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Generation, Characterization, and Kinetics of Triplet Di[1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthryl]carbene

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The title carbene has been generated by photolysis of the corresponding diazo precursors and studied by spectroscopic means, i.e., electron paramagnetic resonance (EPR) and UV/vis spectroscopy in matrixes at low temperature and laser-flash photolysis in solution at room temperature, with the product analysis. The results are compared with triplet di(2,3,5,6-tetramethylphenyl)carbene, an open-chain counterpart, which revealed that bicycloalkyl groups are acting as a fairly good kinetic protector for the triplet carbene as opposed to the open-chain counterpart. The formation of all-hydrocarbon triplet carbenes having a half-life over a second under normal conditions was realized for the first time. Effects of para-substituents on the structure and reactivities of the carbene are also investigated and discussed in terms of polar and spin electronic effects.

The stabilization of a triplet carbene has emerged as a challenging target[1] since the recent syntheses[2,3] of stable singlet carbenes ruled out the long-standing view that carbenes are not stable enough to be isolated in a macroscopic scale at room temperature. Recent growing interest in triplet carbenes as potential organic ferromagnets[4] adds practical meanings to the project.

The stabilization of a triplet carbene is shown to be better accomplished by steric protection than electronic effects. The later strategy does stabilize the singlet state, but at the same time (as a result of the conjugation involved) raises questions with respect to the electronic configuration of the resulting species, i.e., whether one is dealing with a "pure" carbene (one-centered diradical).[3,5] On the other hand, a bulky group, when introduced near the carbene center, is capable of protecting it from external reagents, thus stabilizing the carbene kinetically. At the same time such groups tend to increase the angle at the divalent center simply because of steric congestion. This geometric factor tends to stabilize the carbene thermodynamically, since the wider the angle the more stable the triplet state becomes with respect to the singlet.[6−8]

This strategy, however, encounters a limitation when alkyl groups are employed as protecting groups, since as a result of the highly reactive nature of carbenes, they can abstract even from very poor sources of electrons such as C−H bonds. For instance, di(2,4,6-trimethylphenyl)carbene was shown[9] to decay by undergoing dimerization and have a half-life of 160 ms, some 5 orders of magnitude longer than "parent" triplet diphenylcarbene (DPC). However, when more methyl groups are introduced on the phenyl rings, the carbenic center is more effectively blocked from external reagents because of a buttressing effect, but it becomes more easily trapped by the ortho methyl groups, which are brought closer to the carbene center, to form benzocyclobutene; di(2,3,5,6-tetramethylphenyl)carbene ($t_{1/2}$ = 410 ms) was twice as long lived as di(2,4,6-trimethylphenyl)carbene, while di(2,3,4,5,6-pentamethylphenyl)carbene ($t_{1/2}$ = 180 ms) decayed mainly unimolecularly by abstracting H from the ortho methyl group and hence became shorter lived.[9]

Similarly, the *tert*-butyl group, which has been recognized as one of the most effective kinetic protectors and successfully used to protect many reactive centers, is shown to be ineffective in protecting the triplet carbene center, since it readily reacts with the carbene center. Triplet (2,4,6-tri-*tert*-butylphenyl)phenylcarbene produces 4,6-di-*tert*-butyl-1,1-dimethyl-3-phenylindane as a result of insertion into the C−H bonds of *tert*-butyl groups at the ortho position, and its lifetime is only 120 μs.[9−11]

To realize a stable all-hydrocarbon triplet carbene, it is crucial to develop a protecting alkyl group that is sterically congested but unreactive toward triplet carbenes. Bicycloalkyl groups are very attractive since bridgehead C−H bonds are less susceptible to hydrogen

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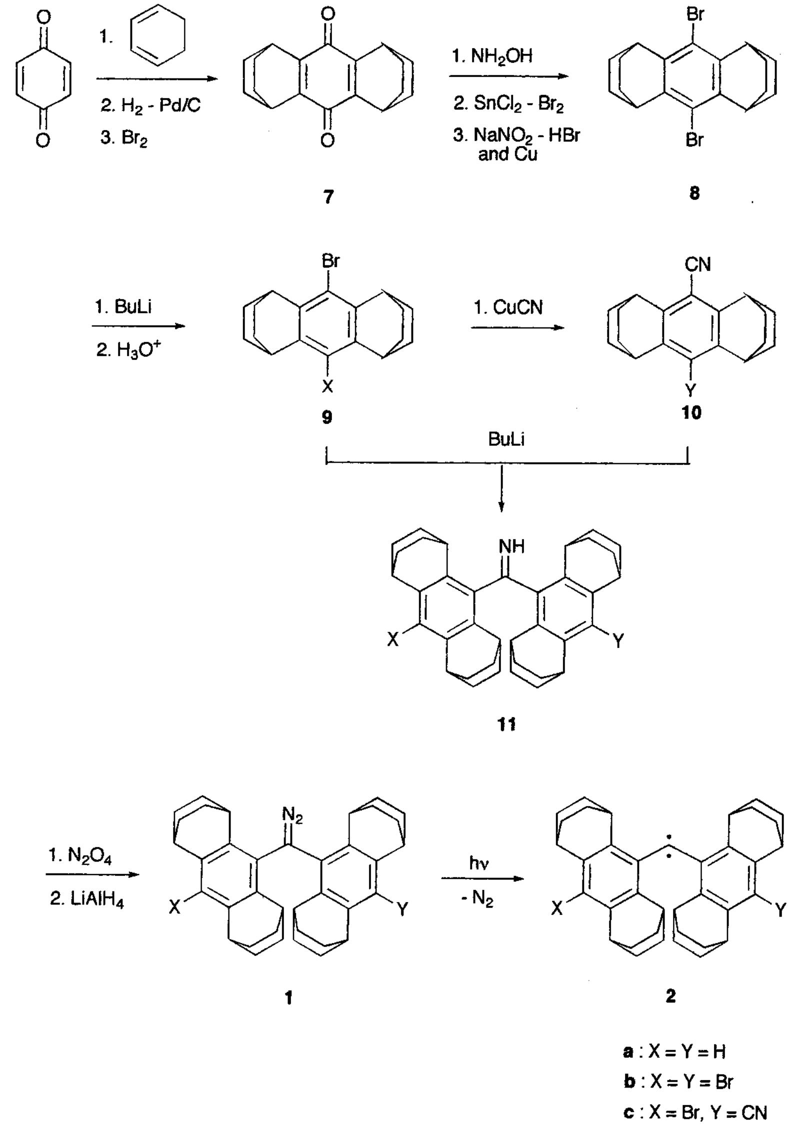
Scheme 1



abstraction, although not entirely inert,[12] and the bridging chains will act as protectors.

In this paper, we wish to report our research on this topic, during which we generated and studied triplet diphenylcarbenes protected by bicyclo[2.2]hexyl groups.[13]

Results

Preparation of Precursor Diazomethanes. The desired precursor diazomethanes (**1a**−**c**) were prepared starting from a benzoquinone-cyclohexa-1,3-diene Diels−Alder adduct according to the reaction procedure outlined in Scheme 1. All of the diazomethanes were purified by silica gel column chromatography at −10 °C followed by repeated chromatography on a gel permeation column; they could be stored in a refrigerator for several months without any appreciable decomposition.

Spectroscopic Studies. (a) EPR Studies in Rigid Matrixes at Low Temperature. Irradiation ($\lambda > 300$ nm) of **1a** in 2-methyltetrahydrofuran (2-MTHF) at 77 K gave rise to a fine-structured EPR line shape characteristic of randomly oriented triplet molecules with a large *D* value attributable to a one-center nπ spin−spin interaction at the divalent carbon of diarylcarbene (Figure 1a).[14,15] The EPR signals were persistent at this low temperature for several hours but disappeared irreversibly when the matrix temperature was raised to around 150 K. The EPR signals were analyzed in terms of zero-field splitting (ZFS) parameters, *D* and *E* values, and are reported in Table 1.

