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Persistent Triplet Carbenes

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1. Introduction

Radical chemistry has had a unique and interesting history. During the late 1800s, most chemists felt that free radicals could not exist. This extreme view was upset in 1900 when Moses Gomberg announced the discovery of triphenylmethyl, the first moderately stable free radical.[1] Naturally, Gomberg's interpretation of his product as free triphenylmethyl was not generally accepted at first, and most organic chemists had little general interest in radical chemistry in these early years. This changed in the 1930s when the idea of small free radicals as intermediates in high temperature gas phase reactions had considerable development and free radicals had been recognized as important species in ordinary liquid-phase organic chemistry. Therefore, the modern history of radical chemistry is usually considered to date from the 1930s. However, Gomberg is still regarded as the "Moses who had led chemists from the wilderness".[2]

The very first attempts to generate carbene (methylene) were made at a time when the quadrivalency of carbon was not yet established.[3] Thus, Duma (1835)[4] and Regnault (1839)[5] tried to dehydrate methanol by means of phosphorus pentoxide or concentrated sulfuric acid. A second period of carbene research was initiated by the discovery of isonitrile and fulminic acid derivatives in the late 19th century. Nef, stimulated by his own work in this field, attempted to interpret organic reactions in terms of a "general methylene theory",[6] in which methylene plays an important role. He even announced that methylene would become available in the near future. Obviously, he thought that methylene, once prepared, would be a stable compound.

It is very interesting to recognize here that two chemists, one having discovered a stable trivalent carbon (radical) and the other hoping to isolate a divalent carbon (carbene), were

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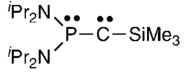
Katsuyuki Hirai was born in Ueno in 1963. He received his M.S. degree at Mie University under the direction of Prof. Hideo Tomioka and obtained his Ph.D. from Nagoya University in 1997. He was appointed as Research Assistant in1986 at the Faculty of Engineering, Mie University, and is now Associate Professor of the Life Science Research Center at Mie University. His current research interests are the isolation of triplet carbene and the construction of magnetic materials using triplet carbene units.

Tetsuji Itoh was born in Mie in 1967. He received his M.S. degree in 1992 from Mie University and his Ph.D. degree in 1996 from the Graduate University for Advanced Studies under the supervision of Prof. Kazuhiro Nakasuji. He worked with Prof. Hiizu Iwamura and Noboru Koga at Kyushu University as a Postdoctoral Fellow in 1996−2001. He joined Professor Tomioka's group at the Department of Chemistry for Materials, Faculty of Engineering of Mie University in 2001 as a Researcher. Since 2007, he has been at Sharp Corporation in the corporate research and development group. His research interests are structural and physical organic chemistry, mainly the construction of organic electronic devices.

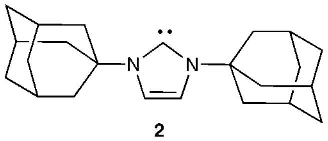
Hideo Tomioka was born in Mie in 1941 and soon moved to a small island floating in the Seto Inland Sea of Yamaguchi. His childhood living close to nature plus reading books and listening to music in this small island have become irreplaceable experiences and contributed much to his career as a scientist. After obtaining his Ph.D. from Nagoya University in 1969, he spent two years as an Assistant at Nagoya Institute of Technology and moved to Mie University, where he was professor until 2005. He is now Visiting Professor of Aichi Institute of Technology and Senior Researcher of Nagoya Industrial Science Research Institute, in addition to Emeritus Professor of Mie University.

working simultaneously at the turn of century. One may wonder if either of them was inspired by each other's reports and might have attempted to stabilize carbenes or even to isolate them.

The pioneering work of Staudinger[7] in the 1910s on the decomposition of diazo compounds and ketenes contributed much to the recognition of carbenes as a new reactive species. Since radicals were the intermediates *en vogue* in the following decades, they started by being generally regarded as diradicals. Therefore, it might not be very surprising that carbene chemistry developed without the upsetting discovery equivalent to the Gomberg's radicals. However, it is rather surprising to note that stable carbenes have attracted little attention until quite recently when two groups announced the discovery of these species, i.e., phosphinocarbene (**1**) as a distillable red oil[8] and imidazol-2-ylidene (**2**) as a crystal with high melting point[9] in 1988 and 1991, respectively.[10] These carbenes are, however, stabilized by heteroatom substituents connected to the carbenic atom and thus have singlet ground states. Their electronic configurations are a topic of debate.[11] Since triplets resemble radicals in terms of reactivity and electronic properties, one may naturally consider that stable triplet carbenes must be the counterpart of the Gomberg's radicals. It is then extremely surprising to note that almost no paper concerning intentional attempts to generate stable carbenes in triplet states under normal conditions has appeared in the literature, except one by Zimmerman and Paskovich in 1964,[12] at least when we started the work in this field in 1990.



1
bp 75~80 °C / 10^{-2} Torr



2
mp 240 °C

Motivated by this rather naive overview of the historical background, we initiated our study to stabilize triplet carbenes to the extent that they are able to survive under normal conditions. However, as one may easily expect from their highly reactive nature with only two modifiable substituents, it turned out to be a very challenging project. For instance, the lifetime of triplet diphenylcarbene in solution at room temperature is 2 orders of magnitude smaller than that of diphenylmethyl and shorter even than methyl. At present, we are still not able to obtain a triplet carbene which is stable enough to be isolated as a crystal or a liquid. So this review is a progress report, not the final summation of our efforts to isolate triplet carbenes.[13]

The first three sections (2−4) are devoted to a brief explanation of the background of these works, which starts with a brief overview of the effect of the substituents and solvents on the ground-state multiplicity of carbenes, mainly based on the modern computational works, which is followed by electron spin resonance works of triplet carbenes and experimental approaches to persistent triplet carbenes. These brief overviews will help readers understand the crucial issues involved in this work. In section 5, we will explain how

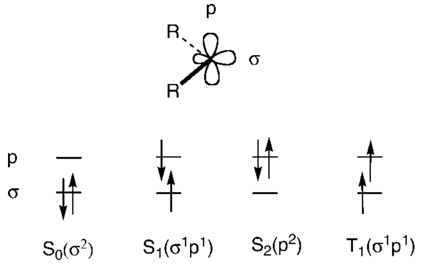


Figure 1. Electronic configurations of carbenes.

persistent triplet carbenes have been generated and characterized. In the last section, behaviors of persistent triplet carbenes in constrained media will be briefly discussed.

2. Relationship between Structure and Ground State Multiplicities

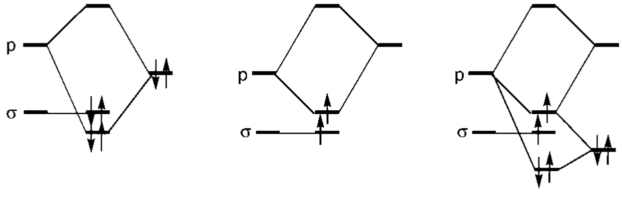
The carbene carbon is linked to two adjacent groups by covalent bonds, and possesses two nonbonding electrons which may have antiparallel spins (singlet state) or parallel spins (triplet state).[14] Therefore, one needs to analyze the factors influencing the stability of both electronic states. We should emphasize here that this requirement is specific to this project. It is usually not necessary in order to stabilize other "simple" transient species and, hence, makes the method rather complicated.

If the carbene unit were linear, it should have two degenerate p orbitals, and Hund's first rule would predict a triplet ground state. Because the carbene unit is not linear, the two orbitals become different. The orbital perpendicular to the plane defined by the three atoms is designated as "p", while that parallel to this plane is called "σ". The σ orbital will acquire s character and thereby become stabilized while the p orbital remains largely unchanged. Actually, most carbenes are not linear, and the ground-state multiplicity varies depending on the structures.

The four lowest energy configurations of carbenes have electronic configuration described as σ^1p^1, σ^2, or p^2. The electron spins in the σ^1p^1 configuration may be paired, a singlet, or parallel to form a triplet, while the σ^2 and p^2 configurations must be an electron-paired singlet. Thus, the triplet state has σ^1p^1 configuration, while the singlet state can have either σ^2 or p^2 or σ^1p^1 configurations, although σ^2 is generally thought to be the lowest energy configuration (S_0) for the singlet (Figure 1).

In the lowest singlet state σ^2 (S) carbene, the electron−electron Coulombic repulsion would be severe, since two electrons are constrained to the same small MO. On the other hand, the triplet state (T) is stabilized by relief of the Coulombic repulsion and "exchange repulsion"; however, the separation of electrons into different MOs does not come without a cost. Thus, the magnitude of the energy difference between the triplet and singlet states (the singlet−triplet splitting, ΔG_{ST}; throughout the text, we will adopt the convention that the positive S−T gaps indicate triplet below singlet in energy) is roughly equal to the electron−electron repulsion minus the energy required to promote an electron from the σ to the p-nonbonding orbital. In other words, as the energy separation between the σ and p states increases, the promotion energy becomes large enough to overcome the repulsion energy, while if the spacing is small, the species will still have a triplet ground state.

Sophisticated and theoretical and experimental works indicate, for the parent carbene, methylene, the triplet was the global minimum with a H−C−H angle of 137°, while the singlet state lies 9 kcal/mol higher with an angle of 102°. The small difference between the energies of S_0 and T_1 may easily be overturned by the effects of substituents on the carbene center. The factors which influence the spacing can be analyzed in terms of electronic and steric effects.[15]



(a) X (b) Z (c) C

Figure 2. A carbene p-orbital interacting with (a) an X substituent, (b) a Z substituent, and (c) a C substituent.

2.1. Mesomeric Effects

Because of a more favorable overlap, the interaction of the carbon 2p orbital with substituent p or π orbitals is expected to dominate. The σ (sp^n) orbital which lies in the nodal plane of the substituent p or π orbital will interact with substituent σ orbitals but weakly.

Substituents interacting with a π system can be roughly classified into three classes, on the basis of the perturbation orbital diagram:[16] namely X (π-electron donors such as -NR_2, -OR, -SR, -F, -Cl, -Br, and -I), Z (π-electron acceptors such as -COR, -SOR, -SO_2R, -NO, and -NO_2), and C (conjugating groups such as alkenes, alkynes, or aryl groups).

As shown in Figure 2a, an X substituent, which has a p orbital, or other suitable doubly occupied orbital which will interact with the π bond, raises the vacancy 2p orbital of the carbene, thereby increasing the separation of the 2p and sp^n (σ) orbitals. The ground-state of an X-substituted carbene becomes singlet. Many carbenes in this class are known. The most familiar are halo carbenes.

Z and C substituents having a p or π* orbital and evenly spaced π and π* orbitals, respectively, on the other hand, either lower the 2p-sp^n gap or leave it about the same as shown in Figure 2(b) and (c). In either case, the ground-state for these carbenes is expected to be T_1 although the magnitude of ΔG_{ST} may vary. It has been demonstrated by ESR studies that most aryl and diarylcarbenes have triplet ground states.

We will briefly show quantitative data from more sophisticated computational works.

2.1.1. Effect of π-Conjugation

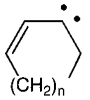
2.1.1.1. Effect of Vinyl Groups. MCSCF calculation predicts the S−T gap of the parent vinylcarbene to be 12−13 kcal/mol.[17a,b] However, at the G2 level of theory, it is found to be 6.4 kcal/mol.[17] This may suggest that the conjugation with the double bond of the carbene center equally stabilizes both states.

This issue has been studied computationally (using *ab initio* and DFT methods) by examining heats of formation and ΔE_{ST} for cyclopenten-3-ylidene (**3**, $n = 1$), cyclohexen-3-ylidene (**3**, $n = 2$), and cyclohepten-3-ylidene (**3**, $n = 3$) and their unconjugated isomers (**4**, $n = 0-2$) (Table 1).[17] Since the central carbenic center is essentially the same when the size of the ring is the same, direct comparison of their relative energies should be primarily associated with the

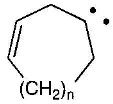
Table 1. Heat of Formation (ΔH_f, kcal/mol) and Derived S−T Splittings (ΔE_{ST}, kcal/mol) for Cycloalkenylidenes (3 and 4)[17]

Carbene	ΔE_{f298}(S)	ΔE_{f298}(T)	ΔE_{ST}
3 (n = 1)	95.7	101.9	-6
3 (n = 2)	88.8	88.7	~0
3 (n = 3)	88.9	85.2	4
4 (n = 0)	104.8	112.1	-7
4 (n = 1)	96.6	101.9	-5
4 (n = 2)	95.0	96.8	-2

stabilization effect of the double bond on the carbenic center. In all three cases, the most stable isomer is the one in which the double bond can conjugate with the carbenic center and the resulting stabilization energy varies between 10.2 and 13.2 kcal/mol for the triplet states. A similar stabilization effect is also found for the singlets, but this stabilization is 5.0−9.1 kcal/mol, which is 10−50% less than that for the triplet.



3 (n=1,2,3)



4 (n=0,1,2)

The small difference in the stabilization between singlet and triplet states can be understood by considering the computed enthalpies (kcal/mol) of the following isodesmic reactions for the singlet (S) and triplet (T) states of vinylcarbene and ethylcarbene:

$$CH_2{=}CH{-}C{-}H + CH_4 \rightarrow H{-}C{-}H + CH_2{=}CH - CH_3\ [S{:}18.2/T{:}17.6] \quad (1)$$

$$CH_3CH_2{-}C{-}H + CH_4 \rightarrow H{-}C{-}H + CH_3CH_2CH_3\ [S{:}16.5/T{:}5.3] \quad (2)$$

$$CH_2{=}CH{-}C{-}H + CH_3CH_2CH_3 \rightarrow CH_3CH_2{-}C{-}H + CH_2{=}CHCH_3\ [S{:}1.7/T{:}12.3] \quad (3)$$

From eq 1, it is seen that a vinyl group stabilizes the singlet somewhat more than the triplet compared to a hydrogen substituent. However, an ethyl group stabilizes the singlet significantly more than the triplet, due to hyperconjugation (eq 2). Equation 3 shows that a vinyl group stabilizes the triplet more than the singlet, as compared to an ethyl group. Thus, in **4**, the singlet is already stabilized by hyperconjugation to a larger extent than the corresponding triplet. Therefore, conjugation of the double bond with the carbenic center in **3** offers little extra stabilization to the singlet, but more to the triplet.[17]

Table 2. Singlet−Triplet Energy Separation and Optimized Bonds (α) and Torsion Angles (θ) of Monoaryl- (5−7) and Diarylcarbenes (8−10)[a,18]

Carbene[b]	ΔE_{ST}(kcal/mol)	α_S(°)	α_T(°)	θ_S/θ_T
Ph−$\ddot{C}$−H (**5a**)	5.59 [2.75]	106.96	135.67	0/0
(*E*)-1-Naph−$\ddot{C}$−H (*E*-α-**6a**)	6.24 [3.40]	106.73	135.48	0/0
9-Anth−$\ddot{C}$−H (**7a**)	8.51 [5.67]	109.72	139.31	0/0
Ph−$\ddot{C}$−Ph (**8a**)	5.78 [2.94]	119.5	142.88	58.5/53.7
1-Naph−$\ddot{C}$−Naph-1 (α-**9a**)	6.58 [3.7]	121.62	173.62	68.9/87.3
9-Anth−$\ddot{C}$−Anth-9 (**10a**)	15.70 7.76[c]	147.28	180.00	78.7/90.0

[a] ΔE_{ST} is estimated at the B3LYP/6-311+G(d,p)+ZPE level of theory, but since the uncorrected gaps overestimated these separations, these values have been adjusted by the 2.84 kcal/mol difference between the experimental and computed S−T gaps for methylene at the same level of theory, which are indicated in square brackets [ ]. [b] Naph = naphthyl, Anth = anthryl. [c] "Nascent" geometry for both singlet and triplet species is used. See text.

Table 3. Enthalpies of the Isodesmic Reactions That Evaluate the Effect of Adding Aryl Groups to Methylene[18]

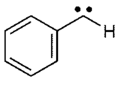
Carbene	E_{sub}/S (kcal/mol)	E_{sub}/T (kcal/mol)	ΔE_{sub} (kcal/mol)
Ph−$\ddot{C}$−H (**5a**)	24.4	18.1	6.3
(*E*)-1-Naph−$\ddot{C}$−H (*E*-α-**6a**)	26.6	20.9	5.7
9-Anth−$\ddot{C}$−H (**7a**)	30.5	26.8	3.7
Ph−$\ddot{C}$−Ph (**8a**)	15.8	16.0	-0.2
1-Naph−$\ddot{C}$−Naph-1 (α-**9a**)	18.6	19.0	-0.4
9-Anth−$\ddot{C}$−Anth-9 (**10a**)	21.5	-	-

2.1.1.2. Effect of Aryl Groups. The geometries and relative stabilities of the singlet and triplet monoaryl- (**5a**−**7a**) and diarylcarbenes (**8a**−**10a**) were computationally investigated (Table 2).[18] ΔE_{ST} for phenylcarbene (**5a**) is estimated to be 2.75 kcal/mol, which means that a single phenyl group reduces ΔE_{ST} by 6.3 kcal/mol relative to methylene. Isodesmic equations (eqs 4 and 5) are used to assess the stabilizing effect of substituents, R, on the singlet (E_{sub}/S) and on the triplet (E_{sub}/T).

