cooled to 77 K. The sample was irradiated for several minutes in the spectrometer with a Halos 300-W high-pressure mercury lamp using a Pyrex filter, and the spectral changes were recorded at appropriate time intervals. The spectral changes upon thawing were also monitored by carefully controlling the matrix temperature with an Oxford Instrument Intelligent Temperature Controller (ITC 4).

Flash Photolysis. All flash measurements were made on a Unisoku TSP-601 flash spectrometer. Three excitation light sources were used, depending on the precursor absorption bands and the lifetime of the transient species. They were (i) a cylindrical 150-W Xe flash lamp (100 J/flash with 10-ms pulse duration), (ii) a Quanta-Ray GCR-11 Nd:YAG laser (355 nm pulses of up to 40 mJ/pulse and 5–6-ns duration; 266 nm pulses of up to 30 mJ/pulse and 4–5-ns duration), and (iii) Lamda Physik LEXTRA XeCl excimer laser (308 nm pulses of up to 200 mJ/pulse and 17-ns duration). The beam shape and size were controlled by a focal length cylindrical lens.

A Hamamatsu 150-W xenon short arc lamp (L 2195) was used as the probe source, and the monitoring beam, guided using an optical fiber scope, was arranged in an orientation perpendicular to the excitation source. The probe beam was monitored with a Hamamatsu R2949 photomultiplier tube through a Hamamatsu S3701-512Q MOS linear image sensor (512 photodiodes used). Timing of the excitation pulse, the probe beam, and the detection system was achieved through an Iwatsu Model DS-8631 digital synchro scope which was interfaced to a NEC 9801 RX2 computer. This allowed for rapid processing and storage of the data and provided printed graphic capabilities. Each trace was also displayed on a NEC CRT N5913U monitor.

Each sample was placed in a long-necked Pyrex tube which had a side arm connected to a quartz fluorescence cuvette and degassed using a minimum of four freeze–degas–thaw cycles at a pressure near 10^{-5} Torr immediately prior to being flashed. The sample system was flame-sealed under reduced pressure, and the solution was transferred to the quartz cuvette which was placed in the sample chamber of the flash spectrometer. A cell holder block of the sample chamber was equipped with a thermostat and allowed to come to thermal equilibrium. The concentration of the sample was adjusted so that it absorbed a significant portion of the excitation light.

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