When the 2-MTHF glass containing carbene ^{3}**2a** was warmed gradually in 10 K increments, a new set of triplet peaks appeared at the expense of the original peaks and took over the original one at 110 K (Figure 1b). These changes were not reversible; when the sample was recooled to 77 K, no change took place except that the

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[13] Preliminary reports on the present study were published: Tomioka, H.; Mizuno, H.; Itakura, H.; Hirai, K. *J. Chem. Soc., Chem. Commun.* **1997**, 2261.

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[15] Weak signals around 270 to 420 mT are not likely to be ascribable to triplet carbene ^{3}**2a**, as *D* values estimated on the signals are too small for triplet diarylcarbenes. These signals were not observed at all in the EPR signals of ^{3}**2b** and ^{3}**2c**.

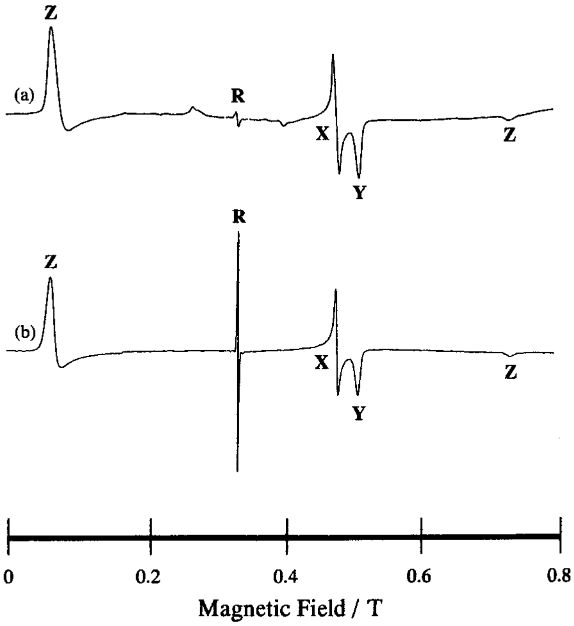

Figure 1. (a) EPR spectra obtained immediately after irradiation of **1a** in 2-MTHF at 77 K. (b) Same sample after annealing to 110 K. The signal at 333.6 mT is due to doublet species.

Table 1. *D* and *E* Values for Triplet Diarylcarbenes in 2-Methyltetrahydrofuran Matrix at 77 K

carbenes	D (cm^{-1})[a]	E (cm^{-1})[a]	E/D[a]	T_d (K)[b]
diphenylcarbene	0.412	0.0191	0.0464	90
4[c]	0.381	0.0106	0.0278	115
	(0.359)	(0.0060)	(0.0168)	
2a	0.400	0.0106	0.0265	150
	(0.376)	(0.0080)	(0.0213)	
2b	0.404	0.0098	0.0242	200
	(0.381)	(0.0084)	(0.0220)	
2c	0.372	0.0087	0.0233	180
	(0.359)	(0.0060)	(0.0168)	

[a] The values in parentheses refer to those observed upon annealing the matrix to 110 K. [b] Temperature at which the triplet signals disappeared in 2-methyltetrahydrofuran matrix. [c] Reference 9.

signal intensity increased according to the Curie law. A signal due to a doublet species also started to appear at 333.6 mT around 110 K. The triplet signals eventually disappeared around 150 K and were taken over by the signals due to doublet species.

In the new set of triplet peaks (Figure 1b), the *x* and *y* lines moved closer together, resulting in a reduction in *E*. Smaller but distinct shifts in the *z* lines were also noted, indicating that *D* has also diminished. The ZFS parameters obtained after annealing to 110 K are reported in the parentheses in Table 1.

The *D* value is related to the separation between the unpaired electrons and is known to vary considerably with the nature of the triplet. The *E* values, on the other hand, when weighed by *D*, are a measure of the deviation from axial symmetry. For diarylcarbene, this value will depend on the magnitude of the central C−C−C angle.

Since the *E* value depends on the magnitude of the central angle, it indicates that the carbene adopts a structure with an expanded C−C−C angle upon annealing. This interpretation seems to be supported by the observation that the reduction of *E* is accompanied by a reduction in *D*, indicating that the electrons are becoming more delocalized.

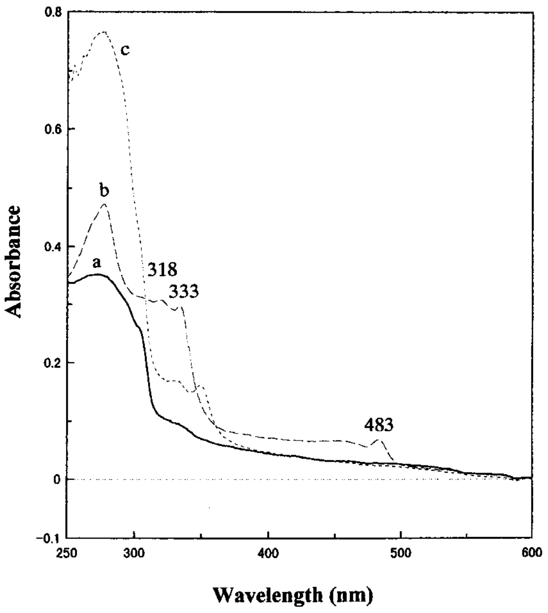

Figure 2. UV/vis spectral changes observed in the photolysis of **1a**. (a) UV/vis spectrum of **1a** in 2-MTHF at 77 K. (b) Same sample after 10-min irradiation ($\lambda > 300$ nm). (c) Same sample after thawing the matrix at 110 K.

Changes of this kind have often been observed for sterically congested triplet diarylcarbenes and are usually interpreted in terms of geometrical changes.[14c,16,17] Thus, when a carbene is generated in rigid matrixes at very low temperature, its initial geometry should be dictated by that of the precursor. Even if the thermodynamically most stable geometry of the carbene is different from that at birth, the rigidity of the matrixes prevents the carbene from achieving its minimum-energy geometry. However, when the matrix is softened by annealing, then the carbene is allowed to relax to its preferred geometry, probably to gain relief from steric compression. In marked contrast, it has been shown that the ZFS parameters of sterically unperturbed triplet DPCs show little sensitivity toward the temperature of the matrix.

A comparison of the ZFS parameters of ^{3}**2a** with that observed for "parent" DPC suggests that the central angle of ^{3}**2a** is significantly expanded, as opposed to DPC, presumably because of the steric influence of bicyclohexyl groups. It is more important to compare the ZFS parameters of ^{3}**2a** with that of triplet di(2,3,5,6-tetramethylphenyl)carbene (^{3}**4**),[9] an open-chain "counterpart" of ^{3}**2a**. Thus ^{3}**4** exhibits smaller *E*/*D* values than ^{3}**2a** especially in the relaxed, minimum-energy ones (Table 1). This can be interpreted as suggesting that ^{3}**4** has more expanded geometry than ^{3}**2a**.