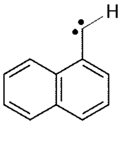
$$H{-}C{-}R(S/T) + CH_4 \rightarrow H{-}C{-}H(S/T) + CH_3{-}R \quad (4)$$

$$H{-}C{-}R(S/T) + CH_4 \rightarrow H{-}C{-}H(S/T) + CH_2R_2 \quad (5)$$

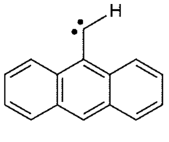
By using these equations, the stabilizing effect of the phenyl group on the singlet (E_{sub}/S) and on the triplet (E_{sub}/T) is calculated to be 24.4 and 18.1 kcal/mol, respectively (Table 3).[18] This means that p−π arene conjugation stabilizes the vacant p-orbital of singlet carbenes more than the singly occupied p-orbitals of the triplet states.



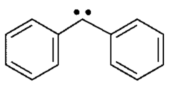
5a



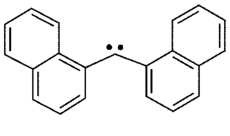
***E*-a-6a**



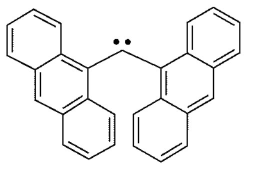
7a



8a



a-9a



10a

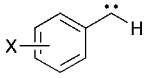
However, for α-naphthyl- (**6a**) and 9-anthrylcarbenes (**7a**), ΔE_{ST} is calculated to be 3.40 and 5.67 kcal/mol, respectively, which means that the reduction of ΔE_{ST} relative to methylene due to the larger α-naphthyl (5.7 kcal/mol) and 9-anthryl groups (3.7 kcal/mol) is smaller. The α-naphthyl group stabilizes the singlet and triplet states by 26.6 and 20.9 kcal/mol, respectively, which are 2−3 kcal/mol greater than those for phenyl, due to the greater resonance stabilization of the larger arene. The 9-anthryl group stabilizes the singlet and triplet states by 30.5 and 26.8 kcal/mol, respectively, and is the most stabilizing aryl-substituent considered.[18]

Note here that the difference in stabilizing effect on the single and the triplet (E_{sub}/S − E_{sub}/T) decreases from 6.3 to 5.7 to 3.7 kcal/mol on going from phenyl- (**5a**) to α-naphthyl- (*E*-α-**6a**) to 9-anthryl-carbenes (**7a**), respectively. The decrease is associated with the increase in the ability to resonance stabilize the triplet states. The exceptional ability of a 9-anthryl group to stabilize the triplet is seen in the NICS values for the central bond of the triplet 9-anthrylcarbene. These values are significantly less those for the adjacent rings, indicating that the substantial overlap between the carbene and 9-anthryl orbitals results in some quinoidal character of the central anthryl rings (vide infra).[18]

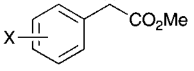
DFT and CAS calculations show that triplet di(9-anthryl-)carbene (^{3}**10a**) prefers D_{2d} symmetry with a linear (180°) carbene angle and allene-like central C=C bond length. It is pointed out that about 65% of the unpaired electron spin density of ^{3}**10a** is displaced from the carbene carbon to the 10 and 10′ positions of the anthryl rings. The DFT closed-shell singlet state has C_2 symmetry, and the triplet is favored 15.7 kcal/mol over this closed-shell singlet. Thus, ^{3}**10a** has a greater degree of delocalized diradical character than of triplet carbene character. However, the broken-symmetry UBS-B3LYP/6-311+G(d,p) open-shell singlet lies only 2.2 kcal/mol above the triplet and shares its D_{2d} symmetry.[18,19]

It has been shown experimentally that triplet di(9-anthryl)carbene has a "nascent" structure when generated in a rigid matrix at low temperature and undergoes geometrical relaxation when the matrix softened (vide infra).[20] When this nascent structure simulated from the precursor diazo compound is used, ΔE_{ST} is calculated to be 7.76 kcal/mol, which is more consistent with the S−T gaps of the other carbenes in Table 2.[18]

2.1.1.3. Effect of Aromatic Ring Substituents. DFT calculations [B3LYP/6-311+G(d,p)//B3LYP/6-31G(d)] show substitution on the aromatic ring has a pronounced effect on the preference for the singlet or triplet electronic state of the substituted phenylcarbene (**5**).[21] As expected from the understanding of phenylcarbene based on valence orbital arguments, strong π-donors (e.g., NH_2, OH, and OCH_3) preferentially stabilize the singlet state relative to the triplet state, while π-acceptors (e.g., CN and NO_2) destabilize the singlet state. Thus, ΔE_{ST} spans 9.6 kcal/mol (from 0.7 kcal/mol for *p*-aminophenylcarbene to 10.3 kcal/mol for *p*-nitrophenylcarbene). The plot of ΔE_{ST} versus σ_p^+ is linear, and the slope (ρ) is 5.0.



5



11

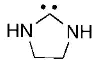
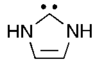
One would expect that the effect of ring substituents on ΔE_{ST} of a more perturbed arylcarbene system, e.g., phenyl(methoxycarbonyl)carbene (**11**), is attenuated due to the participation of the perturbing group, e.g., carboxyl group, in the stabilization of the carbene center. As observed for many other carbonyl carbene systems, the singlet and triplet states of **11** have very different geometries. The triplet carbonyl carbene is planar with an R-C-CO interplanar angle of 0.0°, while the singlet is oriented such that the carbonyl oxygen is perpendicular to the plane defined by the carbene carbon and its adjoining atoms (see Figure 3). Despite the interaction of the methoxycarbonyl group with the carbene center, the substituent effect on the singlet−triplet energy gap is comparable in **11** compared to **5**. The slope (ρ) of ΔH_{ST} versus σ_p^+ is 4.2 for para systems [B3LYP/6-311+G(d,p)//B3LYP/6-31G(d)].[22]

Table 4. Singlet−Triplet Energy Separation of Halocarbenes[a,23a]

Carbene	ΔE_{ST}(kcal/mol)	Carbene	ΔE_{ST}(kcal/mol)
H-C̈-F	-14.3	F-C̈-F	-56.2
H-C̈-Cl	-5.7	Cl-C̈-Cl	-20.0
H-C̈-Br	-5.0	Br-C̈-Br	-16.1
H-C̈-I	-4.5	I-C̈-I	-11.8

[a] Calculated at the CCSD(T)/6-311++G(3df,2p) level of theory.

Table 5. Singlet−Triplet Energy Separation of Carbenes with Heteroatom Substituents

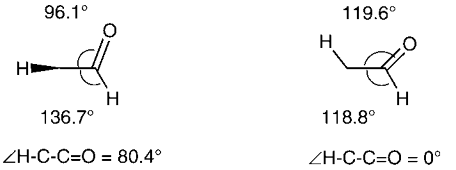
Carbene	ΔE_{ST}(kcal/mol)	Level of Theory	Ref
HS-C̈-SH	-28.0	CCSD(T)/6-311G(3df,2p) +ZPE//MP2/6-31G(d,p)	26
MeO-C̈-OMe (**12**)	-53.02	B3LYP/6-31G(d)	27
$(H_2N)_2P$-C̈-SiH_3 (**13**)	-11.1	B3LYP/6-31G(d)	28
H_2N-C̈-NH_2 (**14**)	-52.6	B3LYP/cc-pVDZ	29
	-69.4	HF/TZ2P	30
 (**15**)	-84.5	HF/TZ2P	30

2.1.2. Effect of π-Electron Donors

The simple carbenes are π-electron-deficient and σ-electron-rich, so that they are effectively stabilized by π-electron-donor, σ-electron-acceptor substituents. A typical example is seen in the halocarbenes (Table 4).[23]

Note that the first-row electron donor F(2p)−C(2p) resonance electron donation of the fluorine group is much more effective than the analogous Cl(3p)−C(2p) interaction of the chlorine group for the singlet.[24] On the other hand, the calculated stabilization energies at a radical center due to F and Cl substituents are 3.3 and 5.5 kcal/mol, respectively, which also account for the observed increase in the splitting on going from chlorocarbene to fluorocarbene.[25]

The S−T energy splittings calculated for a series of carbenes having heteroatom substituents are listed in Table 5, which clearly shows that the splitting is increased as the π-donating ability of the substituents is increased. For instance, the parent diaminocarbene (**14**) has a ΔE_{ST} of −52.6



16 (Singlet State) **16** (Triplet State)

Figure 3. Selected structural parameters for B3LYP/6-31G(d) optimized structures of singlet and triplet formylcarbene (**16**).

kcal/mol, but the stabilizing effect is further increased by incorporating the amino group in an aromatic system; singlet imidazol-2-ylidene (**15**) is stabilized by more than 80 kcal/mol relative to the triplet state.

It is interesting to note here that the kinetic stability of singlet carbene is not closely related with the magnitude of ΔE_{ST}. For instance, while $Me_2N-C-NMe_2$ can be observed by NMR spectroscopy,[31] MeO−C−OMe (**12**, $\Delta E_{ST} = -53.02$ kcal/mol) has only been characterized in matrices at low temperature (lifetime in solution at room temperature is only 2 ms).[32] Also, (phosphino)(silyl)carbene (**1**) is isolated,[8] while ΔE_{ST} of its parent form (**13**) is only −11.1 kcal/mol.

The homodesmic equastion indicates that those π-donor/σ-acceptor substituents not only stabilize the singlet but also *destabilize* the triplet (see Table 8),[33] thus making ΔE_{ST} more negative.

2.1.3. Effect of π-Electron Acceptors

Since simple singlet carbenes are π-electron-deficient species, a π-electron acceptor might not be expected to stabilize a singlet carbene. In accordance with this expectation, ΔE_{ST} of phenylcarbenes is shown to be increased as π-electron acceptors such as nitro and formyl groups are introduced at the para position (vide supra). However, when those π-electron acceptors are introduced directly on the carbene carbon, the situation is changed.

Take formylcarbene (**16**), for instance. The triplet state of this carbene assumes coplanar geometries where the singly occupied p-orbitals of the triplet states are stabilized by conjugation with a formyl carbonyl group. The singlet state differs in an important way from the triplet counterpart in that the formyl group assumes a perpendicular conformation to avoid destabilization of the empty carbenic 2p atomic orbital by the electron-withdrawal carbonyl group. This structure leads to the possibility of donation by an in-plane oxygen lone pair of the carbonyl group to the formally vacant p orbital of the singlet carbene and donation of the sp^2-type lone pair of the carbene to the π* orbital of the carbonyl group. The occurrence of such an interaction is seen in the optimized geometry, which is a nearly orthogonal structure with a ∠HCCO dihedral angle of 80.4° and a narrow ∠CCO bond angle of 96.1° These interactions lead to preferential stabilization of the singlet state. The triplet state is still calculated to be a ground state, but the S−T gap is 2.4 kcal/mol [B3LYP/6-31G(d)], indicating the singlet state is significantly stabilized relative to methylene (H−C−H).[34]

A similar structural change in the singlet state is also found in nitromethylene ($H-C-NO_2$).[35]

2.1.4. Effects of Hyperconjugation

Singlet carbenes are isoelectronic with carbocations, and the same effects that stabilize carbocations also will stabilize singlet carbenes. The triplet carbenes have a singly occupied p orbital, as in the case of radicals. While both carbocations and radicals are stabilized by hyperconjugation, the magnitude is much less for the radicals. Thus, singlet carbenes are stabilized more effectively by alkyl groups than triplet carbenes.

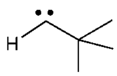
This has been shown by B3LYP/TZ2P calculations (Table 6). The most simple carbene, methylene, is a ground-state triplet with ΔE_{ST} of 9.05 kcal/mol. This value (ΔE_{ST}) decreases as hydrogen is replaced with methyl groups. The calculations yields a ΔE_{ST} of only 2.26 kcal/mol for methylcarbene and predict dimethylcarbene to have a singlet ground-state with a ΔE_{ST} of −2.47 kcal/mol.

Table 6. Singlet−Triplet Energy Separation and Optimized Bond Angles (α) of Alkylcarbenes[a]

Carbene[b]	ΔE_{ST} (kcal/mol)	α_S(°)	α_T(°)	Level of Theory	Ref
$\mathrm{H{-}\ddot{C}{-}H}$	11.32 [9.05]	102	134	B3LYP/TZ2P+ZPVE	36
$\mathrm{H{-}\ddot{C}{-}CH_3}$	4.53 [2.26]	105	131.3	B3LYP/TZ2P+ZPVE	37
$\mathrm{H_3C{-}\ddot{C}{-}CH_3}$	-0.20 [-2.47]	113.5	133.9	TZ2P+fCCSD(T)	38
$\mathrm{H{-}\ddot{C}{-}{}^{t}Bu}$ (**17**)	2.10 [-0.17]			B3LYP/TZ2P+ZPVE	36
$\mathrm{{}^{t}Bu{-}\ddot{C}{-}{}^{t}Bu}$ (**18**)	5.16 [2.65]	125.1	141.9	B3LYP/TZ2P+ZPVE	36
$\mathrm{Ad{-}\ddot{C}{-}Ad}$ (**19**)	9.3	125	149	B3LYP/6-31G(d)	39
$\mathrm{Trp{-}\ddot{C}{-}Trp}$ (**20**)	14.0	129	153.3	B3LYP/6-31G(d)	39

[a] See footnote *a* in table 2. [b] Ad = adamantyl; Trp = triptycyl.

By using isodesmic equations (eqs 4 and 5), the difference in the stabilizing effect of methyl and dimethyl groups on the singlet and the triplet ($E_{sub}/S - E_{sub}/T$) is calculated to be 6.98 and 11.38 kcal/mol, respectively.



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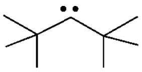

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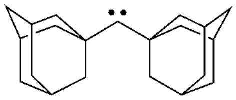

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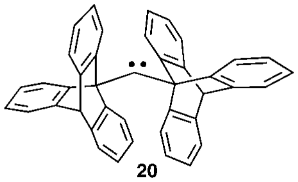

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The effect of *tert*-butyl groups is very informative. The calculation predicts *tert*-butylcarbene (**17**) to have a singlet ground-state with ΔE_{ST} of −0.17 kcal/mol, while di(*tert*-butyl)carbene (**18**) is predicted to have a triplet ground-state with ΔE_{ST} of 2.89 kcal/mol. The *tert*-butyl group stabilizes the singlet state of **17** by 17.8 kcal/mol relative to singlet methylene, but additional stabilization that is obtained by the second *tert*-butyl group in singlet **18** is only 8.8 kcal/mol. The steric repulsion between the two *tert*-butyl groups in **18** widens the central bond angle and influences ΔE_{ST}. The bond angle at the carbene center in the singlet state of **18** is 125.1°, which is 23° larger than that for singlet methylene. From the plot of relative energy with respect to the angle (see Figure 5), one can estimate that singlet **18** raises its energy by 7.2 kcal/mol.[36]

These results clearly show that alkyl groups generally stabilize the singlet state more effectively than the triplet, but this effect is less effective when bulky alkyl groups are used. However, it should be pointed out that ΔE_{ST} of **18** is still significantly smaller than that of methylene.[36]

2.2. Inductive Effect

Since S−T energy gaps are a function of multiple variables including p- as well as σ-contributions, it is not always possible to differentiate each of those contributions. The inductive effects are rationalized qualitatively on the basis of perturbation orbital diagrams (Figure 4). Thus, σ-electron withdrawing substituents inductively stabilize the σ nonbonding orbital by increasing its s character and leave the p

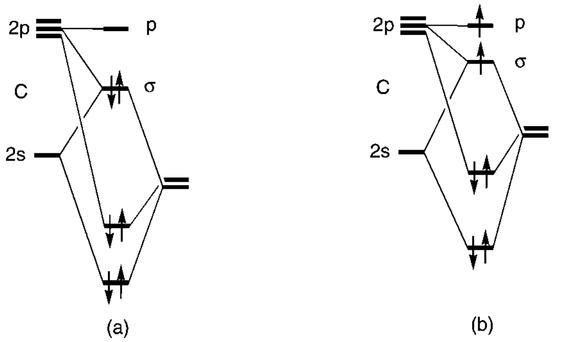


Figure 4. Perturbation orbital diagrams showing the influence of inductive effects.

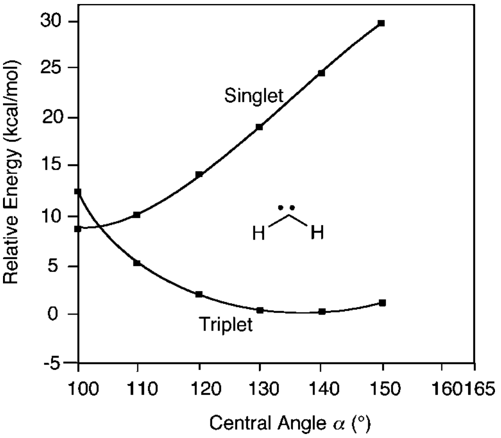


Figure 5. Changes in the relative energy of singlet and triplet methylene with respect to the central bond angle at B3LYP/TZ2P.[36]

Table 7. Singlet–Triplet Energy Separation for Carbenes Symmetrically Substituted with Electropositive Atoms[a,33]

Carbene	ΔE_{ST} (kcal/mol)
$(HO)(O)_2S-\ddot{C}-S(O)_2(OH)$ (**21**)	6.8
$(HO)_2(O)P-\ddot{C}-P(O)(OH)_2$ (**22**)	14.0
$(HO)_2B-\ddot{C}-B(OH)_2$ (**23**)	17.2
$F_2B-\ddot{C}-BF_2$ (**24**)	10.5
$H_3Si-\ddot{C}-SiH_3$ (**25**)	24.7
$F_3Si-\ddot{C}-SiF_3$ (**26**)	29.5
$(HO)_3Si-\ddot{C}-Si(OH)_3$ (**27**)	25.7

[a] Calculated at the CCSD(T)/cc-pVDZ level of theory.