Similarly, irradiation of the other diazomethanes (**1b** and **c**) under identical conditions also gave rise to a similar EPR line shape characteristic of triplet carbenes (^{3}**2b** and ^{3}**2c**), and similar changes in the *D* and *E* values upon annealing were also observed as summarized in Table 1. Interestingly, the temperature (T_d) at which the triplet signals of the relaxed species disappeared

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Scheme 2

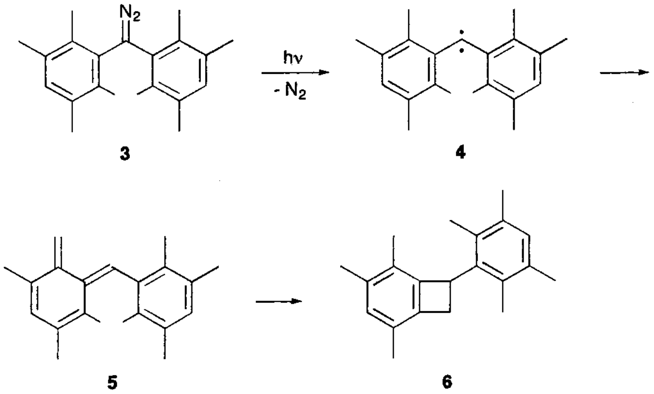

Table 2. Spectroscopic Data for Triplet Diarylcarbenes in 2-Methyltetrahydrofuran Matrix at 77 K

carbenes	λ_{max} (nm)	T_d (K)
diphenylcarbene	300, 465	85
di(2,3,5,6-tetramethylphenyl)-carbene (**4**)[a]	321, 335, 466, 495	110
2a	318, 333, 483	140
2b	322, 336, 474	180
2c	336, 463, 502	160

[a] Reference 9.

was somewhat sensitive to the para-substituents (vide infra).

(b) UV/vis Studies in Rigid Matrixes at Low Temperature. Irradiation of **1a** in 2-MTHF glass at 77 K was then monitored by UV/vis spectroscopy, which revealed the rapid appearance of new absorption bands at the expense of the original absorption due to **1a** (Figure 2). The new absorption consisted of two identifiable features, intense bands in the UV region with maxima at 318 and 333 nm and weak, broad, and structured ones in the visible region with apparent maxima at 483 nm. These features are usually present in the spectra of triplet diarylcarbenes in organic glasses at 77 K.[14a,18] The glassy solution did not exhibit any changes for several hours when kept at 77 K, but the characteristic bands disappeared irreversibly when the matrix was allowed to warm to room temperature. On the basis of these observations, coupled with the EPR data, the absorption spectrum can be safely assigned to triplet carbene ^{3}**2a**.

In the case of the open-chain counterpart (^{3}**4**), a new transient absorption band was observed and increased as carbene absorption bands decreased when the spectral changes of the matrix were more carefully monitored as a function of temperature. The species responsible for the new band was assigned to *o*-quinodimethane (**5**), which was generated as a result of the 1,4 H shift from the *o*-methyl to the carbene center of ^{3}**4** and gave rise to the benzocyclobutene (**6**) (Scheme 2).[9]

When the spectral changes of the matrix containing ^{3}**2a** were monitored as a function of temperature, the transient absorption bands disappeared monotonically showing no new absorption. These observations suggest that intramolecular H abstraction from the bridgehead methine group by triplet carbene is not a prominent process in this case.

Similar spectroscopic measurements on the photolysis of **1b** and **c** gave transient bands ascribable to the carbenes **2b** and **c**, which also decayed monotonically without showing any new absorption. The thermal stability of the transient absorption was again found to be somewhat sensitive to the para-substituents as summarized in Table 2.

(c) Laser Flash Photolysis Studies in Solution at Room Temperature. Laser flash photolysis (LFP) of **1a** in a degassed benzene solution at room temperature with a 10 ns, 70−90 mJ, 308 nm pulse from a XeCl laser produced a transient species absorbing around 320−330 nm and a weak absorption around 480 nm, which appeared to be coincident with the pulse (Figure 3). The transient spectrum was similar to that observed during the photolysis of **1a** in 2-MTHF at 77 K and hence is assigned to the triplet carbene ^{3}**2a**. Support is given to this assignment by the control experiments using trapping reagents for triplet carbenes (vide infra). The inset in Figure 3 shows the decay of ^{3}**2a** at 480 nm, which is found to be second order ($2k/\epsilon l = 8.4$ s^{-1}), and the approximate lifetime of ^{3}**2a** is estimated in the form of half-life, $t_{1/2}$, to be 1.5 ± 0.1 s, which is to be compared with that of ^{3}**4** ($t_{1/2} = 0.41$ s).[9]

In the time-resolved UV/vis studies with ^{3}**4**, a new transient absorption ascribable to *o*-quinodimethane appeared as the original band due to the decayed carbene.[9] No new bands were detected during the decay of ^{3}**2a**. This again indicates that the intramolecular H shift to the carbene center was not a prominent decay process for ^{3}**2a** even in solution at room temperature, where such a hydrogen abstraction reaction is more prominent than in a matrix at low temperature.

In the LFP of a nondegassed benzene solution of **1a**, a broad absorption band with a maximum at 390 nm appeared at the expense of the absorption band due to the carbene (Figure 4). The spent solution was found to contain bis[octahydrodi(ethano)anthryl] ketone (**2**-O) as the main product. It is well documented that diarylcarbenes with triplet ground states are readily trapped with oxygen to generate the corresponding diaryl ketone oxides, which are readily observed directly either by matrix isolation spectroscopy or by flash photolysis techniques and show a broad absorption band centered at 390−450 nm.[19,20] Thus, the observations can be interpreted to indicate that the triplet carbene ^{3}**2a** is trapped by oxygen to form the carbonyl oxide (**2a**-O_2), which confirms that the transient absorption quenched by oxygen is due to ^{3}**2a**.

The appearent built-up rate constant, k_{obs}, of the carbonyl oxide is essentially identical with that of the decay of the carbene, and k_{obs} is expressed as given in eq 1

$$k_{obs} = k_0 + k_{O_2}[O_2] \qquad (1)$$

where k_0 represents the rate of decay of ^{3}**2a** in the absence of oxygen and k_{O_2} is the quenching rate constant of ^{3}**2a** with oxygen. As shown in the inset of Figure 4, the plot of the observed pseudo-first-order rate constant of the formation of **2a**-O_2 against [O_2] is linear. From the

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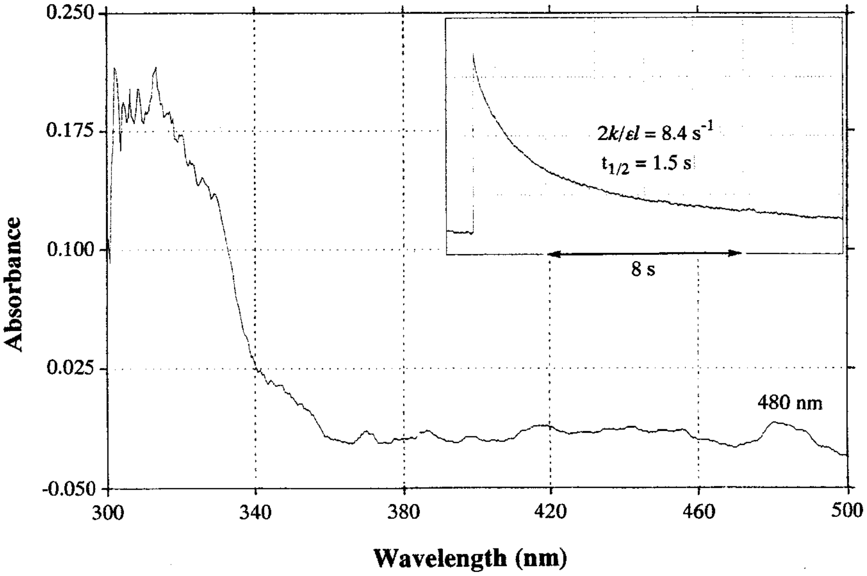

Figure 3. Transient absorption spectra obtained in LFP of **1a** in degassed benzene with a 308-nm excimer laser recorded 50 ms after the pulse. Inset shows oscillogram traces monitored at 450 nm.

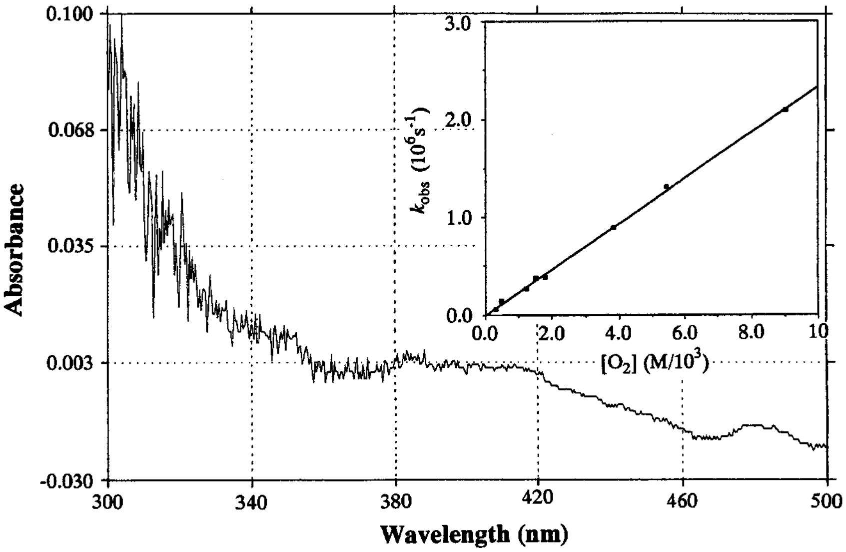

Figure 4. Transient absorption spectra obtained in LFP of **1a** in nondegassed benzene with a 308-nm excimer laser recorded 50 ms after the pulse. Inset shows a plot of the growth rate of the oxide (**2a**-O_2) monitored at 390 nm as a function of the concentration of oxygen.

slope of this plot, the rate constant for the quenching of ^{3}**2a** by oxygen was determined to be 2.3 × 10^8 M^{-1} s^{-1}. When a degassed benzene solution of **1a** containing 1,4-cyclohexadiene (CHD) was excited, a new species was formed, showing an absorption with $\lambda_{max} = 340$ nm, which had formed as the 330 nm signals of ^{3}**2a** decayed (Figure 5). The decay of ^{3}**2a** was shown to be kinetically correlated with the growth of the new species. Thus, this new band was attributable to the diarylmethyl radical (**2a**-H) formed as a result of H abstraction of ^{3}**2a** from the diene. It is also well documented that triplet arylcarbenes, generated in the presence of a good hydrogen donor, undergo H abstractions leading to the corresponding radicals which show transient absorptions at longer wavelengths than those of the precursor carbenes.[21]

A plot of the observed pseudo-first-order rate constant of the formation of the radical against [CHD] is linear as shown in the inset of Figure 5, and the slope of this plot yields the absolute rate constant for the reaction of ^{3}**2a** with the diene, $k_{CHD} = 3.6 \times 10^2$ M^{-1} s^{-1}.

The rate (k_{obs}) of decay of the carbenes (**2a**) also increased upon addition of methanol. However, the plot of k_{obs} vs methanol concentration was not linear for the concentration range of 50 to 200 mM.[22] Plots of better linearity were observed when k_{obs} was plotted against the dimer concentration of methanol, and the quenching rate constant (k_{MeOH}) by methanol was estimated to be 4.3 × 10^4 M^{-2} s^{-1} from the slope of this plot.

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(22) Previously nonlinear plots of decay rate vs methanol concentrations have been observed in the reaction of phenyl(chloro)carbene and better linearity is found when plotted against the concentration of methanol oligomers. Griller, D.; Liu, M. T. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5549.

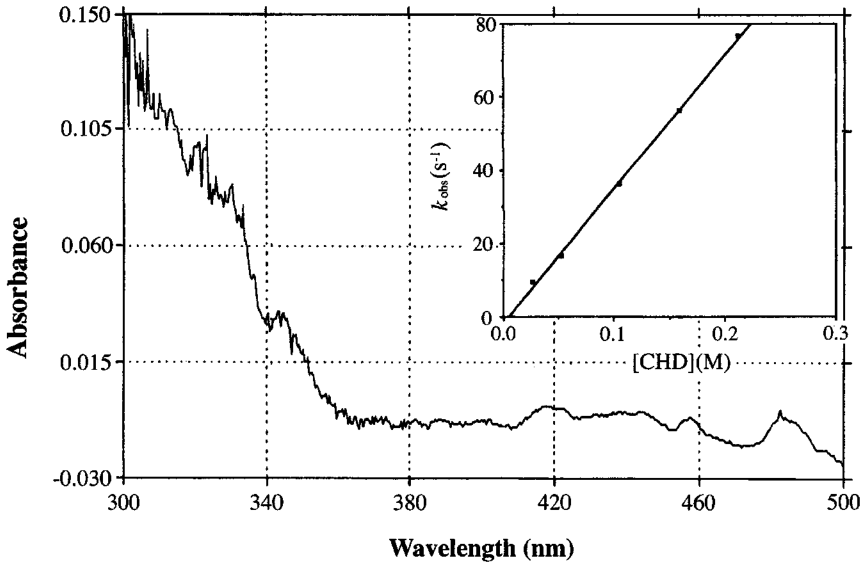

Figure 5. Transient absorption spectra obtained in LFP of **1a** in degassed benzene in the presence of 1,4-cyclohexadiene (CHD) with a 308-nm excimer laser recorded 50 μs after the pulse. Inset shows a plot of the growth of the radical (**2a**-H) monitored at 350 nm as a function of the concentration of the diene.

Scheme 3

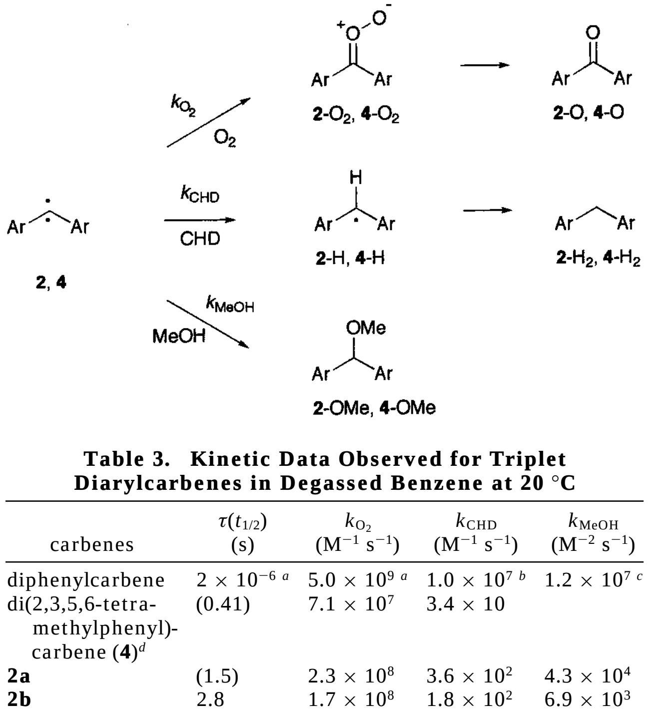

Table 3. Kinetic Data Observed for Triplet Diarylcarbenes in Degassed Benzene at 20 °C

carbenes	$\tau(t_{1/2})$ (s)	k_{O_2} ($M^{-1}\,s^{-1}$)	k_{CHD} ($M^{-1}\,s^{-1}$)	k_{MeOH} ($M^{-2}\,s^{-1}$)
diphenylcarbene	2×10^{-6} [a]	5.0×10^{9} [a]	1.0×10^{7} [b]	1.2×10^{7} [c]
di(2,3,5,6-tetramethylphenyl)carbene (**4**)[d]	(0.41)	7.1×10^{7}	3.4×10	
2a	(1.5)	2.3×10^{8}	3.6×10^{2}	4.3×10^{4}
2b	2.8	1.7×10^{8}	1.8×10^{2}	6.9×10^{3}
2c	1.4	1.2×10^{8}	6.7×10	2.9×10^{2}

[a] Reference 19. [b] Reference 21c. [c] Reference 29; in $M^{-1}\,s^{-1}$ unit. [d] Reference 9.