Table 8. Reaction Energies (ΔE_S for Overall Singlet, ΔE_T for Overall Triplet Multiplicity) of Isodesmic Eq 6 at B3LYP/6-311++G(d,p)[33]

R in $R-\ddot{C}-R$	ΔE_S (kcal/mol)	ΔE_T (kcal/mol)
NH_2	-48.3	15.9
CH_3	-27.8	-15.3
CF_3	-1.4	-0.5
$S(O)_2(OH)$	-3.2	3.1
$P(O)(OH)_2$	-10.8	-7.6
$Si(OH)_3$	-10.5	-21.9
SiH_3	-12.6	-23.8
SiF_3	1.9	-15.7

orbital unchanged. The σ–p gap is increased, and the singlet is favored. In contrast, σ-electron donating substituents induce a small σ–p gap, which favors the triplet ground state.

The influence of the electronegativity of carbenic substituents on ΔE_{ST} of the carbene was studied already in the 1970s. For instance, Harrison estimated approximate S–T gaps for Li–C–Li, H–C–H, and F–C–F to be 23, 11, and −45 kcal/mol, respectively, and suggested that the ground state goes from triplet to singlet as the substituents are changed from electropositive lithium to hydrogen to electronegative fluorine[40] (although the mesomeric effect plays an important role in the case of fluorine).

It has been shown that the carbenes having substituents of the first to third group of the periodic table (i.e., Li–C–Li, BeH–C–BeH, and BH–C–BH) are unusual in that they have linear structures in both singlet and triplet states. This is because the substituents have empty p-orbitals that can interact with electrons on the carbene carbon.[41]

More systematic studies have been carried out by calculating the S–T gaps of a series of substituted carbenes X–C–Y, where X and Y are H, F, Cl, Br, I, and SiH_3 by generalized valence bond (GVD) calculations. The magnitude of the singlet–triplet energy gap is shown to be rationalized in terms of the change on the carbenic carbon atom and π-donation from the substituents. It is concluded that σ-donating and π-back-bonding act synergistically.[42]

Electronic stabilization of the triplet state has been examined recently by using ab initio [CCSD(T)/cc-pVDZ] methods for a series of carbenes (**21**–**27**) symmetrically substituted with electropositive atoms (Si, B, P, and S) at the α-position (Table 7).[33] ΔE_{ST} values do not strictly follow the electronegativities of the α-atom, since contributions from other factors are also included. However, in accordance with Si's electronegativity, silylcarbenes (**26**) exhibit the largest splittings among the model carbenes.

The charges on the carbene carbon indicate that all substituents less electronegative than C stabilize carbene by σ-donation. They are proportional to the electronegativity of the α-substituents, and the overall stabilization by Si is the largest. From the homodesmic eq 6, it has been shown that Si groups stabilize the triplet states significantly more than the singlet state (Table 8).

$$H-C-H + R-CH_2-R \rightarrow R-C-R + CH_4 \tag{6}$$

It is concluded that σ-donor substituents lacking p-interactions with the carbene center preferentially stabilize triplet carbenes, while strongly hyperconjugating alkyl groups favor singlet multiplicity and the classical p-donor/σ-acceptor substituents stabilize the singlet and simultaneously destabilize the triplet.[33]

The group electronegativity of CF_3 is 2.98 Pauling unit,[43] which is larger than that of CH_3 (2.47 Pauling unit). Substitution of a CF_3 group on methylene increases ΔE_{ST} from 10.5 to 13.5 kcal/mol. A similar small change upon substitution with CF_3 groups is also seen in a singlet ground-state carbene. For instance, ΔE_{ST} changes from −15.4 to −16.7 kcal/mol on going from H–C–F to CF_3–C–F (Table 9). These results indicate that the influence of CF_3 substitution on the gap is very small, about 2 kcal/mol.[44] Isodesmic equations clearly indicate that CF_3 groups show very small stabilizing effects to both states, while the CH_3 group stabilizes both states by more than 15 kcal/mol but with $E_{sub}/S - E_{sub}/T = 12.5$ kcal/mol (Table 8). This is seen in the difference of ΔE_{ST} between CH_3–C–CH_3 and

Table 9. Effect of CF_3 Group on Singlet−Triplet Energy Separation of Carbenes

Carbene	ΔE_{ST}(kcal/mol)	Level of Theory	Ref
$\mathrm{H{-}\ddot{C}{-}H}$	10.5	DDCI	44
$\mathrm{F_3C{-}\ddot{C}{-}H}$	13.5	DDCI	44
$\mathrm{H{-}\ddot{C}{-}F}$	-15.4	DDCI	44
$\mathrm{F_3C{-}\ddot{C}{-}F}$	-16.7	DDCI	44
$\mathrm{H_3C{-}\ddot{C}{-}CH_3}$	1.6	CCSD(T)/cc-pVDZ	33
$\mathrm{F_3C{-}\ddot{C}{-}CF_3}$	11.2	CCSD(T)/cc-pVDZ	33

CF_3-C-CF_3 (Table 9). The results clearly suggest that pure inductive electron withdrawing effects are very small.

2.3. Steric Effect

The magnitude of ΔG_{ST} is expected to be sensitive to the carbene−carbon bond angle. A linear carbene has two degenerate p orbitals, which is expected to provide the maximum value of ΔG_{ST}. Bending the carbene removes the orbital degeneracy and reduces ΔG_{ST}. As the carbene−carbon bond angle is further contracted, the σ-orbital achieves stronger s-character and consequently moves even lower in energy. The smaller the bond angle, the more energy it takes to promote an electron from the σ to the p-orbital, and the smaller ΔG_{ST} becomes.

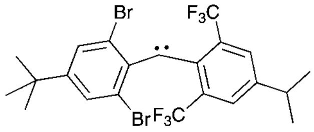
This is shown more quantitatively by calculations for methylene (Figure 5).[36] The calculations predict that the energy of singlet methylene will drop below that of the triplet state for carbenes with bond angles less than about 104°. On the other hand, theory also suggests that opening of the central angle strongly destabilizes the singlet state but requires very little additional energy for the triplet, thus making ΔG_{ST} larger.

Typical examples are seen in di(adamantly)carbene (**19**) and di(triptycyl)carbene (**20**). DFT [B3LYP/6-31G(d)] calculations predict that ΔE_{ST} for **19** and **20** is 9.3 and 14.0 kcal/mol, respectively[39] (Table 6), which is to be compared with the ΔE_{ST} value of 12 kcal/mol calculated with the same level of theory for methylene.

As alkyl substitution usually stabilizes the singlet state significantly more than the triplet state, the observed increase in ΔE_{ST} by those bulky substituents is ascribable either to stabilization of the triplet state or to destabilization of the singlet state, both due to widening of the central bond angle.

The effect of ortho substituents on the singlet−triplet energy gap of phenylcarbene is analyzed [B3LYP/6-311+G(d,p)//B3LYP/6-31G(d)].[21] The range spanned by ΔE_{ST} for ortho substituents is 13.5 kcal/mol (from −4.4 kcal/mol for *o*-aminophenylcarbene to 9.1 kcal/mol for *o*-trifluoromethylphenylcarbene), which is larger than that observed in the para case (vide supra). It is to be noted that the largest ΔE_{ST} was observed for trifluoromethyl substitution, not for nitro substitution, in the ortho system. This probably arises from a combination of inductive effects and steric effects limiting conjugation into the aromatic ring, both destabilizing the singlet state.[21]

The effect of sterically more congested ortho substituents on the singlet−triplet energy gap of diphenylcarbene was analyzed [B3LYP/6-311+G(d,p)].[45] The energy gap for the parent diphenylcarbene (**8a**) and (2,6-dibromo-4-*tert*-butylphenyl)[2,6-di(trifluoromethyl)-4-isopropylphenyl]carbene (**28**) is predicted to be 5.8 and 12.2 kcal/mol, respectively. The optimized geometries show that the central C−C−C bond angles in **8a** and **28** are bent significantly more in **8a** than in **28**: ^{1}**8a** (119.5°) versus ^{1}**2828** (134.2°) and ^{3}**8a** (143.1°) versus ^{3}**28** (176.3°). So, one may suppose that the triplet state in **28** is thermodynamically more stabilized with respect to the singlet, since bulky substituents are introduced. However, a suitable isodesmic reaction reveals that both ^{1}**28** and ^{3}**28** are destabilized by 12.5 and 6.3 kcal/mol, respectively, by additional bulky substituents. In other words, the substituents actually destabilize both ^{1}**28** and ^{3}**28** with respect to **8a**, but do so more for ^{1}**28** than for ^{3}**28**.[45]



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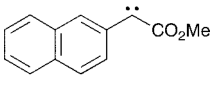
The potential energy surfaces of the triplet states are extremely flat, and changes in the carbene angles have little effect on the energies. For instance, only 1.4 kcal/mol is required to linearize triplet diphenylcarbene from its 143° equilibrium geometry.[36] The intramolecular steric interactions are more adverse in the singlet, with its smaller internal bond angle, than in the triplet states.

2.4. Solvent Effect

Singlet carbenes have closed-shelled singlet electronic configurations and hence might have zwitterionic character.[46] Thus, singlet states are expected to be stabilized more than the triplet states in polar solvents. This issue has been computationally examined by using polarizable continuum model (PCM) calculations.

Solvent effects on the S−T energy gaps are calculated for β-naphthyl(methoxycarbonyl)carbene (**29**) in six solvents with different polarities.[47] Again, the energy gaps decrease as the solvent polarity is increased. The difference in calculated dipole moment between ^{1}**29** and ^{3}**29** ($\Delta\mu_{ST}$) increases with solvent polarity. This increase is mainly due to the solvent effect on the singlet carbene's dipole moment and results in preferential stabilization of the singlet in polar solvents. The plot of experimentally derived S−T gaps as a function of solvent polarity parameter $E_T(30)$[48] is linear, suggesting that specific carbene−solvent complexes (vide infra) do not play a significant role in the present system.



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The effect of solvent on the S−T energy gaps is experimentally verified by measuring the intersystem crossing rate. The rate of singlet to triplet conversion (k_{ST}) of diphenylcarbene decreases as the solvent polarity is increased. The plot of k_{ST} as a function of $E_T(30)$ is again linear, indicating that k_{ST} decreases as ΔE_{ST} is decreased. Since the usual behavior exhibited by other molecules is that the smaller the energy gap, the faster the rate of intersystem crossing, diphenylcarbene exhibits an inversed gap effect. This effect is explained by an off resonance coupling model.[49]

Apart from the solvent polarity, the singlet carbenes also undergo specific stabilization by solvents having nonbonding electrons such as ethers,[50] haloalkanes, and halobenzene[51] and π-electrons such as benzene.[52]

3. Electron Spin Resonance Spectroscopy

Electron spin resonance (ESR) spectroscopy not only unambiguously identifies triplet carbenes but also provides valuable information on their molecular and electronic structures.[53,54] Here we will first give the types of information obtained from ESR and how the information can be used. And then we will show the information on the triplet ground-state carbenes that is discussed computationally in the previous section. We will also refer to the observations that are encountered in the studies of persistent triplet carbenes.

A triplet state is characterized by three values of the spin-magnetic quantum numbers, $m_s = 1$, 0, and -1. The three levels of a triplet are split even in the absence of an external magnetic field, since a dipole coupling of the two spins creates an internal magnetic field in the molecule, which splits the energy levels. The $m_s = 0$ level is stabilized and the $m_s = 1$ and -1 levels are destabilized. This energy separation is called D. Each electron moves in the magnetic field of the other. If the molecule has less than cylindrical symmetry, there will be two different values of the internal field. These fields do not affect the $m_s = 0$ level, which has no overall spin. They cause, however, a further splitting of the $m_s = 1$ and $m_s = -1$ levels. This splitting is called E.

These splittings persist in the absence of an external magnetic field, and hence the constants D and E are termed zero-field splitting (ZFS) parameters. Each energy level is associated with a principal magnetic axis in the molecule, because its energy will not change with magnetic field when the field is parallel to that axis. Triplet EPR spectroscopy provides a direct measure of the distribution of spins in the molecule. D and E are obtained in gauss from the spectrum, but usually they are converted to energy units (cm^{-1}) and reported as D/hc and E/hc. The absolute value signs indicate the fact that D can be positive or negative, and the sign is not known.

The parameter D measures the magnetic dipole interaction along the z axis and is related to the average $1/r^3$, where r is the average separation between the spins. A high value of D implies a large spin−spin interaction and a close proximity of the two spins. The parameter E, on the other hand, is a measure of the difference between similar magnetic dipole interactions along the x and y axes. A consequence of this is that a molecule with three different axes should have a finite E, whereas this quantity vanishes for linear molecules with degenerate p orbitals. Spin−orbit coupling is also capable of affecting ZFS parameters.[23b,c]

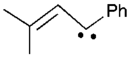
More plainly, the more the two electrons are delocalized in carbenes with a conjugated π-system, the smaller the value of the repulsive interaction D will be. On the other hand, increasing the bond angle at the carbene center leads to a higher p-orbital contribution and a smaller value for E. Although the values D and E depend on the electronic distribution, it has been shown[55] that there is a correlation between the E/D ratio and the bond angle at the divalent carbon atom.

Table 10. ESR Data of Alkylcarbenes[a]

Carbene	Matrix/Temp(K)	$\|D/hc\|$ (cm^{-1})	$\|E/hc\|$ (cm^{-1})	E/D	ref
$\mathrm{H{-}\ddot{C}{-}H}$	Xe/4	0.6881	0.00346	0.005	55
$^t\mathrm{Bu{-}\ddot{C}{-}Bu}^t$ (**18**)	MTHF/20-70	0.689	0.039	0.057	56
$\mathrm{Ad{-}\ddot{C}{-}Ad}$ (**19**)	EtOH/4-75	0.6832	0.038	0.056	57
$\mathrm{Trp{-}\ddot{C}{-}Trp}$ (**20**)	MTHF/77-130	0.720	0.0263	0.0365	39

[a] MTHF = 2-methyltetrahydrofuran.

Table 11. ESR Data of Vinylcarbenes[a]

Carbene	Matrix/Temp(K)		$\|D/hc\|$ (cm^{-1})	$\|E/hc\|$ (cm^{-1})	E/D	ref
 (**30a**)	MTHF/6	(Z)	0.4578	0.0193	0.0442	58
		(E)	0.4093	0.0224	0.0547	
 (**30b**)	Neat/NS	(Z)	0.357	0.00194	0.0543	59

[a] NS = not specified.

3.1. Relationship between Structure and Zero-Field Splitting Parameters

3.1.1. Alkylcarbenes

Some D and E values for triplet alkylcarbenes are collected in Table 10. The ZFS parameters for methylene, the parent compound of all carbenes, clearly indicated that it has a bent structure. The bond angle is estimated to be 136°, which is in agreement with most theoretical calculations.[55]

Since alkyl groups usually stabilize singlet carbenes more effectively than triplet carbenes, only alkylcarbenes substituted with bulky groups have a triplet ground-state and show ESR signals. As predicted by theoretical calculations, di(*tert*-butyl)carbene (**18**), di(adamantyl)carbene (**19**), and di(triptycyl)carbene (**20**) show triplet ESR signals. From the E/D ratio, a bond angle at the carbene center of 143° was estimated for **18**. Carbenes **19** labeled with ^{13}C at the carbene carbon were generated, and a bond angle of 152° was estimated from the hyperfine splitting. Carbene **20** showed the largest D and the smallest E values.

3.1.2. Vinylcarbenes

Introduction of vinyl groups on methylene results in a significant decrease in D values; thus, D values decrease from 0.69 to 0.4093 cm^{-1} (and 0.4578 cm^{-1}) on going from methylene to vinylcarbene (**30a**). Geometrical isomerism is observed in this case (vide infra). This is again in accord with the theoretical prediction that a vinyl group significantly stabilizes the triplet compared to a hydrogen substituent. For **30b**, where the vinylcarbene hydrogen is replaced with a phenyl group, the D value further reduces to 0.357 cm^{-1} (Table 11).

3.1.3. Arylcarbenes

Introduction of aryl groups on methylene results in a significant decrease in D values (Table 12); thus, D values decrease from 0.69 to 0.515 cm^{-1} on going from methylene to phenylcarbene (**5a**). The D values decrease further as an aromatic ring is changed from phenyl to naphthyl to anthryl. These trends are interpreted in terms of an increase in spin delocalization into the aromatic rings. The trends are in

Table 12. ESR Data of Monoaryl- and Diarylcarbenes[a]

Carbene	Matrix/Temp(K)		$\lvert D/hc \rvert$ (cm^{-1})	$\lvert E/hc \rvert$ (cm^{-1})	E/D	ref
Ph−$\ddot{\text{C}}$−H (**5a**)	DCB/77		0.5150	0.0251	0.04873	60
α-Naph−$\ddot{\text{C}}$−H (α-**6a**)	BZP/77	(*Z*)	0.4426	0.0208	0.0470	61
		(*E*)	0.4629	0.0202	0.0436	
β-Naph−$\ddot{\text{C}}$−H (β-**6a**)	BZP/77	(*Z*)	0.4926	0.0209	0.0424	61
		(*E*)	0.4711	0.0243	0.0516	
9-Anth−$\ddot{\text{C}}$−H (**7a**)	BZP/77		0.3008	0.0132	0.0439	61
Ph−$\ddot{\text{C}}$−Ph (**8a**)	BZP/77		0.4055	0.0194	0.0478	60
α-Naph−$\ddot{\text{C}}$−Naph-α (α-**9a**)	MTHF/77		0.3232	0.0105	0.0325	62
β-Naph−$\ddot{\text{C}}$−Naph-β (β-**9a**)	MTHF/77	(*Z*)	0.3971	0.0158	0.0398	63
		(*E*)	0.3832	0.0182	0.0475	
9-Anth−$\ddot{\text{C}}$−Anth-9 (**10a**)	MTHF/77		0.1038	0.0000	0.0000	20

[a] DCB = *p*-dichlorobenzene. BZP = benzophenone.