Similar measurements were conducted for the carbenes **2b**,**c**, and the values of $t_{1/2}$, k_{O_2}, k_{CHD}, and k_{MeOH} are summarized in Table 3.

(d) Product Analysis Studies. Irradiation of **1** in a degassed benzene containing either methanol or 1,4-cyclohexadiene resulted in the formation of either methyl ether (**2**-OMe), probably produced as a result of the interaction of the carbene (**2**) with the O−H bond of methanol, or diarylmethane (**2**-H$_2$), presumably formed by the double-hydrogen abstraction reaction of **2** from the diene. Photolysis of **1** in an oxygen-saturated benzene solution afforded diaryl ketone (**2**-O) as the main product. However, irradiation of **1** in a degassed benzene solution always resulted in complex mixtures from which no particular products were isolated. When the photolysis was carried out in a degassed C_6D_6 solution sealed in an NMR tube and was monitored by ^{1}H NMR (300 M Hz), new signals appeared at the initial stage of the irradiation but did not grow significantly even though the starting compound decomposed. The product signals gradually disappeared when the sample was allowed to stand overnight.

Discussion

Comparison of Di[octahydrodi(ethano)anthryl]carbene (2) to Di(2,3,5,6-tetramethylphenyl)carbene (4). It is interesting to examine the effect of bicyclohexyl groups on the reactivity and structure of diphenylcarbenes as opposed to that of dimethyl groups in more detail. ZFS parameters indicate that ^{3}**4** has more opened geometry than ^{3}**2a**, at least in the relaxed, minimum energy one (Table 1). This may suggest that methyl groups are bulkier than bicyclohexyl groups. It is likely that the interaction between rigidly tied bicyclohexyl groups is less severe than that between free-rotating methyl groups. Actually comparison of the optimized geometries between ^{3}**4** and ^{3}**2a** obtained by the UPM3 method[23] reveals that there is slightly more space around the carbene center in ^{3}**2a** compared to that in ^{3}**4**. This suggests that ^{3}**2a** is subject to the attack of a small particle such as hydrogen more easily than ^{3}**4**. In accordance with this observation, the reactivity of ^{3}**2a** toward typical triplet quenchers, i.e., oxygen and 1,4-cyclohexadiene, is higher than that of ^{3}**4** (Table 3).

The half-life of ^{3}**2a** in degassed benzene in the absence of proper trapping reagents is, however, slightly longer than that of ^{3}**4**. This is probably ascribable to the difference in decay pathway between the two carbenes.

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(23) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209, 221; MOPAC version 6.01 (JCPE NO. P044) was used. Optimized geometries for ^{3}**2a** and ^{3}**4** are included in Supporting Information.

Spectroscopic observations suggest that the H migration is one of the prominent decay pathways for ^{3}**4** but that this is a less prominent decay pathway for ^{3}**2a**. It has been shown that the intramolecular H migration is rather sensitive to the distance between the migrating hydrogen and carbene center.[9] For instance, the ratios of the migration to dimerization in the reaction of polymethylated diphenylcarbenes decrease from 94:6 to 46:54 to 4:96 on going from di(pentamethylphenyl)- to di(2,3,5,6-tetramethylphenyl)- to di(2,4,6-trimethylphenyl)carbenes where the distance increases from 2.34 to 2.38 to 2.41 Å. The distance calculated (UPM3) for ^{3}**2a** is 2.67 Å.[23] This suggests that the H migration in ^{3}**2a** would be less significant than that in ^{3}**4**.

The diradical centers of the 1,4-diradical generated as a result of the H migration in ^{3}**4**, on the other hand, would be stabilized by benzylic resonance, which eventually results in the formation of *o*-quinodimethane. Such a resonance stabilization in the diradical would lower the energy of the transition state for the H migration. In the 1,4-diradical from ^{3}**2a**, the radical center on the bridgehead carbon atom undergoes little resonance stabilization.

These considerations suggest that the H migration is not likely to be a prominent decay pathway for ^{3}**2a**, at least, compared with the open-chain counterpart ^{3}**4**.

Dimerization of ^{3}**2a** seems to be more likely a decay process as the decay kinetics of ^{3}**2a** cleanly follows second-order kinetics. Moreover, even di(2,4,6-tribromophenyl)carbene, where the carbene center is more effectively shielded than that in ^{3}**2a**, undergoes dimerization to give a carbene dimer. Therefore, a second factor that may be taken into account is the difference in steric restriction during the dimerization between ^{3}**2** and ^{3}**4**. Inspection of the optimized geometry indicates that dimerization of the carbene center of ^{3}**4** is hindered but still attained as the facing methyl groups can rotate about one another in order to minimize the interaction potential during dimerization. The relatively easy isolation of the dimer of ^{3}**4** supports this view. On the other hand, in ^{3}**2a**, the flexible motion of bulky and rigid "three-dimensional" bicyclic substituents during the dimerization is not attained. It is intriguing that while the decay kinetics of ^{3}**2a** cleanly follows second-order kinetics, all attempts to isolate and/or detect the expected dimer of ^{3}**2a** have been unsuccessful. Although we have not been able to characterize products, the fact that the reaction always resulted in a complex reaction mixture may suggest that there is severe steric restriction during dimerization, and hence the reaction cannot end up with a final stable product.

Bicyclohexyl groups thus act as an ideal kinetic protector for triplet carbene not only by quenching the intramolecular hydrogen-donating process but also by forcing steric restriction during the dimerization of the carbene center.

Effect of para-Substituents. The substituents at the para-position of ^{3}**2** exhibit subtle but distinct effects on the reactivity on ^{3}**2**.

It is worth examining how the para-substituents affect the electronic structure of ^{3}**2**. The dominant interaction of the unpaired electron in a p-radical is with the electron pairs in the π-bonds. Such interactions are characterized by the delocalization of the spin throughout the π-system. To estimate the relative abilities of substituents to delocalize the spin, sigma-dot substituent constants (σ•) have been proposed.[24] Among the various approaches to the definition of a σ• scale,[25] Arnold's σ•$_{\alpha}$ scale is the most suitable for the analysis of the substituent effect on the D values of diarylcarbenes, as this scale is a nonkinetic measure of radical-stabilizing effects based on hyperfine coupling constants in the benzylic radical.[26]

Inspection of the data in Table 1 indicates that the D values of ^{3}**2** appreciably decrease as well when a strongly spin-delocalizing substituent, i.e., the 4-cyano group (σ•$_{\alpha}$ = 0.040),[25] is introduced, although a moderate spin-delocalzing group, i.e., 4-bromine (σ•$_{\alpha}$ for 4-Cl = 0.011),[25,26] shows little effect on the D values. Obviously, more data with well-distributed substituents are required in order to analyze the D values more quantitatively in terms of σ•$_{\alpha}$.[27,28]

It is also interesting to note that the thermal stability (T_{d} in Tables 1 and 2) and half-life ($t_{1/2}$ in Table 3) of ^{3}**2** are sensitive to the para-substituents. As spin-delocalizing groups are introduced at para-positions, carbenes tend to become more stable, judging from T_{d} and $t_{1/2}$ values. There is, however, some uncertainty in those values since T_{d} reflects overall decomposition pathways of ^{3}**2** in an organic matrix upon annealing, whereas $t_{1/2}$ is just a measure of lifetime in solution at room temperature and is dependent on the initial concentration of ^{3}**2**. The kinetic data for the specific reactions is a more reliable indication of the reactivity of ^{3}**2**.