Table 13. ESR Data of Diarylcarbenes Incorporated in Rings

Carbene	Matrix/Temp(K)		$\lvert D/hc \rvert$ (cm^{-1})	$\lvert E/hc \rvert$ (cm^{-1})	E/D	ref
31	Paraffin/77	n =9	0.4787	0.0233	0.04867	64
		n =11	0.4290	0.0220	0.05128	
		n =12	0.4199	0.0214	0.05096	
32	Neat/77		0.3932	0.0170	0.0432	65
33	Neat/77		0.3787	0.0162	0.0428	65
34	BZP/77		0.365	0.0177	0.048	66
35	MTHF/14		0.2662	0.0175	0.0657	67

accord with the theoretical predictions that the ability to resonance stabilizes the triplet states' increases as arene groups become larger and that the 9-anthryl group is the most stabilizing aryl-substituent considered.

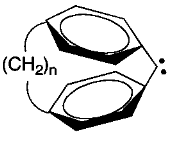
It is interesting to note here that there are only small changes in *E*/*D* values among those monoarylcarbenes, indicating that the central bond angles of the carbenes are not affected significantly by a change in those aromatic rings.

The effect of the second aryl group on the *D* values is much smaller than that expected from simple additivity. This is obviously due to the geometrical distortion in diarylcarbenes, as optimized geometries suggested. The twist of the aryl rings forces them to take a geometry which is far from an optimal interaction between the carbene center and the substituent.

However, di(9-anthryl)carbene (**10a**) exhibits unusual properties, most probably due to steric repulsion between four peri hydrogens and a great ability to delocalize unpaired electron. ZFS parameters represent the smallest *D* and nearly zero *E* values, suggesting almost linear and perpendicular structure where optimal interaction between the carbene center and a substituent in the triplet state may be attained.

The influence of the carbene bond angle on ZFS parameters was investigated for groups of cyclophane diphenylcarbenes (**31**), where diphenylcarbene units are incorporated in the [1.*n*]paracyclophane skeleton (Table 13). A small para bridge forces the ring to be parallel and practically perpendicular to the p-carbene orbital. Actually, the *D* value of 0.4787 cm^{-1} for a carbene with $n = 9$ is one of the highest values ever reported for diarylcarbenes. *D* values decrease upon increasing *n* from 9 to 12.[64]

Similar decreases in the *D* values are observed for a series of diarylcarbenes where two phenyl rings are bridged at the ortho position with various types of units (**32**−**35**). Anthronylidene (**34**) has a small *D* value, which indicates that one of the unpaired electrons is mainly delocalized in the σ-plane at the carbene center, as in the phenyl radical, while the other is delocalized in the π-system, as in the phenoxy radical.[66] 7*H*-Benzo[*de*]anthracen-7-ylidene (**35**) is most interesting, since it shows very small *D* values of 0.2662 cm^{-1}, which is the second smallest *D* value ever reported for diarylcarbenes. The π-spin densities calculated by HMO theory indicate that the spin density is found to be delocalized mostly in the naphthalene moiety of themolecule.[67]



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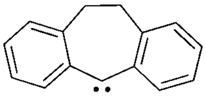

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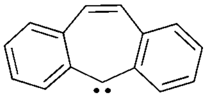

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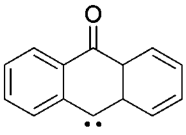

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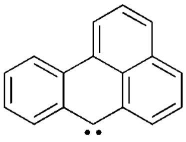

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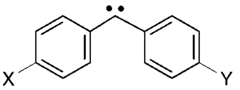
3.1.4. Effect of Aromatic Ring Substituents

Effects of para substituents on the ESR spectrum have been investigated for triplet diphenylcarbenes **8** (Table 14).[68,69] Two trends become obvious when the *D* values are compared for mono- and dipara-substituted diphenylcarbenes. First, substitution generally causes a decrease in *D* over that in the parent molecule. This is obviously due to extended π-delocalization of spin density.



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Second, the decrease in *D* is largest when ^{3}**8** is substituted with one para-electron-withdrawing group and one para′-

Table 14. ESR Data of Substituted Diphenylcarbenes (8)[a,68,69]

p-Substituent X	*p*-Substituent Y	|*D*/*hc*| (cm^{-1})	|*E*/*hc*| (cm^{-1})
H	H	0.4088	0.0170
H	OMe	0.4043	0.0191
OMe	OMe	0.4022	0.0189
H	CN	0.3906	0.0193
CN	CN	0.3879	0.0178
H	NMe_2	0.3876	0.0168[b]
NMe_2	NMe_2	0.3748	0.0180[c]
H	NO_2	0.3778	0.0173[d]
NO_2	NO_2	0.3773	0.0177[b]
CN	NMe_2	0.3518	0.0163[d]
NO_2	NMe_2	0.3351	0.0164[b]

[a] All measurements were made in a methylcyclohenxane/isopentane (4:1) matrix at 77 K unless otherwise noted. [b] In tetrahydrofuran at 77 K. [c] In methylcyclohexane/tetrahydrofuran (4:1) at 77 K. [d] Neat at 77 K.

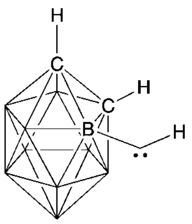
electron-donating group. The decrease in *D* in unsymmetrically disubstituted ^{3}**8** is always larger than that predicted taking the sum of the effects in the monosubstituted derivatives. These observations are explained in terms of merostabilization, a term first suggested by Katritzky[70] to describe increased delocalization in radicals.

3.1.5. Effect of π-Electron Acceptors

The triplet state of carbonyl carbene is predicted to assume coplanar geometries where the singly occupied p-orbitals of the triplet states are stabilized by conjugation with the carbonyl group. This is clearly seen in the significant decrease in the *D* values as methylene hydrogens are successively replaced with methoxycarbonyl groups, i.e., on going from **36** to **37** (Table 15). A similar appreciable decrease in the *D* values is also observed in **38**, where the phenylcarbene hydrogen is replaced with a benzoyl group.

3.1.6. Inductive Effect

ZFS parameters of carbenes with electropositive substituents are reported in Table 16, which also includes the data for carbenes with electronegative substituents. The *D* values of silylcarbenes are appreciably smaller than that of simple alkylcarbenes including methylene, although theory[33] predicts that spin densities on the carbenic carbon of silylcarbenes and alkylcarbene are very similar. 3-*o*-Carboranylcarbene (**40**), a boron-substituted carbene, has the *D* value of 0.657 cm^{-1}, which is however smaller than that (0.6860 cm^{-1}) of carboranylcarbene (**41**), where the carbene carbon is connected to a carbon in the ring.



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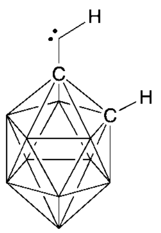

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Interestingly, carbenes with electronegative substituents such as a CF_3 group also show large *D* values of >0.7, which are larger even than that of the parent methylene.

Table 15. ESR Data of Carbonylcarbenes[a]

Carbene	Matrix/Temp(K)	|*D*/*hc*| (cm^{-1})	|*E*/*hc*| (cm^{-1})	*E*/*D*	ref
$MeOOC-\ddot{C}-H$ (**36**)	MCH/10 (*Z*) (*E*)	0.663 0.617	0.030 0.053	0.0452 0.0859	71
$MeOOC-\ddot{C}-COOMe$ (**37**)	MTHF/NS	0.604	0.031	0.0513	58
$Ph-\ddot{C}-COPh$ (**38**)	Neat/77 (*Z*)	0.3916	0.0158	0.1323	72

[a] MCH = methylcyclohexane.

Table 16. ESR Data of Carbenes with Electropositive Substituents[a]

Carbene	Matrix/Temp(K)	|*D*/*hc*| (cm^{-1})	|*E*/*hc*| (cm^{-1})	*E*/*D*	ref
$Me_3Si-\ddot{C}-H$	Ar/4	0.613	0.00145	0.002	73
$Me_3Si-\ddot{C}-SiMe_3$	Ar/4	0.614	0.00252	0.004	73
$Ph-\ddot{C}-P(O)(OMe)_2$ (**39**)	MTHF/77	0.4866	0.0206	0.0423	74
$CF_3-\ddot{C}-H$	PFDH/4	0.712	0.021	0.029	75
$CF_3-\ddot{C}-CF_3$	PFDH/4	0.7444	0.0437	0.059	75
3-*o*-Carboranylcarbene (**40**)	MCH/10	0.657	<0.0002	<0.0003	76
Carboranylcarbene (**41**)	MTHF/5	0.6860	0.0302	0.044	77

[a] PFDH = perfluorodimethylhexane.

3.2. Geometrical Isomerism

Triplet carbenes whose divalent carbon atom is substituted with an sp^2 hybridized carbon atom may exist in two rotameric forms, which are stable at very low temperatures.[61] In favorable cases, the ESR spectra of these carbenes exhibit two sets of triplet signals with sufficiently different ZFS parameters to detect and characterize the isomers.[77,78]

The magnitude of the ZFS parameters D is largely determined by the spin−spin dipolar interaction of the two electrons at the divalent carbon atom. In spite of the predominance of this one-center interaction, the spin density at atoms several bonds removed from the divalent carbon atom can also have a significant effect on the ZFS parameters.

This was first observed for the pairs of α- and β-naphthylcarbenes (see Table 12),[61] and then reports of geometric isomerism in triplet carbenes have appeared with increasing frequency, where two sets of triplet signals having similar but nonidentical ZFS parameters are observed (see Tables 11 and 15).[59] The spectra are assigned to the two conformations of the carbene in which the σ orbital at the divalent carbon and the aromatic moiety are coplanar. When the distribution of the spin in the p orbital is unsymmetric, the dipole spin−spin interaction of the π electron with the electron localized in the σ orbital is different for the two conformations. The assignment of the ZFS parameters to a specific conformer is made possible by a point spin model.[77,78]

3.3. Structural Relaxation

Geometrical changes upon warming the matrix are observed, especially for sterically hindered carbenes.[79] For instance, the E/D value obtained for di(α-naphthyl)carbene (α-**9a**) in 2-methyltetrahydrofuran (MTHF) at 15 K is 0.0109/0.3157. A new set of triplet signals with a smaller E/D value (0.0051/0.2609) ascribable to the linear configuration of ^{3}α-**9a** is observed at the expense of the original peaks when the matrix is annealed to ca. 80 K. This observation is interpreted in terms of steric strain in triplet carbenes.[62,80] Thus, when the carbene is formed in a rigid matrix at low temperature, it should have the bent geometry presumably dictated by that of the precursor. Even if the thermodynamically most stable geometry of the carbene is different from the nascent structure, the rigidity of the matrix prevents it from assuming its minimum energy geometry. However, when the matrix is softened on annealing, the carbene relaxes to a structure that is closer to linear, as evidenced by the substantial reducing in E. The small reductions in D are also consistent with this picture, as they indicate that the unpaired electrons are more efficiently delocalized in the relaxed geometry. A detailed analysis of the change in ZFS parameters indicates that an initial decrease of the parameters D is observed, which is followed by a decrease in the E value. It is suggested that molecular relaxation occurs initially by twisting the aromatic ring, which is followed by the opening of the central bond angle upon further heating.[80]

A similar dependence of the ZFS parameters on the rigidity of matrices is observed for many other sterically congested triplet carbenes and hence can be considered as an indication of such steric strain.

4. Strategy and Experimental Methods

Stabilization of triplet carbenes is more difficult to obtain than the singlet manifolds. Theoretical calculations show that even σ-donating substituents lacking p-interactions with the carbene center preferentially stabilize triplet carbine and the maximum ΔE_{ST} obtained by using such substituents is approximately 30 kcal/mol, which is to be compared with the ΔE_{ST} of over -80 kcal/mol estimated for singlet carbenes. ESR data clearly suggest that unpaired electrons are significantly delocalized into the π-systems of the substituents. However, the dimerization reactions of triplet methylene, phenylcarbene, and vinylcarbene are exothermic by 174.0, 150.0, and 145.7 kcal/mol, respectively. These numbers indicate that conjugation with π systems will not lead to thermodynamically stable triplet carbenes. Steric congestion about the resulting double bond is also insufficient. The (hypothetical) dimerization of di(*tert*-butyl)carbene was computed to be exothermic by 73.6 kcal/mol.[81] Hence, kinetic stabilization is the only promising strategy to obtain persistent triplet carbenes.

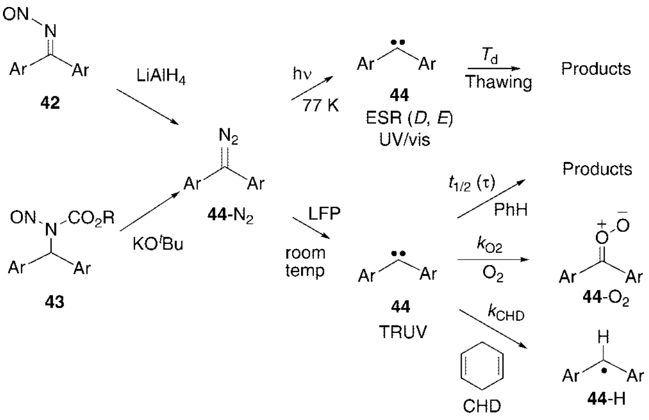


Figure 6. Procedures to generate and characterize a persistent triplet carbene.

Triplet carbenes are not easily stabilized to an extent that they are isolated, unlike the singlet counterparts. Therefore, spectroscopic techniques to observe and study transient species have been extensively used in this study. We will briefly describe here how we have generated and characterized those species.

Carbenes are conveniently generated from nitrogenous precursors such as diazo compounds[82] or diazirines[83] upon irradiation or thermolysis, which takes place very cleanly and efficiently. Therefore, it is possible to generate carbenes even at very low temperature in a rigid matrix once those precursors are prepared. This makes it very easy to assign and characterize the carbenes spectroscopically, which is a very important point, since we will then have to assign only triplet states of carbenes and to estimate their stability.

The first step of the research was to establish the method to prepare the precursors. We decided to use diazo compounds as precursors, as they have been much better investigated than other nitrogenous compounds. It was not easy, however, to prepare highly congested diazomethanes (**44**-N_2). Fortunately, the methods developed by Zimmerman and Paskovich,[12] that is, either reduction of *N*-nitrosoketimine (**42**) with $LiAlH_4$ or acyl cleavage of the corresponding *N*-alkyl-*N*-nitrosourethane (**43**) by potassium *tert*-butoxide, were found to be very useful to prepare the required diazo precursors (Figure 6).

Once desired diazomethanes were prepared, they were irradiated in rigid organic glasses, e.g., 2-methyltetrahydrofuran (MTHF), at 77 K. The photoproducts showed a fine-structure ESR line shape characteristic of randomly oriented triplet molecules, with a large *D* value attributable to one-center nπ spin−spin interaction at a divalent carbon of triplet carbenes (**44**). The ESR signals were analyzed in terms of zero-field splitting (ZFS) parameters, *D* and *E* values, which give us information on the molecular and electronic structure of triplet carbenes. The irradiation was then monitored by optical spectroscopy under identical conditions, which enables us to observe and characterize the UV−vis spectra of the triplet carbenes (**44**). Thermal stability of triplet carbenes can be estimated by measuring the temperature (T_d) at which the triplet signals and/or absorption completely disappeared when thawing the matrix containing triplet carbenes. Thus, the sample temperature is raised in 10 K increments to the desired temperature, allowed to stand for 1 min, and then recooled to the original temperature (usually at 77 K) to measure the signals and/or absorption. This procedure will minimize possible errors due to weakening of the signals originating from the Curie law and softening of the matrix.

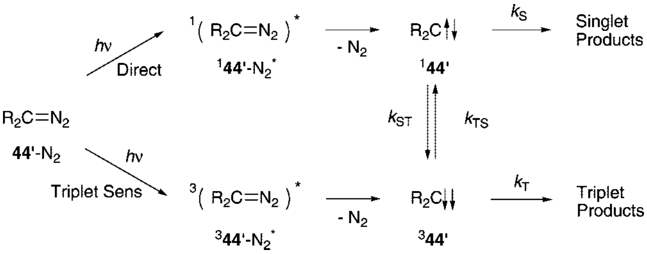
In order to estimate the stability of triplet carbenes (**44**) under ambient conditions, laser flash photolysis (LFP)[84] was carried out on the precursor diazomethanes (**44**-N_2) in solution at room temperature. The transient absorption bands formed upon the flash photolysis were recorded by a multichannel detector. These bands were assigned to the triplet carbenes (**44**) by comparison with those obtained in a matrix at low temperature. The kinetic information was then available by monitoring the decay of the transient absorption with an oscillographic tracer. When triplet carbenes decayed unimolecularly, lifetime (τ) can be determined. However, when the decay did not follow a single exponential, which is often the case, τ cannot be determined. Many persistent triplet carbenes decay by dimerization. In this case, second-order fitting of transient absorption data for triplet carbenes yields $2k_d/\varepsilon l$ values, where $2k_d$ is the dimerization reaction rate constant, ε the extinction coefficient at the wavelength of the monitoring band, and l the optical path length. A half-life ($t_{1/2}$) is also estimated from the decay curve as a rough measure of the stability.