In this light, it is more useful to compare the rate constants of ^{3}**2** with oxygen ($k_{\mathrm{O_2}}$) and 1,4-cyclohexadiene (k_{CHD}). Inspection of the data in Table 3 clearly shows that the reactivity of ^{3}**2** decreases as more spin-delocalizing groups are introduced. The quenching rate constant (k_{MeOH}) by methanol also decreases in the same order. Similar ongoing decrease in k_{MeOH} by methanol from *p*-H to *p*-Br to *p*-CN is also observed for *o*-unsubstituted diphenylcarbene systems.[29,30]

The mechanism of the reaction of triplet carbenes with methanol to form methyl ether is of considerable interest.[31] The insertion reaction of carbenes with alcohols to form ethers is usually considered to occur from the singlet states of these species. However, LFP studies have shown that the ground state of diphenylcarbene is efficiently quenched by methanol.[32]

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[24] For a review, see: Jiang, X.-K. *Acc. Chem. Res.* **1997**, *30*, 283.

[25] (a) Dust, J. M.; Arnold, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 1221 and 6531. (b) Wayner, D. D. M.; Arnold, D. R. *Can. J. Chem.* **1984**, *62*, 1164; **1985**, *63*, 2378.

[26] Creary's σ_{c}• scale is also useful since it is based on the thermal rearrangement that is devoid of polar character in the transition state. (a) Creary, X. *J. Org. Chem.* **1980**, *45*, 280. (b) Creary, X.; Mehrsheik-Mohammadi, M. E.; McDonald, S. *J. Org. Chem.* **1987**, *52*, 3254. In this scale, σ_{c}• for 4-Cl and 4-Br is 0.12 and 0.13, respectively.

[27] The effect of *p*-substituents on the *D* values of *o*-unsubstituted DPCs has been systematically studied by Arnold and co-workers. (a) Humphreys, R. W. R.; Arnold, D. R. *Can. J. Chem.* **1979**, *57*, 1979. (b) Arnold, D. R.; Humphreys, R. W. R. *J. Chem. Soc., Chem. Commun.* **1978**, 181.

[28] Fairly good correlation with σ• was found for the *D* values of triplet di(2,6-dimethylphenyl)carbenes bearing para disubstituents. Hu, Y.-M.; Hirai, K.; Tomioka, H. *J. Phys. Chem. A* **1999**, *103*, 9280.

[29] Hadel, L. M.; Maloney, V. M.; Platz, M. S.; McGimpsey, W. G.; Scaiano, J. C. *J. Phys. Chem.* **1986**, *90*, 2488.

[30] For a review, see: Platz, M. S.; Maloney, V. M. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; pp 320−348.

[31] For a review, see: Kirmse, W. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press: Stamford, 1994; Vol. 1, p 1.

[32] (a) Closs, G. L.; Rabinow. B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190. (b) Eisenthal, K. B.; Turro, N. J.; Sitzmann, E. V.; Gould, I. R.; Hefferon, G.; Langan, J.; Cha, Y. *Tetrahedron* **1985**, *41*, 1543.

In either mechanism, the decrease in k_{MeOH} is considered to reflect a larger free-energy difference between the ground triplet states and their singlet states as a function of the para-substituent.[33,34] In other words, the data in Table 3 suggest that free-energy difference between the ground triplet and singlet states increases on going from **2a** to **2b** to **2c**.

The trend is in accordance with the expectation that electron-donor groups stabilize the electrophilic singlet carbene more than they do the radical-like triplet and that electron-withdrawing groups destabilize the singlet.[35] Moreover, the electron-withdrawing groups employed here are also spin-delocalizing groups, which stabilize the triplet states thermodynamically by delocalizing the unpaired electrons. Thus, two electronic effects operating in the same directions would result in the observed changes.

Conclusion

We have shown that bicycloalkyl groups shield the triplet carbene center quite well from external reagents yet show little reactivity toward it and hence have the capability to act as very promising kinetic protectors for triplet carbene. Once the decaying pathways of the diphenylcarbenes protected by bicyclo alkyl groups in inert solvents are clarified more clearly, it will be possible to modify these groups to so as to block the quenching pathways, which will enable us to realize stable all-hydrocarbon triplet carbenes in future.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on JEOL JNM-AC300FT/NMR spectrometer in $CDCl_3$ with Me_4Si as an internal reference. IR spectra were measured on a JASCO−Herschel FT/IR-600H spectrometer, and UV−vis spectra were recorded on a JASCO CT-560 spectrophotometer. The mass spectra were recorded on a JEOL JMS-600H mass spectrometer. Gel permeation chromatography (GPC) was carried out on a JASCO, model HLC-01 instrument. The GPC column was a Shodex H-2001. Thin-layer chromatography was carried out on a Merck Kieselgel 60 PF_{254}. Column chromatography was performed on silica gel (Fuji Davidson) for column chromatography or ICN for dry column chromatography.