The half-life ($t_{1/2}$) is just a measure of lifetime and cannot be regarded as a quantitative measure of reactivity. T_d cannot also be taken as such a scale unless the decay process is demonstrated to be essentially the same over the carbenes studied. In this respect, the rate constant of the triplet carbene with a typical triplet quencher can be employed as a more quantitative scale of the reactivity. It is well documented that carbenes with triplet ground states are readily trapped with oxygen or a good hydrogen donor such as 1,4-cyclohexadiene (CHD) to generate the corresponding carbonyl oxides (**44**-O_2)[85] or radicals (**44**-H),[84b] which are also detected by LFP techniques. Therefore, the rate constants of the trapping reactions, i.e., k_{O_2} or k_{CHD}, are obtained by plotting the observed pseudo-first-order rate constant of the formation of the carbonyl oxides or radicals as a function of [O_2] or [CHD]. These rate constants are used as a more quantitative scale to estimate the reactivities of the triplet carbenes.

5. Persistent Triplet Carbenes

In this chapter, we will summarize persistent triplet carbenes in three groups, that is, dialkyl-, aryl(alkyl)-, and diarylcarbenes. In each section, we will start by referring to triplet ground-state carbenes which are not "persistent", so that readers may recognize how far persistent triplet carbenes

Scheme 1



are stabilized. These "reactive" triplet carbenes, on the other hand, usually decay by reacting with solvents in which they are generated. Thus, the intrinsic lifetime is not obtained. The rate constants for the trapping reagents for the triplet state such as oxygen and 1,4-cyclohexadiene (CHD) can be used when available, as mentioned earlier. Otherwise, the stability may be judged by the reactivities (the rate of the reaction) toward an appropriate substrate. We will briefly describe the kinetic procedures of the reactions of carbenes.

Although carbenes have two electronic states of different stability, it is not always the ground-state multiplicity that is involved in the reaction. Take the reaction of carbenes generated by photolysis of diazo compounds (Scheme 1), for example. Direct irradiation of a diazo compound (**44′**-N_2) is believed to generate the carbene initially in singlet state (^{1}**44′**) via the singlet excited-state of the precursor (^{1}**44′**-N_2*). Triplet sensitization, on the other hand, is presumed to give the triplet carbene (^{3}**44′**) directly via the triplet excited-state of the diazo compound (^{3}**44′**-N_2*) without first forming its singlet state.

Generally speaking, the rate of reaction in the singlet state (k_S) is larger than that of the triplet (k_T). The rate of singlet to triplet (k_{ST}) intersystem-crossing and the reverse rate (k_{TS}), also important factors, are related to the S−T energy gaps (ΔG_{ST}). Thus, $k_{ST} > k_{TS}$ if ΔG_{ST} is large, but $k_{ST} \cong k_{TS}$ when ΔG_{ST} is less than ~3 kcal/mol. In the latter case, singlet−triplet equilibration is usually assumed (vide infra).

Of course, the rate constants (k_S and k_T) are dependent on the substrates, and hence, the above criteria should be taken only as a general guide. For instance, if one chooses a quencher that efficiently reacts with the triplet state, such as O_2, carbenes with triplet ground states react efficiently with the quencher to give products such as the corresponding ketones, regardless of ΔG_{ST} values.[85]

Rate measurement is straightforward if the carbenes can be monitored directly.[84] The decay of carbene absorption is mostly (pseudo) first-order, due to rearrangement and/or reaction with solvent. In the presence of a quencher, the decay is accelerated, and the rate constant k_q is obtained from a plot of k_{obs} versus [Q].

$$k_{obs} = k_0 + k_q[Q] \qquad (7)$$

Spectroscopically invisible carbenes can be monitored by the ylide method.[86] Here, the carbene reacts with heteroatom compounds (Y:) such as amines and ketones to form a ylide which usually exhibits a strong and stable absorption band in the visible regions. This process occurs competitively with all other routes of decay. Pyridine (py) is the most frequently used compound, and the term pyridine probe is used. In the presence of an additional quencher (Q), the observed pseudo-first-order rate constant for ylide formation is given by eq 8. A plot of k_{obs} vs [Q] at constant [Y:] will provide k_q.

$$k_{obs} = k_0 + k_y[Y:] + k_q[Q] \qquad (8)$$

If the growth of ylide absorption is too rapid to be monitored, relative rates can still be obtained by a Stern−Volmer approach (eq 9). The yield of ylide, measured as the change in optical density (ΔOD), decreases in the presence of a carbene quencher. By plotting 1/ΔOD as a function of [Q], the ratio k_q/k_{py}[Y] can be derived. This ratio corresponds to the $k_q\tau$ term of the Stern−Volmer equation. Here, τ is the lifetime of the carbene in the absence of Q. By means of $k_q\tau$, the reactivity of an individual carbene toward Q can be established, but different carbenes cannot be compared.

$$\frac{\Delta OD_0}{\Delta OD} = 1 + \frac{k_q[Q]}{k_y[Y:]} = 1 + k_q\tau[Q] \qquad (9)$$

As mentioned above, even if carbenes have a triplet ground state, the reactions take place at the singlet state if the energy gap between the single and the triplet state is a few kilocalories per mole, since the reaction rates of the corresponding singlet states with many general reagents are usually much larger than that of the triplet. For instance, the optical absorption spectrum of triplet diphenylcarbene (^{3}DPC, ^{3}**8a**) is quenched by methanol and yields the product of O−H insertion, which is believed to be formed from the singlet state. The quenching rate constant (k_T) is determined to be 6.8 × 10^6 M^{-1} s^{-1} in benzene.[87]

Pre-equilibrium[88] and surface crossing[89] mechanisms have been proposed for the relatively slow reaction of ^{3}DPC with O−H bonds. Actually, any process leading to a singlet product from a triplet must involve surface crossing, and it is the timing of spin inversion and chemical events that distinguishes these two mechanisms. According to the pre-equilibrium mechanism, triplet to singlet interconversion occurs prior to O−H insertion of the singlet carbene. On the other hand, in the surface crossing mechanism, triplet carbene can react directly with alcohol, with surface crossing occurring after the carbene has begun to interact with the O−H bond.

According to Scheme 1, the observed rate constant (k_{obs}) for the reaction of the triplet carbene with methanol is

$$k_{obs} = \frac{k_{TS}k_S}{k_{ST} + k_S[CH_3OH]} \qquad (10)$$

where K is the equilibrium constant, which is simply the ratio of the singlet equilibrium population to that of the triplet. At relatively low concentration of methanol, with $k_{ST} > k_S[CH_3OH]$, k_{obs} reduces to

$$k_{obs} = k_S K,\ \text{where } K = \frac{k_{TS}}{k_{ST}} = \frac{[S]}{[T]} \qquad (11)$$

Because $k_S < k_{diff}$, measurement of k_{obs} immediately yields the lower limit of K, from which the maximum free energy separation between the singlet and the triplet (ΔG_{ST}) can be estimated.[90]

In some cases, a species derived from the triplet carbene is detected and used to obtain kinetic data.[84b] For instance, radicals are formed in a hydrogen-donating solvent as a result of hydrogen abstraction and carbonyl oxides are formed from reaction with oxygen in an aerated solvent. In this case, the observed rate constant (k_{obs}) of a triplet carbene reaction obtained by monitoring the secondary species is the sum of all decay rate constants of the triplet, which may include decay via an associated but invisible singlet with which the triplet is in rapid equilibrium.

$$k_{obs} = k_T + Kk_S \qquad (12)$$

Therefore, the reactivities obtained for triplet carbenes toward substrates which react with the singlet more efficiently than the triplet are those for the spin-equilibrated mixtures.

5.1. Dialkylcarbenes

Before describing dialkylcarbenes, we will summarize the nature of the parent carbene. Triplet methylene (H−C−H) was detected and characterized by ESR in a noble gas matrix at extremely low temperature (4 K).[55] The absolute reactivity of $^3CH_2$ appears to be considerably lower than that of $^1CH_2$. In the gas phase, the bimolecular rate constant of CH_2 quenching by ethylene is 9 × 10^{10} M^{-1} s^{-1} for $^1CH_2$, while it is only 4 × 10^5 M^{-1} s^{-1} for $^3CH_2$.[91a] Extrapolation of the gas-phase quenching data of $^1CH_2$ by He to the solution phase leads to the expectation that the lifetime of $^1CH_2$ will be on the order of picoseconds in the condensed phase.[91b]

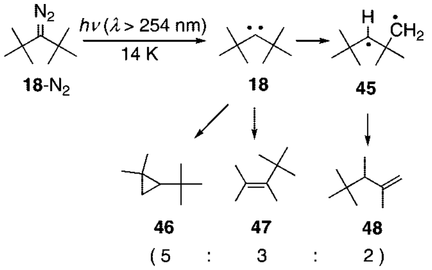
Singlet methylene is trapped by acetonitrile to give a nitrile ylide, which absorbs at 280 nm. Since it was not possible to resolve the growth of the ylide, a Stern−Volmer analysis was used to estimate the relative reactivities of singlet methylene toward various quenchers (alcohols, chloroform, benzene, alkenes, and ethers), which indicates that a large numbers of quenchers all have nearly the same value of $k_q\tau$. Since τ is constant in neat acetonitrile, the data support the epithet that methylene is the "most indiscriminating reagent in organic chemistry".[92,93]

Turro et al. discovered that direct photolysis of diazomethane in 2-pentene or chloroform afforded the product distribution consistent with $^1CH_2$ chemistry (stereospecific cyclopropanation and C−H insertion or C−Cl abstraction), while triplet-sensitized photolysis gave a mixture consistent with $^3CH_2$ chemistry (nonstereospecific cyclopropanation, or C−H abstraction). The result is explained as indicating that intersystem crossing from $^1CH_2$ to $^3CH_2$ is irreversible and slow relative to capture of singlet methylene. The rate (k_{ST}) is estimated to be 8 × 10^8 s^{-1}, which is substantially lower than the rate constant of intersystem crossing of DPC (k_{isc} = 1.0 × 10^{10} s^{-1}). This is reasonable, since ΔG_{ST} in methylene (9 kcal/mol) is larger than that in DPC and since methylene possessing only one carbon and two hydrogen atoms cannot benefit from the rich vibrational density of states present in the phenyl rings of DPC to facilitate intersystem crossing.[92,93]

Since alkyl groups usually the stabilize singlet state more than the triplet, most dialkylcarbene have singlet ground states. Also, due to their ability to undergo rapid intramolecular rearrangements, there appear to be very limited data concerning the interception and detection of dialkylcarbenes.[94]

ESR as well as IR and UV−vis spectroscopic studies of triplet ground-state methylcarbene (Me−C−H) failed to provide experimental evidence of its presence.[94] Attempts to detect the singlet state of methylcarbene in solution at room temperature by using a pyridine probe method were unsuccessful, which predicted a possible calculated lifetime of less than 500 ps. Thus, it is suggested that the intersystem crossing from the singlet methylcarbene to the triplet does not compete with the 1,2-H shift.[95] The barrier to the 1,2-H shift is calculated by the [TZ2P(f,d) CCSD(T)] method to

Scheme 2



be 1.2 kcal/mol.[96] The rates of H-shift might be enhanced by quantum mechanical tunneling,[97] and hence, the experimental barriers are estimated to be even lower, especially at low temperature.

These observations clearly show that it will be extremely difficult to detect the triplet state of a simple alkylcarbene. In other words, dialkylcarbenes can only be intercepted or detected or both by slowing down the rearrangement rate. For instance, dialkylcarbenes that lead to highly strained products as a result of rearrangement can be intercepted and detected. However, they are mostly the ground-state singlet.[86a,98] In this respect, only dialkylcarbenes with bulky substituents are expected to have a triplet ground-state that can be detected and characterized.

5.1.1. Di(tert-butyl)carbene

In accord with this expectation, the first triplet dialkylcarbene directly observed by ESR was di(*tert*-butyl)carbene (**18**) (Scheme 2).[56] Irradiation of di(*tert*-butyl)diazomethane (**18**-N_2) in a degassed MTHF glass at 20 K produced the characteristic ESR spectrum of a triplet. The ZFS parameters ($D/hc = 0.689$ cm^{-1}, $E/hc = 0.039$ cm^{-1}) fully support the assignment of the triplet spectrum as ^{3}**18**. The ESR spectrum is stable even at temperatures of 70 K (Table 10). The ZFS parameters indicate that this carbene is not linear, and a bond angle about the central carbon is predicted to be ~143° based on the E/D ratio. Like other dialkylcarbenes, **18** also appeared to decay exclusively by intramolecular rearrangement. Irradiation (254 nm) of **18**-N_2 in an Ar matrix at 14 K, followed by collection and separation, allowed the separation of three major products, 1,1-dimethyl-2-*tert*-butylcyclopropane (**46**), 2,3,4,4-tetramethyl-2-pentene (**47**), and 2,3,4,4-tetramethyl-1-pentene (**48**) in a 5:3:2 ratio.[56] The azine was not formed under these conditions. Products **46** and **47** represent classical reactivity of a carbene such as **18**. The origin of **48** is not obvious. Diradical **45** presumably generated by hydrogen atom transfer is proposed as an intermediate.[56]

5.1.2. Di(1-adamantyl)carbene

Triplet di(1-adamantyl)carbene (**19**) was the second dialkylcarbene that was also found to be stable enough to allow direct ESR observation (Scheme 3).[57] Irradiation of diadamantyldiazomethane (**19**-N_2) labeled with ^{13}C at the central position in an ethanol matrix at 14 K gave a persistent triplet signal. From the hyperfine components, the bond angle about the central carbon was estimated to be ~152°. Triplet signals of di(1-adamantyl)carbene (**19**) were long-lived in ethanol matrices between 4 and 75 K (Table 10).

In sharp contrast with **18**, **19** showed substantial intermolecular triplet reactivity, even in solution at 25 °C. Thus, LFP of an aerated solution of **19**-N_2 produced the transient absorption band at 307 nm attributable to carbonyl oxide **19**-O_2. The transient is formed after the flash with a rise time of 200 ns. The lifetime is consistent with the expected, nearly diffusion controlled reaction of a triplet carbene with the low concentration of oxygen present in solution.

Carbene **19** also reacts with the singlet carbene quencher methanol to give O−H insertion product **49**. Since **19** has a triplet ground state, this reaction most probably occurs from spin equilibrium. The rate constant of this reaction was determined from the slope of the observed rate constant of carbonyl oxide formation versus [CH_3OH] to be $(3.16 \pm 0.81) \times 10^7$ M^{-1} s^{-1}, which is about the same as that of DPC (Table 17).[99]

Irradiation of **19**-N_2 in hexane at room temperature gave di(adamantyl)methane (**19**-H_2) as a main product.[100] Similar irradiation of **19**-N_2 in (*Z*)-2-butene also led to **19**-H_2 as the major product along with small amounts of 1:1 adducts **50a,b** produced from **19** and (*Z*)-2-butene (Scheme 3). **19**-H_2 is surely a product of triplet carbene. Thus, **19** becomes the first dialkylcarbene to react as a triplet in solution.

Intramolecular migration reaction of **19** was observed only when it was generated at high temperature in the gas phase. Flash vacuum pyrolysis (420 °C) of **19**-N_2 with rapid trapping at −196 °C afforded 4-(1-adamantyl)homoadamant-3-ene (**51**) in >85% yield (Scheme 3). Not surprinsingly, **51** is thermally stable; heating of **51** in benzene-d_6 results in no change over 24 h at 185 °C.[101]

The 1-adamantyl group is not as prone to rearrangement as is the *tert*-butyl group.