Preparation of Di[1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthryl]diazomethane (1a). 9,10-Diamino-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthracene dihydrobromide (500 mg, 1.16 mmol),[36] prepared by bishydroxyamination of 1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthraquinone (**7**)[37] followed by treatment with $SnCl_2$ in EtOH and HBr aqueous solution, was added to a solution of NaBr (5.0 g, 48.6 mmol) in 48% hydrobromic acid (50 mL) for 5 h. To the stirred suspension was added dropwise a solution of sodium nitrite (4.8 g, 69.6 mmol) in water (20 mL) at 0 °C over 30 min. After the solution was stirred at 0 °C for 3 h, activated Cu powder (0.22 g, 6.96 mmol) was added, followed by stirring at room temperature overnight. The solution was poured into water (200 mL), and the solid was filtered and washed with water. The crude product was chromatographed over silica gel with hexane as an eluent to afford **9,10-dibromo-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthracene** (**8**) (204 mg, 22%) as a white crystal: mp 258−261 °C; ^{1}H NMR ($CDCl_3$) δ 1.31−1.37 (m, 8 H), 1.56−1.77 (m, 8 H), 3.61 (bs, 4 H); HRMS calcd for $C_{18}H_{20}Br_2$ 393.9931, found 393.9933. To a solution of the dibromide **8** (1.6 g, 4.04 mmol) in anhydrous Et_2O (80 mL) was added 1.7 M *n*-BuLi in hexane (2.4 mL, 4.04 mmol) at room temperature under argon atmosphere. After stirring for 1 h, the resulting white suspension was treated with water. The organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. Removal of the solvent afforded **9-bromo-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthracene** (**9**, X = H) in quantitative yield (1.3 g) as a white crystal: mp 199−202 °C; ^{1}H NMR ($CDCl_3$) δ 1.36−1.45 (m, 8 H), 1.64−1.81 (m, 8 H), 2.96 (bs, 2 H), 3.54 (bs, 2 H), 6.85 (s, 1 H); HRMS calcd for $C_{18}H_{21}Br$ 316.0826, found 316.0850. A solution of the monobromide (**9**, X = H) (1.1 g, 3.47 mmol) and CuCN (0.48 g, 5.21 mmol) in anhydrous DMF (20 mL) was heated at 120 °C overnight. The reaction mixture was poured into ice−water, and the solid was filtered and dissolved in a mixture of ethylenediamine and water (1:2). The solution was extracted with CH_2Cl_2, washed with water, and dried over anhydrous Na_2SO_4. Removal of the solvent and chromatography of the crude product over silica gel with hexane−CH_2Cl_2 (1:2) as eluent afforded **9-cyano-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthracene** (**10**, X = H) (0.65 g, 72%) as a white crystal: mp 190−193 °C;^{1}H NMR ($CDCl_3$) δ 1.31−1.45 (m, 8 H), 1.60−1.88 (m, 8 H), 3.01 (bs, 2 H), 3.44 (bs, 2 H), 7.11 (s, 1 H); IR (KBr) 2218 cm^{-1}; HRMS calcd for $C_{19}H_{21}N$ 263.1674, found 263. 1677. To a solution of monobromide (**9**, X = H) (880 mg, 2.78 mmol) in anhydrous Et_2O (20 mL) was added 1.6 M *n*-BuLi in hexane (1.7 mL, 2.78 mmol) at room temperature under argon atmosphere. After the suspension was refluxed for 4 h, the cyano compound (**10**, X = H) (655 mg, 2.49 mmol) was added, followed by refluxing overnight. The mixture was treated with aqueous NH_4Cl, and the organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. Removal of the solvent and chromatography of the crude product over silica gel with hexanes−Et_2O (10:1) as eluent afforded **di[1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethane)anthryl]ketimine** (**11a**) (1.0 g, 80%) as a white solid: mp 238−241 °C; ^{1}H NMR ($CDCl_3$) δ 1.26−1.37 (m, 16 H), 1.55−1.76 (m, 16 H), 2.94 (bs, 4 H), 3.25 (bs, 4 H), 6.93 (s, 2 H); HRMS calcd for $C_{37}H_{43}N$ 501.3395, found 501.3377. N_2O_4 gas (455 mg, 4.95 mmol) was bubbled into anhydrous CCl_4 (10 mL) cooled at −20 °C, and AcONa (1.1 g, 1.0 mmol) was added to it. After a solution of the ketimine **11a** (500 mg, 0.99 mmol) in anhydrous CCl_4 (20 mL) was added, the mixture was stirred at 0 °C for 3 h. The mixture was poured into cold aqueous Na_2CO_3, and the organic layer was separated, washed with cold water, and dried over anhydrous Na_2SO_4. Removal of the solvent afforded the nitroso compound as a blue solid. The nitroso compound was dissolved in anhydrous Et_2O (10 mL), cooled with dry ice−MeOH and a suspension of $LiAlH_4$ (46 mg, 0.99 mmol) in anhydrous Et_2O (5 mL) was added. The mixture was stirred at 0 °C for 10 min, cooled with dry ice−MeOH again and these operations were repeated two more times. After addition of 138 mg of $LiAlH_4$ was completed, the mixture was stirred at 0 °C for 30 min, and then cooled with dry ice−MeOH, quenched with EtOAc (10 min) and water (20 mL) and filtered with suction. The organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. Removal of the solvent and flash chromatography of the crude product over alumina with hexane as eluent at −20 °C, and then GPC purification with $CHCl_3$ as an eluent afforded **di[1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthryl]diazomethane** (**1a**) (76 mg, 15%) as a red solid: mp 183−186 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.17−1.39 (m, 16 H), 1.59−1.76 (m, 16 H), 2.93 (bs, 4 H), 3.16 (bs, 4 H), 6.89 (s, 2 H); IR (KBr) 2032 cm^{-1}.

Preparation of Di[10-bromo-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthryl]diazomethane (1b). A solution of the dibromide **8** (1.0 g, 2,53 mmol) and CuCN (0.23 g, 2.53 mmol) in anhydrous DMF (20 mL) was heated at 120 °C overnight, and the reaction mixture was worked up as described above. Chromatography of the crude product over silica gel with hexane−CH_2Cl_2 (2:1) as eluent afforded **9-bromo-10-cyano-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthracene** (**10**, X = Br) (330 mg, 38%) as a white crystal: mp

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223−225 °C; ^{1}H NMR (CDCl$_3$) δ 1.36−1.45 (m, 8 H), 1.64−1.81 (m, 8 H), 3.48 (bs, 2 H), 3.62 (bs, 2 H); IR (KBr) 2218 cm^{-1}; HRMS calcd for $C_{19}H_{20}NBr$ 341.0779, found 341. 0743. The reaction mixture obtained from the dibromide (410 mg, 1.04 mmol) and 1.7 M *n*-BuLi (0.61 mL, 1.04 mmol) was treated with **10** (X = Br) (260 mg, 0.75 mmol) as described above, which was followed by chromatography over silica gel to afford **di[10-bromo-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthryl]ketimine** (**11b**) (346 mg, 72%) as a white solid: mp 310−312 °C; ^{1}H NMR (CDCl$_3$) δ 1.15−1.34 (m, 16 H), 1.57−1.73 (m, 16 H), 3.27 (bs, 4 H), 3.62 (bs, 4 H); HRMS calcd for $C_{37}H_{41}NBr_2$ 657.1605, found 657.1556. The ketimine (200 mg, 0.30 mmol) was subjected to nitrosation followed by $LiAlH_4$ reduction as described above to afford **di[10-bromo-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthryl]diazomethane** (**1b**) (27 mg, 13%) as a red solid: mp 230−233 °C dec; ^{1}H NMR (CDCl$_3$) δ 1.11−1.39 (m, 16 H), 1.57−1.77 (m, 16 H), 3.17 (bs, 4 H), 3.59 (bs, 4 H); IR (KBr) 2032 cm^{-1}.

Preparation of [10-Bromo-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthryl][10′-cyano-1′,2′,3′,4′,5′,6′,7′,8′-octahydro-1′,4′-5′,8′-di(ethano)anthryl]diazomethane (1c). A solution of the dibromide **8** (300 mg, 0.76 mmol) and CuCN (168 mg, 1.93 mmol) in anhydrous DMF (10 mL) was heated at 120 °C overnight, and the reaction mixture was worked up as described above. Chromatography of the crude product over silica gel with hexane−CH_2Cl_2 (4:1) as eluent afforded **9,10-dicyano-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthracene** (**10**, X = CN) (190 mg, 87%) as a white crystal: mp 220−223 °C; ^{1}H NMR (CDCl$_3$) δ 1.39−1.42 (m, 8 H), 1.81−1.91 (m, 8 H), 3.51 (bs, 4 H); IR (KBr) 2218 cm^{-1}; HRMS calcd for $C_{20}H_{20}N_2$ 288.1626, found 288.1632. The reaction mixture obtained by treating the dibromide **8** (275 mg, 0.69 mmol) and 1.6 M *n*-BuLi (0.52 mL, 0.83 mmol) was reacted with **10** (X = CN) (200 mg, 0.69 mmol), which was followed by chromatography over silica gel to give **[10-bromo-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthryl][10′-cyano-1′,2′,3′,4′,5′,6′,7′,8′-octahydro-1′,4′-5′,8′-di(ethano)anthryl]ketimine** (**11c**) (210 mg, 50%) as a white solid: mp 325−328 °C; ^{1}H NMR (CDCl$_3$) δ 1.13−1.91 (m, 32 H), 3.19 (bs, 2 H), 3.29 (bs, 2 H), 3.49 (bs, 2 H), 3.63 (bs, 2 H); IR (KBr) 2218 cm^{-1}; HRMS calcd for $C_{38}H_{41}N_2Br$ 604.2452, found 604.2443. The ketimine (200 mg, 0.33 mmol) was treated with N_2O_4 followed by $LiAlH_4$ reduction and GPC purification to afford **[10-bromo-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)-anthryl][10′-cyano-1′,2′,3′,4′,5′,6′,7′,8′-octahydro-1′,4′-5′,8′-di(ethano)anthryl]diazomethane** (**1c**) (14 mg, 7%) as a red solid: mp 265−268 °C dec; ^{1}H NMR (CDCl$_3$) δ 1.14−1.34 (m, 16 H), 1.56−1.81 (m, 16 H), 3.12 (bs, 2 H), 3.18 (bs, 2 H), 3.46 (bs, 2 H), 3.60 (bs, 2 H); IR (KBr) 2032, 2218 cm^{-1}.