5.1.3. Di(9-triptycyl)carbene

The triptycyl (Trp) group is very interesting in this respect because it is not prone to rearrangement and also contains a repulsive nonbonded interaction when two Trps are attached on one carbon.[102] Precursor diazomethane, di(9-triptycyl-)diazomethane (**20**-N_2), cannot be prepared by any traditional procedures employed to prepare diazomethanes, since the central carbon atom surrounded by two Trp groups is too hindered to be attacked by any reagents. The only plausible approach to **20**-N_2 is addition of 2 equiv of benzyne to di(9-anthryl)diazomethane (**10a**-N_2) (Scheme 4. The reaction is realized only by using (phenyl)[*o*-(trimethylsilyl)phenyl]-iodonium triflate,[103] which can generate benzyne under very mild and neutral conditions.[39]

Irradiation of **20**-N_2 in a degassed MTHF glass at 77 K afforded di(9-triptycyl)carbene (**20**) ($D/hc = 0.720$ cm^{-1} and $E/hc = 0.0263$ cm^{-1}) (Table 10).[39] A comparison of the values with those reported for other sterically congested hydrocarbon dialkylcarbenes suggests that **20** has the largest D and the smallest E values. The thermal stability of **20** is remarkable. When the irradiation of **20**-N_2 was monitored by UV−vis spectroscopy, a weak absorption band around 426 nm due to **20** was observed.[39] When the matrix containing **20** was gradually warmed, the band did not disappear appreciably until 120 K, and it then disappeared completely at around 150 K. LFP of **20**-N_2 in degassed benzene at room temperature produced **20**, showing an apparent maximum at 430 nm. The transient band decayed in a second-order kinetics ($2k/\varepsilon l = 5.8 \times 10^5$ s^{-1}), and the rough first half-life of **20** is estimated to be 40 μs. Triplet carbene was trapped by oxygen to the corresponding ketone oxide. The quenching rate constant (k_{O_2}) of **20** was determined to be 1.6×10^9 M^{-1} s^{-1} (Table 17).[39]

Scheme 3

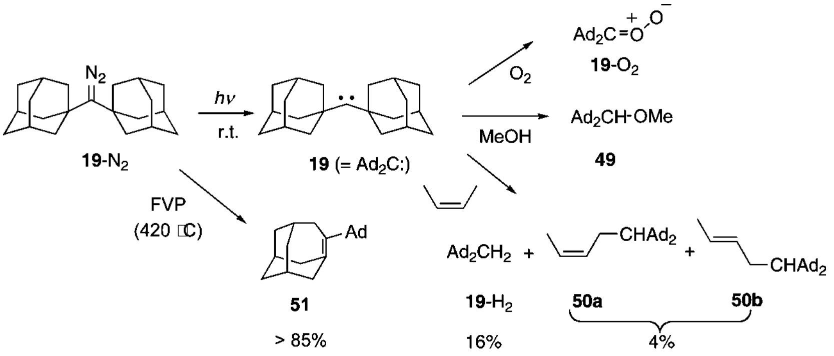
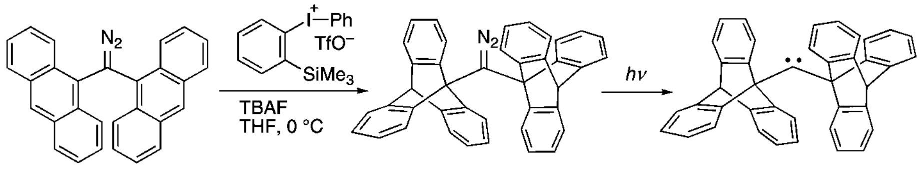


Table 17. ESR, UV−Vis Spectroscopic, and Kinetic Data of Dialkylcarbenes

Carbene	Matrix/Temp (K)	$\lvert D/hc \rvert$ (cm^{-1})	$\lvert E/hc \rvert$ (cm^{-1})	E/D	λ_{max} (nm)	T_d (K)	$2k/\varepsilon l$ (s^{-1})	$t_{1/2}$ (μs)	k_{O2} (M^{-1}s^{-1})	k_{MeOH} (M^{-1}s^{-1})
18	MTHF/20-70	0.689	0.039	0.057	–	–	–	–	–	–
19	EtOH/4-75	0.6823	0.038	0.056	–	–	–	–	–	$(3.16 \pm 0.81) \times 10^7$
20	MTHF/77-130	0.720	0.0263	0.0365	426	150	5.8×10^5	40	1.6×10^9	–

Scheme 4



10a-N$_2$ **20**-N$_2$ **20**

The S−T gap usually decreases as the alkyl groups are introduced on methylene; the S−T gap decreases from 2 to −2 kcal/mol in going from Me−C−H to Me−C−Me. However, when bulky groups are introduced, the steric repulsion between the substituents widens the C−C−C bond angle and influences the S−T splitting, increasing the p character of the doubly occupied sp^2 orbital and destabilizing the singlet. For instance, the S−T gap increases from 2 to 5 kcal/mol on going from ^{t}Bu−C−H to ^{t}Bu−C−^{t}Bu. In the case of the triptycyl group, a hyperconjugative effect is considered to be less important, as all the C−C bonds are tightly tied back to phenyl rings. Moreover, a repulsive nonbonding interaction between the Trp groups in **20** must result in a significant widening of the central C−C−C bond angle (α). This will result in a larger gap in α_{ST} as well as G_{ST} than that for **18** and **19**.

5.2. Arylcarbenes

5.2.1. Phenylcarbenes

The ZFS parameters of phenylcarbene (**5a**) indicate spin delocalization within the phenyl ring. The fluorescence of **5a** in a 3-methylpentane (MP) matrix was measured at 77 K in a laser-induced fluorescence study, which showed that **5a** is stable in organic matrices but only on a time scale of minutes even under these conditions.[104]

The UV spectrum of **5a** in an Ar matrix exhibits a long-wavelength band with a prominent maximum at 430 nm,[105] but LFP study of the precursor diazomethane (**5a**-N$_2$) showed that the spectrum falls underneath that of **5a**-N$_2$. However, ^{1}**5a** reacts with pyridine to produce an easily detectable ylide. The lifetime of the spin-equilibrated mixture of **5a** in pentane and CF$_2$ClCFCl$_2$ (Freon-113) and the ΔG_{ST} value were determined by the pyridine-ylide method[106] and are listed in Table 18, which also includes the analogous data obtained for other monophenylcarbene derivatives. These data indicate that the stability (as judged from reactivities of the spin-equilibrated mixture) of monophenylcarbenes is little affected by ortho methyl[107] and fluoro groups.[106] Only the *o*,*o*-dimethyl group increases the lifetime by at least ten times.[107] However, note that the main decay pathway of mesitylcarbene (**5c**) in pentane is still insertion into the C−H bond of pentane.

Table 18. Kinetic Data of Monophenylcarbenes[106−109]

Carbene	k_{py} (M^{-1}s^{-1})	τ(ns)	ΔG_{ST}(kcal/mol)^a	Solvent	ref
5a	$(1.9 \pm 0.3) \times 10^7$	205	2.3	CF$_2$ClCFCl$_2$	106
	9.3×10^6	74		Pentane	
5b		70		Pentane	107
5c	1.35×10^7	580	2.6	Pentane	107
52	5.1×10^6	500	3.1	CF$_2$ClCFCl$_2$	106
		22		MeCN	
53	4×10^8	190	0.5-1.5	CF$_2$ClCFCl$_2$	108
		2		MeCN	
54	2×10^7	833	2.3	Heptane	109

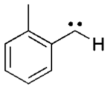
[a] Determined from $k_{py} = {}^1k_{py}K$, where $^1k_{py}$ is assumed to be 1×10^9 M^{-1} s^{-1}.

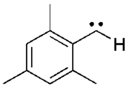
Phenyl(methyl)carbene (**54**) decays mainly by 1,2-H shift, like methylcarbene, to form styrene. Crabene **54** can also be trapped by pyridine, which enables one to measure the rate constant of this process to be 6 × 10^6 s^{-1} in heptane.[109] Since the barriers to 1,2-shift of fluorine are large,[110] the

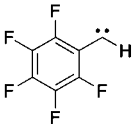
Table 19. Kinetic Data of Phenyl(methoxycarbonyl)carbene (11)[111]

Quencher	k_q ($M^{-1}s^{-1}$)
$CF_2ClCFCl_2$	(461 ns)
MeOH	2.7×10^8
Cyclohexane	(< 10 ns)
Oxygen	8.6×10^8

migration process is suppressed when a methyl group is replaced with trifluoromethyl, but the stability of *p*-tolyl(trifluoromethyl)carbene (**53**) seems to decrease. This is partly because this carbene also decays by reacting with solvents.


5b


5c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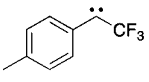
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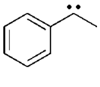
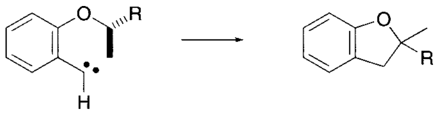

54

Phenyl(methoxycarbonyl)carbene (**11**) showed transient absorption bands at 240−400 nm with a maximum below 270 nm. The lifetime in Freon-113 is 461 ns, which is appreciably longer than that for the parent phenylcarbene (200 ns). The bimolecular rate constants of the reaction with typical carbene quenchers are measured (Table 19). These kinetic data indicate that the stability of this carbene is regarded as an intermediate between diphenylcarbene and fluorenylidene.[110]

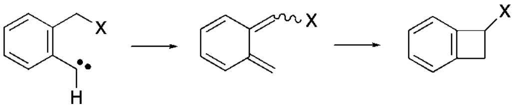
In the photochemical decomposition of nitrogeneous precursors such as diazo compounds to carbenes, the chemistry resulting from many carbenes has been shown to be accompanied by a significant amount of precursor chemistry. This is especially so when intramolecular processes are involved. For instance, the photochemistry of aryl(alkyl)diazomethanes is complicated by the involvement of rearrangement in the excited states (RIES).[86,109] This has been demonstrated spectroscopically by using the pyridine probe method. When a series of phenyl(alkyl)diazomethanes having C−H bonds adjacent to the diazo group were irradiated above the saturating concentration of pyridine, the optical yield of pyridine ylides increases with increasing bond dissociation energies of the C−H bond adjacent to the diazo group. A very large optical yield of ylide is obtained with phenyl(*tert*-butyl)carbene, a system in which there is no C−H bond adjacent to the diazo moiety. 1,2-Carbon migration is also important in the excited-state chemistry of phenyl(cycloalkyl)diazo compounds.

When alkyl groups are introduced at the ortho position, phenylcarbenes are trapped by the C−H bonds to form benzocycloalkanes. For these reactions, the ring size of the cyclic transition state appears to be a major factor in determining the multiplicity involved in the reaction. For example, the reaction of optically active (2-ethoxyphenyl)carbene (**55**) affords a five-membered product (**56**) almost exclusively, but with the significant loss of enantiomeric purity (Scheme 5).[112]

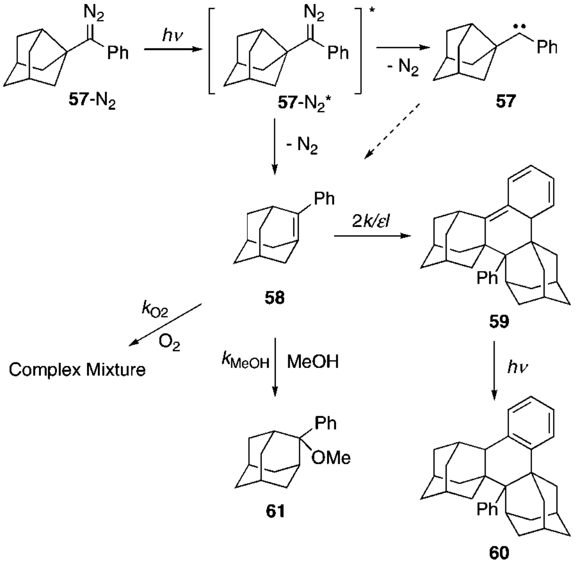
Scheme 5


55 **56** (~30% ee)

Scheme 6



Scheme 7



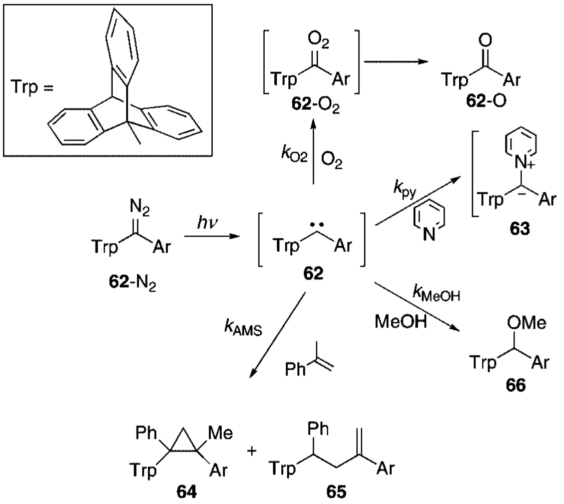
This result is explained in terms of hydrogen abstraction by a triplet followed by recombination of the radical pairs, rather than a concerted insertion from the singlet. Presumably, the concerted insertion reaction of the singlet involves the p orbital as well as the σ orbital of the carbene. For the interaction of both orbitals with δ-C−H bonds, rotation must occur about the bond connecting the divalent carbon to the benzene ring, with concomitant loss of benzylic stabilization and deformation of bond angles. In contrast, transfer of the δ-hydrogen to the half-filled, in-plane σ orbital of the triplet carbene can proceed by way of a favorable six-membered transition state in which the benzylic resonance is not disturbed.[112]

When various CH_2X (X = H, Me, CMe_3, $SiMe_3$, CF_3, and F) groups have been attached to the ortho position of phenylcarbene, benzocyclobutenes are formed. The effects of sensitization and of solvent polarity suggest that benzocyclobutenes arise from singlet arylcarbenes. Reaction is interpreted in terms of 1,4-hydrogen transfer followed by cyclization of an *o*-quinodimethane (Scheme 6).[113]

Like the dialkylcarbene case, a phenyl(alkyl)carbene having a bulky alkyl group that is not prone to migration is expected to be persistent.

5.2.1.1. Phenyl(3-noradamantyl)carbene. Since di(1-adamantly)carbene (**19**) is found to undergo migration only at very high temperature, the 3-noradamantyl group appears to be a very attractive kinetic protector. Attempts to generate phenyl(3-noradamantyl)carbene (**57**) were made (Scheme 7). LFP of 3-noradamantyl(phenyl)diazomethane (**57**-N_2) in degassed benzene at room temperature generated a fairly strong absorption band at 434 nm. This band decayed with a second-order kinetics ($2k/\varepsilon l = 1.5 \times 10^2$ s^{-1}) with a half-life of 5.6 ms to generate a new species showing an absorption band at 323 nm, which is too long to be monitored. The transient band at 434 nm was quenched by methanol ($k_{MeOH} = 8.7 \times 10$ M^{-1} s^{-1}) and oxygen ($k_{O_2} = 7.0 \times 10^6$ M^{-1} s^{-1}).[114] Those rate constants are however too small for triplet carbenes.

Scheme 8

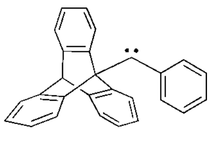


Product analysis showed that the structure of the dimer is not a dimer of the carbene, but a dimer (**60**) of 2-phenyladamantene (**58**), which is formed by dimerization in [4 + 2] fashion including the aromatic ring to form the initial dimer (**59**), followed by hydrogen migration. Also, the main product obtained after photolysis of methanol is 2-phenyl-2-methoxyadamantane (**61**), and phenyl(noradamantyl) methyl ether, expected to be formed from carbene **57**, was also detected but in a minor amount.

These observations clearly indicate that the transient band at 434 nm is not ascribable to the carbene but is most likely to be adamantene **58**, which is likely to be formed not by way of carbene. Thus, the excited-state of **57**-N_2 decays almost exclusively by 1,2-C migration with concerted loss of nitrogen to form adamantene directly.

5.2.1.2. Phenyl(triptycyl)carbene. The triptycyl (Trp) group is also expected to act as a kinetic protector. Phenyl(triptycyl)carbene (**62a**) was generated by irradiation of the corresponding diazo compound (**62a**-N_2) in MTHF glass at 77 K and characterized by ESR (Scheme 8). The *D* value of **62a** is essentially the same as that of phenylcarbene, but a slight increase in the *E* value (and hence *E*/*D* value) upon replacement of hydrogen with a Trp group is rather unexpected, since one might expect a larger bond angle for **62a** than for **5a**. This is interpreted as indicating that the three phenyl rings on the tertiary carbon atom in the Trp group are held back tightly, allowing little steric interference with the phenyl ring on the carbenic carbon.

LFP of **62a**-N_2 in degassed benzene at 20 °C afforded the transient absorption bands at 314 nm ascribable to triplet **62a**. The transient band decayed in first-order ($k = 1.2 \times 10^3$ s^{-1}), and the lifetime is estimated to be 840 μs. Thus, the lifetime increase of phenylcarbene by addition of a Trp group is some 3 to 4 orders of magnitude.[115]



62a

Although analysis of the spent solution indicates the presence of rather complex mixtures, no possible products arising from tribenzobicyclo[3.2.2]nonatetraene or -triene as a result of rearrangement in **62a** were detected. Thus, the Trp group plays its role as a kinetic protector.

Table 20. ESR and UV−Vis Spectroscopic Data of Phenyl(triptycyl)carbene[115]

Carbene	Matrix/Temp (K)	$\lvert D/hc \rvert$ (cm^{-1})	$\lvert E/hc \rvert$ (cm^{-1})	*E*/*D*	λ_{max} (nm)	T_d (K)
62a	MTHF/77	0.510	0.0288	0.0564	314	120

Table 21. Kinetic Data of Phenyl(triptycyl)carbene[115]

Carbene	*k* (s^{-1})	τ (μs)	k_{O2} (M^{-1}s^{-1})	Kk_{py} (M^{-1}s^{-1})	Kk_{MeOH} (M^{-1}s^{-1})	k_{AMS} (M^{-1}s^{-1})
62a	1.2×10^3	840	1.6×10^9	1×10^4	3.2×10^5	3.3×10^3

Table 22. Kinetic Data of Naphthylcarbenes 6a

Carbene	Quencher	k_q (M^{-1}s^{-1})	ref
α-**6a**	MeOH	$(1.6 \pm 0.2) \times 10^7$	116
	Cyclohexane	$(8.93 \pm 0.11) \times 10^5$	116
	Oxygen	$(3.5 \pm 0.7) \times 10^9$	117
β-**6a**	MeOH	$(7.25 \pm 0.5) \times 10^6$	117
	Cyclohexane	$(1.48 \pm 0.04) \times 10^5$	117
	Oxygen	1.5×10^9	116

A remarkable thermal stability of ^{3}**62a** is noted in monitoring the spectral changes as a function of temperature under matrix conditions. No appreciable changes were observed for the UV−vis spectrum of ^{3}**62a** in MTHF up to 115 K, and significant decay began only at 120 K (Table 20). It should be noted that triplet monophenylcarbene (^{3}**5a**) is not observable in MTHF at 77 K and that triplet DPC (^{3}**8a**) can be observed in MTHF at 77 K but its absorption starts to disappear even below 90 K.