Irradiation for Product Identification. In a typical run, a solution of the diazo compound (ca. 10 mg) in solvent was placed in a Pyrex tube and irradiated with a high-pressure, 300-W mercury lamp until all of the diazo compound was destroyed. The irradiation mixture was then concentrated on a rotary evaporator below 20 °C. Individual components were isolated by column chromatography or by preparative TLC and identified by NMR and MS. In this way, the following products were isolated and characterized.

Di[1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthryl]-(methoxy)methane (2a-OMe): mp 212−215 °C; ^{1}H NMR (CDCl$_3$) δ 1.00−1.08 (m, 8 H), 1.23−1.31 (m, 8 H), 1.49−1.69 (m, 16 H), 2.87 (bs, 4 H), 3.47 (s, 3 H), 3.58 (bs, 4 H), 6.26 (s, 1 H), 6.80 (s, 2 H); HRMS (El) calcd for $C_{38}H_{46}O$, 518.3548, found 518.3617 (M$^+$).

Di[10-bromo-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)-anthryl](methoxy)methane (2b-OMe): mp 361−365 °C; ^{1}H NMR (CDCl$_3$) δ 0.96−1.05 (m, 8 H), 1.23−1.31 (m, 8 H), 1.48−1.55 (m, 8 H), 1.63−1.71 (m, 8 H), 3.42 (s, 3 H), 3.57−3.62 (m, 8 H), 6.19 (s, 1 H); HRMS (El) calcd for $C_{38}H_{44}OBr_2$, 674.1758, found 674.1730 (M$^+$).

[10-Bromo-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)-anthryl][10′-cyano-1′,2′,3′,4′,5′,6′,7′,8′-octahydro-1′,4′:5′,8′-di(ethano)anthryl](methoxy)methane (2c-OMe): mp 358−362 °C; ^{1}H NMR (CDCl$_3$) δ 0.85−0.88 (m, 4 H), 1.04−1.71 (m, 28 H), 3.42 (s, 3 H), 3.44 (bs, 2 H), 3.51 (bs, 2 H), 3.59 (bs, 2 H), 3.69 (bs, 2 H), 6.23 (s, 1 H); HRMS (El) calcd for $C_{39}H_{44}NOBr$, 621.2606, found 621.2616 (M$^+$).

Di[1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthryl]-methane (2a-H$_2$): mp 208−211 °C; ^{1}H NMR (CDCl$_3$) δ 1.07−1.18 (m, 8 H), 1.25−1.37 (m, 8 H), 1.55−1.67 (m, 16 H), 3.24 (bs, 4 H), 3.62 (bs, 4 H), 4.25 (s, 2 H), 6.76 (s, 2 H); HRMS (El) calcd for $C_{37}H_{44}$, 488.3443, found 488.3433 (M$^+$).

Di[10-bromo-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)-anthryl]methane (2b-H$_2$): mp 364−368 °C; ^{1}H NMR (CDCl$_3$) δ 0.97−1.01 (m, 8 H), 1.23−1.30 (m, 8 H), 1.48−1.71 (m, 8 H), 1.64−1.71 (m, 8 H), 3.25 (bs, 4 H), 3.55 (bs, 4 H), 4.19 (s, 2 H); HRMS (El) calcd for $C_{37}H_{42}Br_2$, 644.1652, found 644.1605 (M$^+$).

[10-Bromo-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)-anthryl][10′-cyano-1′,2′,3′,4′,5′,6′,7′,8′-octahydro-1′,4′-5′,8′-di(ethano)anthryl]methane (2c-H$_2$): mp 361−366 °C; ^{1}H NMR (CDCl$_3$) δ 0.83−0.88 (m. 4 H), 0.99−1.15 (m, 4 H), 1.25−1.37 (m, 8 H), 1.46−1.75 (m, 16 H), 3.18 (bs, 2 H), 3.28 (bs, 2 H), 3.41 (bs, 2 H), 3.56 (bs, 2 H), 4.26 (s, 2 H); HRMS (El) calcd for $C_{38}H_{42}NBr$, 591.2500, found 591.2445 (M$^+$).

Di[1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthryl] ketone (2a-O): mp 213−216 °C; ^{1}H NMR (CDCl$_3$) δ 1.11−1.68 (m, 24 H), 1.72−1.78 (m, 8 H), 2.97 (bs, 4 H), 3.17 (bs, 4 H), 6.94 (s, 2 H); HRMS (El) calcd for $C_{37}H_{42}O$, 502.3235, found 502.3263 (M$^+$).

Di[10-bromo-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)-anthryl] ketone (2b-O): mp 358−362 °C; ^{1}H NMR (CDCl$_3$) δ 1.56−1.72 (m, 16 H), 1.68−1.81 (m, 16 H), 3.49 (bs, 4 H), 3.68 (bs, 4 H); HRMS (El) calcd for $C_{37}H_{40}OBr_2$, 658.1445, found 658.1380 (M$^+$).

[10-Bromo-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)-anthryl][10′-cyano-1′,2′,3′,4′,5′,6′,7′,8′-octahydro-1′,4′-5′,8′-di(ethano)anthryl] ketone (2c-O): mp 363−365 °C; ^{1}H NMR (CDCl$_3$) δ 1.18−1.62 (m, 16 H), 1.67−1.89 (m, 16 H), 3.48 (bs, 2 H), 3.51 (bs, 2 H), 3.55 (bs, 2 H), 3.69 (bs, 2 H); HRMS (El) calcd for $C_{38}H_{40}NOBr$, 605.2293, found 605.2267 (M$^+$).

EPR Measurements. The diazo compound was dissolved in 2-methyltetrahydrofuran (2-MTHF) (5×10^{-4} M), and the solution was degassed in a quartz cell by four freeze−degas−thaw cycles. The sample was cooled in a optical transmission EPR cavity at 77 K and irradiated with a Wacom 500-W Xe lamp using a Pyrex filter. EPR spectra were measured on a JEOL JES TE200 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 2704) 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 by four freeze−degas−thaw cycles at 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 500-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).

Laser Flash Photolysis. All flash photolysis measurements were made on a Unisoku TSP-601 flash spectrometer. The excitation source for the laser flash photolysis was a XeCl excimer laser. A Hamamatsu 150-W xenon short arc lamp (L2195) 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 linear image sensor (512 photodiodes used). Timing of the laser excitation pulse, the probe beam, and the detection system was achieved through an Iwatsu model DS-8631 digital synchroscope which was interfaced to a NEC 9801 RX2 computer. This allowed for rapid processing and storage of the data and provided printed graphics capabilities. Each trace was also displayed on a NEC CRT N5913U monitor.

A sample was placed in a long-necked Pyrex tube that had a sidearm connected to a quartz fluorescence cuvette and degassed using a minimum of four freeze−degas−thaw cycles at pressure near 10^{-5} Torr immediately prior to being flashed. The sample system was sealed, and the solution was transferred to the quartz cuvette, which was placed in the sample chamber of the flash spectrometer. The concentration of the sample was adjusted so that it absorbed a significant portion of the laser light.

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Supporting Information Available: Optimized UPM3 geometries for **2a** and **4** and calculated exothermicities of dimerization of ^{3}**2a** and ^{3}**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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