Marked reduction in the reactivity by introduction of a Trp group is also seen in the reaction with typical carbene quenchers, such as oxygen, methanol, and α-methylstyrene (Table 21). From the rate constant with methanol, ΔG_{ST} is estimated to be 5.7 kcal/mol, which is larger than that (3.2−3.9 kcal/mol) estimated for diphenylcarbene.[113]

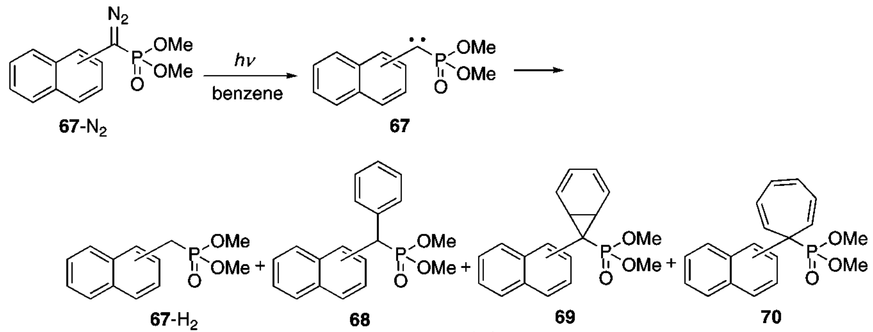
5.2.2. Naphthylcarbenes

Since naphthylcarbenes (NC, **6a**) are more easily detected by time-resolved UV−vis spectroscopy, the rate constants of the reactions with typical substrates such as methanol, cyclohexane, and oxygen are obtained (Table 22).

A comparison of the data available on the reaction with hydrocarbons shows that α-NC exhibits the lower reactivity and the higher singlet character and possesses a smaller singlet−triplet energy gap than β-NC. Two key molecular structure differences are responsible for the reactivity. First, the α-position of the naphthyl moiety has the largest HOMO orbital coefficient (Hückel, 0.425 vs 0.263). This will lead to greater stabilization of the carbene center π−p overlap, thus making the carbene center less electrophilic. A second factor which should be taken into account is the interaction between the carbene center and the peri-hydrogen. Differences in the reaction pattern and the reactivities are seen in the reaction of naphthyl(phosphonyl)carbenes **67**.

Naphthyl(phosphonyl)carbenes **67** are generated and investigated both by product analysis and by spectroscopic means.[118] In the reaction with (*Z*)-2-butene, α-**67** produced

Scheme 9



Carbene	67-H₂	68	69	70
	yield(%)			
α-**67**	0.9	96.6	0	0
β-**67**	2.4	0	52.6	23.5

Table 23. UV−Vis Spectra and Lifetimes of Naphthyl(phosphonyl)carbenes 67[118]

Carbene	λ_{max}[a] (nm)	τ[b] (μs)
α-**67**	375, 490, 530, 570	20 (3.0)
β-**67**	370, 510, 543, 590	37 (2.0)

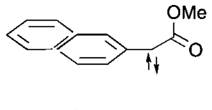
[a] In MTHF at 77 K. [b] In degassed benzene at room temperature. The values in the parentheses are in aerated benzene.

only stereospecific cyclopropanation products, while *β*-**67** also afforded the cyclopropane, but alkene product as a result of the C−H insertion of the methyl group was also formed. The formation of the latter can be explained as indicating either that the *β*-isomer is more electrophilic and hence attacks even the C−H bonds of the alkene or that, because of the higher singlet−triplet energy gap, the singlet state of the *β*-isomer decays to the triplet, which reacts by abstracting allylic hydrogens from the alkene before it undergoes intersystem crossing to the singlet.[118]

Carbenes **67** also added to benzene to give norcaradiene **69** and cycloheptatriene **70**. A product derived formally from an insertion into the C−H bonds of benzene was also formed (Scheme 9). This product (**68**) is derived from the singlet rather than the triplet, since the kinetic isotope effect (k_H/k_D) is very small. Again, the product ratios are very different between the two isomers. The α-isomer produced the C−H insertion product (**68**) as major product, while the *β*-isomer gave the diene (**69**) and the triene compounds (**70**). This difference is also explained in terms of electronic and steric factors.

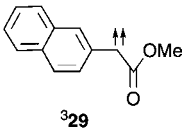
Triplet carbenes **67** were observed by UV−vis spectroscopy in MTHF glass at 77 K and by LFP in degassed benzene at room temperature. Surprisingly, there is no significant difference in the lifetime of the triplet carbene between the α- and *β*-isomers of the ester carbenes **67** in benzene (Table 23). These results indicate that most of the reactions occur with the singlet state carbene, but not the triplet state.[118]

β-Naphthyl(methoxycarbonyl)carbene (**29**) attracts special attention, since the singlet and triplet states of this carbene show very different IR spectra (1590, 1625, 1640 cm^{-1} for ^{1}**29** and 1660 cm^{-1} for ^{3}**29**) and, more importantly, both states are observable. Thus, photolysis of precursor diazomethane in an argon matrix at 12 K at 450 nm yielded primarily the triplet ground-state of **29**. Bleaching of the weak visible band of ^{3}**29** generated singlet **29**. The triplet state was recovered either upon irradiation of the singlet with 515 nm light or upon leaving at 12 K in the dark.



^{1}**29**

(1590, 1625, 1640 cm^{-1})



^{3}**29**

(1660 cm^{-1})

In the singlet state, the methoxycarbonyl group assumes a conformation perpendicular to the naphthylcarbene plane, while, in the triplet, the methoxycarbonyl group is in the same plane. For this reason, there is a barrier between the two states and hence both of them are observable under these conditions.[119]

The two states are monitored in solution by using time-resolved IR techniques.[120] This allows a direct experimental estimate of the (solvent-dependent) singlet−triplet energy gap of **29** in solution at ambient temperature as only 0.2 ± 0.1 kcal/mol.[47] Also, the measurements of the rate constant of the reaction with methanol and 2,3-dimethyl-2-butene of both states are separately made, which demonstrates that the rate constants observed for both states are the same within experimental error (Table 24), supporting the fast singlet−triplet spin equilibrium mechanism.[120] The rate of intersystem crossing of **29** is estimated to be >10^{11} s^{-1}, which is 1 order of magnitude greater than that of most diarylcarbenes.[121]

The lifetime (monitored at either 1650 or 1584 cm^{-1}) is 830 ns in argon saturated Freon-113 solution but reduces to 120 ns when oxygen is saturated.[120]

5.2.2.1. Naphthyl(triptycyl)carbenes. The only persistent triplet naphthyl(alkyl)carbene thus far reported is naphthyl(triptycyl)carbene **62b**, which showed stable ESR signals in MTHF at 77 K (Table 25). Very small changes in the *D* values and a rather slight increase in the *E* values are noted compared to the parent naphthylcarbene (**6a**) not only in *β*- but also in α-naphthylcarbene systems. This observation suggests that a naphthyl group is located in the cavity of a Trp group in order to avoid interaction between the peri hydrogens, although the peri hydrogens on the α-naphthyl group can potentially interact with the peri hydrogens on the Trp group.

In the case of parent systems, a mixture of two rotational isomers, *Z* and *E*, is usually distinguished by ESR spectroscopy.[61] The ESR spectra of the *β*-isomer (*β*-**62b**) also consisted of two sets of triplet peaks of similar intensities, assignable to *Z* and *E* rotamers. However, only one set of triplet signals was observed in the ESR spectra of α-**62b** under the same conditions. It has been shown that the *Z* isomer of α-**6a** is higher in energy than the *E* isomer due to steric interaction of the peri hydrogen with the hydrogen on

Table 24. Kinetic Data of *β*-Naphthyl(methoxycarbonyl)carbene (29)[120]

Quencher	k_q ($M^{-1}s^{-1}$)
MeOH	$(1.0 \pm 0.1) \times 10^8$ (1650 cm^{-1}) $(9.2 \pm 0.9) \times 10^7$ (1584 cm^{-1})
2,3-Dimethyl-2-butene	$(4.2 \pm 0.4) \times 10^7$ (1650 cm^{-1}) $(4.9 \pm 0.5) \times 10^7$ (1584 cm^{-1})

Table 25. ESR and UV−Vis Spectroscopic Data of Naphthyl(triptycyl)carbenes 62b[115]

Carbene	Matrix/Temp (K)		$\lvert D/hc \rvert$ (cm^{-1})	$\lvert E/hc \rvert$ (cm^{-1})	E/D	λ_{max} (nm)
α-**62b**	MTHF/77		0.455	0.0237	0.0522	347, 364
β-**62b**	MTHF/77	(*Z*)	0.491	0.0258	0.0525	358, 376
		(*E*)	0.3898	0.0195	0.0500	

Table 26. Kinetic Data of Naphthyl(triptycyl)carbenes 62b[115]

Carbene	k (s^{-1})	τ (ms)	k_{O2} ($M^{-1}s^{-1}$)	Kk_{py} ($M^{-1}s^{-1}$)	Kk_{MeOH} ($M^{-1}s^{-1}$)	k_{AMS} ($M^{-1}s^{-1}$)
α-**62b**	4.8×10	21	5×10^8	1.2×10^2	1.2×10^4	7.2×10
β-**62b**	9.1×10^2	1.1	1.6×10^9	6.0×10^3	2.1×10^5	1.9×10^3

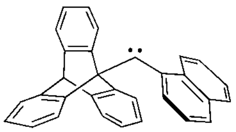
the carbene center.[61] In α-**62b**, this hydrogen is replaced with the bridgehead tertiary carbon and hence the steric repulsion with the peri hydrogen in the *Z* isomer must be much more severe. Therefore, the energy difference between the two rotamers becomes large enough to form the more stable rotamer almost exclusively.

Carbene α-**62b** decayed in first-order fashion and has a lifetime of 21 ms, which is 10^5 times longer lived than the parent α-naphthylcarbene (α-**6a**, $\tau \sim 0.1$ μs), and 10^3 times longer liver even than di(α-naphthyl)carbene (α-**9a**, $\tau \sim 70$ μs).

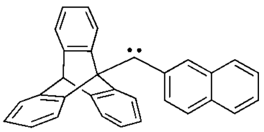
The effect of a Trp group on the stability of triplet *β*-naphthylcarbene is rather smaller than that of the α-isomer and similar with that of **62a**. The carbene center in *β*-**62b** is essentially the same as in phenylcarbene with respect to steric factors.

Reactions with typical trapping reagents for carbenes are also highly retarded (Table 26). For instance, k_{O_2} for α-**62b** is approximately 1 order of magnitude smaller than that for most other triplet diarylcarbenes, including di(α-naphthyl-)carbene (α-**9a**), which are usually trapped with a nearly diffusion-controlled rate constant.

From the rate constants of quenching studies with methanol, ΔG_{ST} for α- and *β*-**62b** is estimated to be 7.7 and 6.0 kcal/mol, respectively.



α-**62b**



β-**62b**

5.2.3. Anthrylcarbenes

Although theoretical calculations predict that the 9-anthryl group shows exceptional ability to stabilize the triplet state,[18] very few reports have been published concerning the chemistry of this carbene. The very small *D* value reported for 9-anthrylcarbene (**7a**)[61] indicates great ability to delocalize unpaired electrons, thus supporting theoretical predictions.

Table 27. ESR and UV−Vis Spectroscopic Data of 9-Anthryl(9-triptycyl)carbene (62c)[115b]

Carbene	Matrix/Temp (K)	$\lvert D/hc \rvert$ (cm^{-1})	$\lvert E/hc \rvert$ (cm^{-1})	E/D	λ_{max} (nm)
62c	MTHF/77	0.348	0.0075	0.0215	335, 403, 426

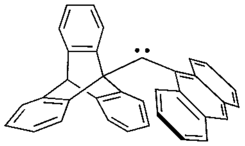
Table 28. Kinetic Data of 9-Anthryl(9-triptycyl)carbene (62c)[a,115b]

Carbene	$2k/\varepsilon l$ (s^{-1})	$t_{1/2}$ (μs)
62c	2.4×10^4	280

[a] Measured in benzene at room temperature.

5.2.3.1. 9-Anthryl(9-triptycyl)carbene.

9-Anthryl(9-triptycyl)carbene (**62c**) shows a stable triplet signal in a MTHF matrix at 77 K (Table 27). The difference of the ZFS parameters of **62c** compared to 9-anthrylcarbene (**7a**) indicates a rather significant decrease in *E* value. This suggests that the central bond angle undergoes opening of the central bond angle as a Trp group is introduce at the 9-position. Presumably, the anthryl group has peri hydrogens at both the 1- and 8-positions and hence cannot avoid steric interaction with the bridgeheadcarbon.[115]



62c

Transient absorption bands ascribable to triplet **62c** decay in second-order ($2k/\varepsilon l = 2.4 \times 10^4$ s^{-1}), and the half-life ($t_{1/2}$) is estimated to be 280 μs (Table 28). Thus, the half-life of **62c** is significantly shorter than that of the naphthyl derivatives (**62b**, $\tau = 1-21$ ms) and shorter even than that of the phenyl derivative (**62a**, $\tau = 840$ μs). This is rather surprising, since the 9-anthryl group is expected to stabilize the triplet state not only thermodynamically by delocalizing unpaired electrons but also kinetically by shielding the carbene center with the two peri hydrogens. This is most probably interpreted by assuming that the reaction at the carbene center must suffer from severe steric hindrance and hence the carbene is forced to react at the aromatic rings where the unpaired electrons are delocalized. Such reactions are expected to become more facile as the numbers of fused aromatic rings are increased; the loss of the resonance energy as a result of such a reaction on the first aromatic ring is estimated to decrease from 36 to 25 to 11 kcal/mol on going from benzene to naphthalene to anthracene.[122]

5.3. Di(aryl)carbenes

5.3.1. Di(phenyl)carbenes

When two phenyl groups are introduced on the carbene carbon, the reaction patterns change rather dramatically. The reaction of the simplest diarylcarbene, DPC (**8a**), for instance, with alkenes gives cyclopropanes but in a nonstereospecific manner with considerable amounts of alkenic products,

Table 29. Bimolecular Quenching Rate Constants for Triplet Diphenylcarbene (8a)

Quencher/Solvent	k_q ($M^{-1}s^{-1}$)	ref
MeOH/Benzene	$(6.8 \pm 2.1) \times 10^6$	88
Oxygen/Benzene	1.0×10^9	88
Oxygen/Acetonitrile	5×10^9	85b,128
1,4-Cyclohexadiene/ Cyclohexane	$(1.0 \pm 0.1) \times 10^7$	129
TEMPO/Benzene	2.7×10^8	130

obviously produced as a result of hydrogen abstraction, followed by recombination of the resulting radical pair. The ratio of hydrogen-abstraction to cycloaddition increases as alkyl substition on the alkene is increased. These observations clearly indicate that **8a** is reacting mainly in the triplet state.[123]

The reaction of **8a** with cyclohexane produces C−H insertion products (15%) along with a large amount of 1,1,2,2-tetraphenylethane (82%) and diphenylmethane (4%). In the reaction with an equimolecular mixture of cyclohexane and cyclohexane-d_{12}, some crossed products (d_1 and/or d_{11} compounds) are formed. Thus, intervention of the triplet state is also indicated in the C−H insertion reaction.[124]

When **8a** is generated in benzene by photolysis of the precursor diazomethane (**8a**-N_2), tetraphenylazine is formed, resulting from the reaction of **8a** with unreacted **8a**-N_2. When the irradiation is carried out using an intense light (a laser lamp) on a dilute solution of **8a**-N_2 in benzene, tetraphenylethene, the dimer of the carbene **8a**, becomes the major product. These results indicate that, unlike other simpler carbenes thus far mentioned, **8a** is essentially unreactive toward benzene.[87]

Reaction of **8a** with methanol is normal in that it gives an O−H insertion product, like other carbenes. However, LFP study shows that the transient absorption band due to a ground-state triplet ^{3}**8a** is efficiently quenched by methanol.[87] This is explained in terms of a spin-equilibrium mechanism[88] (vide supra).

The lifetime of triplet **8a** is 1−2 μs in cyclohexane. Under these conditions, the observed rate of carbene decay would be a composite of both singlet and triplet elementary reactions. Thus, the lifetime is dependent on an equilibrium concentration of singlet carbene.[125] The experimental ΔE_{ST} values in acetonitrile and isooctane are 2.6 and 4.1 kcal/mol, respectively.[126]

Singlet and triplet DPCs (**8a**) have bands centered at 370[87] and 300 nm,[127] respectively. The lifetime of ^{1}**8a** in cyclohexane and cyclohexane-d_{12} is 120 ± 10 and 110 ± 10 ps, respectively, thus suggesting that cyclohexane does not scavenge ^{1}DPC prior to relaxation to ^{3}**8a**. The singlet **8a** deactivates by intersystem crossing to ^{3}**8a** and decays to baseline within 3 ns. This demonstrates that ^{1}**8a** has a negligibly small concentration relative to ^{3}**8a** in the singlet−triplet equilibrium mixture.[52]

The bimolecular rate constants of **8a** with typical trapping reagents are indicated in Table 29.

The effects of ring substituents on the reactivities of DPCs (**8**) have been investigated (Table 30). The bimolecular rate constants of O−H insertion into methanol span 10^2 [from 0.87×10^6 M^{-1} s^{-1} for phenyl(*p*-cyanophenyl)carbene to $10^4 \times 10^6$ M^{-1} s^{-1} for di(*p*-methylphenyl)carbene] and thus are sensitive to substituents effects.[131] Since O−H the insertion reaction is thought to proceed through the singlet, this is explained in terms of the substituent effects on ΔG_{ST} as well as on the energy of probably the polar transition state of the O−H insertion reaction. In sharp contrast, the rate of hydrogen abstraction of ^{3}**8** in cyclohexane as judged from the lifetimes of the corresponding benzhydryl radicals is all in the range of 1.5−7.8 μs, indicating a virtual absence of a polar substituent effect on the hydrogen abstraction reaction. Only for those cases where considerable delocalization into the substituent is possible are the τ values longer.[125]

Table 30. Effects of para-Substituents on the Bimolecular Quenching Rate Constants of Triplet Diphenylcarbenes 8 with Methanol[131] and Cyclohexane[125]

X	Y	$10^{-6}k_{MeOH}$ ($M^{-1}s^{-1}$)	τ (μs in Cyclohexane)
H	H	12 ± 1	1.5
H	Br	5.1 ± 0.6	2.1
Br	Br	2.0 ± 0.8	1.6
H	Cl	6.9 ± 0.8	2.0
Cl	Cl	2.9 ± 0.3	2.1
Me	Me	104 ± 7	1.2
Me	CN	6.2	3.8
H	CN	0.87	5.4
H	COOMe	1.3	5.0
H	Ph	7.9	7.8

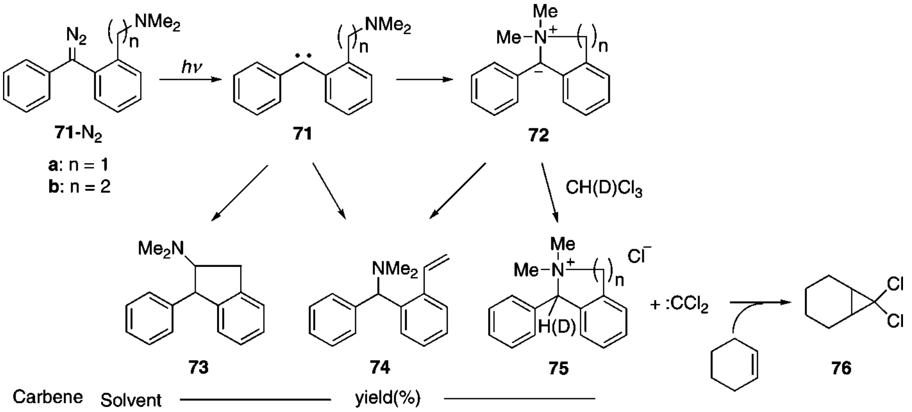
Although the reactivities of diphenylcarbenes toward many substrates are appreciably reduced compared to phenylcarbene, they are relatively efficiently trapped once those groups are introduced at the ortho position. We will see here two examples, where diphenylcarbenes are quenched almost exclusively by the ortho substituents.

5.3.1.1. (*o*-Dimethylaminoalkylphenyl)(phenyl)carbenes.

Irradiation of [2-[(*N*,*N*-dimethylamino)methyl]phenyl]phenyldiazomethane (**71a**-N_2) in $CDCl_3$ produced *N*,*N*-dimethyl-1-deuterio-1-phenylisoindolium chloride (**75a**-*d*) as a single major product in ~80% yield (Scheme 10).[132] This observation indicates that carbene **71a** undergoes intramolecular interaction with the dimethylamino nitrogen at the ortho position to generate ammonium ylide **72a**, which is protonated to form the isoindolium trichloromethide (**75a**) as an initial product. Since it is well-known that $^-CCl_3$ anion easily undergoes elimination of Cl^- to give dichlorocarbene,[133] trichloromethide salt must undergo similar degradation to afford the chloride salt **75a**. This mechanistic scenario was easily confirmed by the observation that photolysis of **71a**-N_2 in $CHCl_3$ in the presence of cyclohexene produced dichloronorcarane **76** (26%) as a dichlorocarbene adduct. Photolysis of **71a**-N_2 in a MTHF matrix at 77 K produced the ammonium ylide **72a**, having a broad intense band with a maximum near 540 nm along with sharp intense bands at 381 and 400 nm.[132]

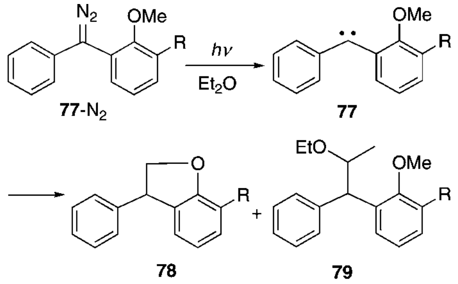
Diphenylcarbene **71b** generated from [2-[(*N*,*N*-dimethylamino)ethyl]phenyl]phenyldiazomethane (**71b**-N_2) gave somewhat different results (Scheme 10). Thus, irradiation of **71b**-N_2 in benzene afforded two major products, 1-phenyl-2-(*N*,*N*-dimethylamino)indan (**73**, 62%) and 2-[α-(*N*,*N*-dimethylamino)benzyl]styrene (**74**, 36%).[132] The formation of **73** is interpreted in terms of CH insertion of carbene **71b**. On the other hand, **74** must be produced from the ylide (**72b**) by intramolecular Hofmann-type degradation, since it is well-known that ammonium ylides that bear a α-hydrogen atom often undergo an elimination reaction to provide the corresponding amine and alkene.[134]

Scheme 10



Carbene	Solvent	73	74	75
		yield(%)		
71a	$CH(D)Cl_3$	–	–	80
71b	benzene	62	36	–
	$CHCl_3$	40	0	44

Scheme 11



	78	79
	yield(%)	
a: R= H	62.6	37.4
b: R = Me	>99	<1

5.3.1.2. 2-Alkoxyphenyl(phenyl)carbenes. Irradiation of 2-methoxyphenyl(phenyl)diazomethane **77a**-N_2 in diethyl ether at 10 °C gave 3-phenyldihydrobenzofuran **78a** along with the ether adduct **79a** (Scheme 11). The reaction patterns were dramatically changed as an alkyl group was introduced into the 3-position of diazo compounds (**77**-N_2). Thus, irradiation of 2-methoxy-3-methylphenyl(phenyl)diazomethane (**77b**-N_2) in diethyl ether at 10 °C afforded the corresponding benzofuran **78b** at the complete expense of the ether adduct **79b**.[135] The results are nicely explained in terms of the buttressing effect of the 3-alkyl group. It is well know that, in 1,2-disubstituted benzene derivatives, introduction of substituents in the 3 position exerts a large effect on the reactivity of the molecule through steric and electronic effects. In other words, the substituents at the 3-position can be thought of as being buttressing the 2-substituents.[136] Thus, 3-methyl group prevents the 2-methoxy group from lying in the plane of the phenyl ring in the precursor molecules and assists the methoxy group in rotating around the C−O bond toward the carbene center after elimination of N_2.

The extent of buttressing is roughly proportional to the bulk of the 3-alkyl substituent; in 3-*tert*-butyl derivative **77** (R = ^{t}Bu), the carbene center is almost completely covered by the ortho substituents so that it becomes unreactive even toward very reactive carbene-trapping reagents, *e.g.* methanol.[135]

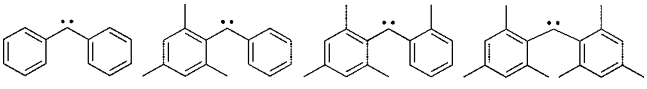
5.3.1.3. Polymethylated Diphenylcarbenes. *(a) Polymethylated Diphenylcarbenes.* Di(2,4,6-trimethylphenyl)carbene (**81a**) and di(2,6-dimethyl-4-methoxyphenyl)carbene were first generated also by Zimmerman and Paskovich in 1964.[12] Although these carbenes were not stable enough to be isolated, the congestion at the carbene center in **81a** is reflected in its unique behavior. Thus, in solution at room temperature, these carbenes dimerized to give tetraarylethene as the main product and, at high temperature, it decayed by attack at an ortho methyl group to form benzocyclobutene, a reaction that is not observed for di(2-methylphenyl)carbene under similar conditions. The chemistry found for **81a** is in sharp contrast with that found for other diarylcarbenes and is interpreted in terms of steric effects.

Table 31. Values of *D* and *E* for Diarylcarbenes

Carbene	|*D/hc*| (cm^{-1})	|*E/hc*| (cm^{-1})	*E/D*
8a	0.4069 [a]	0.01901 [a]	0.04672 [a]
80a	0.3846 [b]	0.01568 [b]	0.04077 [b]
80b	0.3736 [b,c]	0.01334 [b,c]	0.03571 [b,c]
81a	0.3482 [c,d]	0.01468 [c,d]	0.04216 [c,d]

[a] Average values reported for a variety of glasses in ref 138. [b] Average values from ref 137e. [c] After annealing. [d] Average values from refs 137b and 137d.

Later, Griller et al. studied the effect of the methyl group on the reactivities of diphenylcarbene by using spectroscopic techniques in combination with product analysis.[137] The ZFS parameters of diphenylcarbene (**8a**), (2,4,6-trimethylphenyl)(phenyl)carbene (**80a**), (2,4,6-trimethylphenyl)(2-methylphenyl)carbene (**80b**), and di(2,4,6-trimethylphenyl)carbene (**81a**) are measured in organic glass at 77 K (Table 31). The data indicate that the *D* values decrease as more methyl groups are introduced, although the change in *E* is relatively small. It is also noted that the ZFS parameters of **80a** and **81a** decrease as the temperature is increased, while a similar change in the parameters is not observed for **8a** and **80a**. This suggests that carbenes **80b** and **81a** relax to a structure with an expanded central C−C−C angle to gain relief from steric compression, while, in carbenes **8a** and **81a**, there is little steric compression.



8a 80a 80b 81a

In order to know whether there is a smooth gradation in chemistry as the central angle is increased, a product analysis study was also carried out. Photolysis of precursor diazo-

Scheme 12

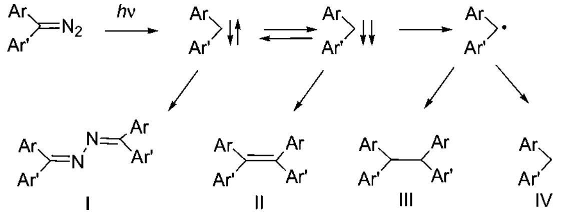


Table 32. Product Distribution Obtained by Photolysis of Diaryldiazomethanes in Isooctane at 298 K[137e]

Ar(Ar')CN$_2$	[Ar(Ar')C=N]$_2$ I	[Ar(Ar')C]$_2$ II	[Ar(Ar')CH]$_2$ III	Ar(Ar')CH$_2$ IV	yield of I/yield of (II + III + IV)
8a-N$_2$	39	< 1	39	29	0.64
80a-N$_2$	19	4	47	30	0.23
80b-N$_2$	5	14	57	24	0.05
81a-N$_2$		85	15		0.00

Table 33. Rate Constants for Reaction of Diarylcarbenes with Methanol in Isooctane at 298 K[137e]

Carbene	k_1 (M^{-1}s^{-1})	ΔG_{ST} (kcal/mol)
8a	6.4×10^6	5.9
80a	8.2×10^4	6.5
80b	2.1×10^4	7.3
81a	$< 2 \times 10^3$	>8

Scheme 13

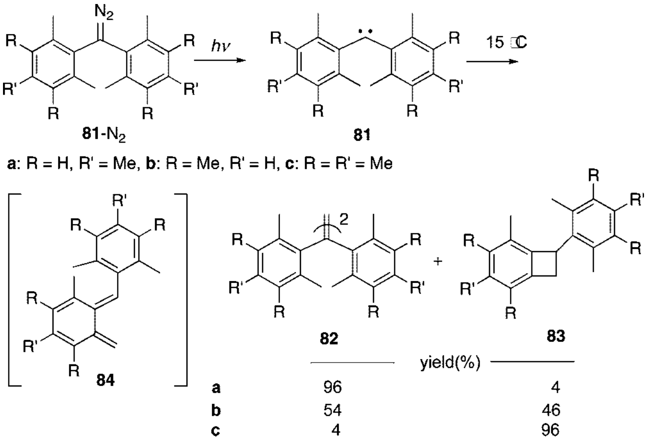


Table 34. ESR Data of Polymethylated Diphenylcarbenes 81

Carbene **81**	Matrix[a]	T (K)	$\lvert D/hc\rvert$ (cm^{-1})	$\lvert E/hc\rvert$ (cm^{-1})	E/D	T_d (K)	ref
a	IP/Et$_2$O	5.8	0.3460	0.0082	0.0237		140
	IP/Et$_2$O	77[b]	0.3558	0.0125	0.0351		140
	MTHF	77	0.3551	0.0116	0.0327	120	139
	MP	77	0.347	0.0059	0.0170		141
	PT	77	0.381	0.0121	0.0318	210	141
		77[b]	0.331	2.6×10^{-6}	7.9×10^{-6}		141
b	MTHF	77	0.3805	0.0106	0.0279		139
c	MTHF	77	0.3636	0.0095	0.0261		139

[a] IP, isopentane; PT, 1,2,3-propanetriol triacetate. [b] After annealing.

Table 35. UV−Vis Spectroscopic Data of Polymethylated Diphenylcarbenes 81[139]

Carbene **81**	λ_{max} (nm)	T_d (K)
a	318, 330, 449, 461	105
b	321, 335, 466, 495	
c	325, 338, 458, 485	

methane in isooctane at room temperature gives tetraarylketazine (I) along with tetraarylethene (II), tetraarylethane (III), and diarylmethane (IV) (Scheme 12). If one assumes that the azine (I) is formed from the singlet state of the carbene, while all others are the products from the triplet, the ratio of singlet−triplet derived products [I/(II + III + IV)] is highest for **8a** and decreases with increasing substitution at the ortho positions of the aryl group (Table 32).

The rate constants of those carbenes with methanol indicate that the rates decrease smoothly as more methyl group is introduced. From the observed quenching rate constants, ΔG_{ST} is estimated (Table 33), which is clearly in accord with the prediction, based on ESR and theoretical studies, that the singlet−triplet energy gap becomes greater as the central bond angle of the carbene is expanded.[137]

The chemistries of di(2,3,5,6-tetramethylphenyl)carbene (**81b**) and di(2,3,4,5,6-pentamethylphenyl)carbene (**81c**) were studied and compared with that of di(2,4,6-trimethylphenyl)carbene (**81a**) in order to know the effect of *m*- and *p*-methyl groups on the reactivities of di(2,6-dimethylphenyl)carbene.[139] The product distributions were significantly different. A key difference is found in the formation of benzocyclobutene **83**. Thus, irradiation of **81a**-N$_2$ in benzene at 15 °C gave the dimer (**82a**) as a major product (>90%), but the yield of the dimer decreases sharply as more methyl groups are introduced; carbene **81c** produced benzocyclobutene **83c** at the almost complete expense of the dimer (**82c**) (Scheme 13).

The ZFS parameters of **81** (Table 34) indicate that the *E*/*D* values are considerably smaller than those in diphenylcarbene (**8a**) and steadily decrease as one introduces more methyl groups on the aromatic rings, suggesting that the carbene becomes less bent due to increased steric interaction between the four ortho methyl groups in going from **81a** to **81b** to **81c**.[140]

Optical spectroscopy in the frozen medium gives more intriguing results. Irradiation of **81b**-N$_2$ in a MTHF glass at 77 K gave a spectrum consisting of an intense UV band (321 and 335 nm) and a weak visible transition (466 and 495 nm), characteristic of triplet diarylcarbenes (Table 35). When the matrix temperature was slowly warmed, a new broad absorption at 375 nm appeared and increased as carbene absorption bands decreased. The species responsible for this new absorption was assigned to *o*-quinodimethane **84b** formed as a result of intramolecular hydrogen abstraction of triplet carbene **81b**. Since the product analysis of the spent solution showed the presence of benzocyclobutene **83b** along with the dimer **82b**, **83b** is likely to be produced from the *o*-quinodimethane **84b** as a result of cyclization.

A similar spectrum was obtained in the photolysis of **81a**,**c**-N$_2$ in MTHF glass at 77 K, where **81a**,**c** showed two sharp, intense UV bands at 318 and 330 nm, and 325 and 338 nm, respectively, and generated the *o*-quinodimethane **84**, showing broad absorptions at 380 and 370 nm, respectively (Table 35).[139]

The decay kinetics of the transients observed by LFP of **81b**-N$_2$ in a degassed benzene solution at room temperature showed that the absorption at 330 nm decayed within 1 s to generate a new species with an absorption maximum around 370 nm. On the basis of the low-temperature spectrum coupled with chemical analysis, the initially formed transient with a maximum at 330 nm was assigned to carbene **81b**, while the second was assigned to *o*-quinodimethane **84b**.[139]

Table 36. Kinetic Data of Polymethylated Diphenylcarbenes 81[a,139]

Carbene **81**	λ_{max} (nm)	$2k/\varepsilon l$ (s^{-1})	k_i[b] (s^{-1})	$t_{1/2}$ (ms)	k_{O2} ($M^{-1}s^{-1}$)	k_{CHD} ($M^{-1}s^{-1}$)
a	330	1.1×10	1.5	160	2.0×10^8	4.6×10^2
b	330	-	2.2	410	7.1×10^7	3.4×10
c	328	-	4.1	180	1.0×10^8	9.8×10
c-d_{12}	340	-	0.85	1200		

[a] Measured in benzene. [b] Growth rate of *o*-quinodimethane.

The decay of **81b** was kinetically correlated with the growth of the *o*-quinodimethane **84b**; the decay rate was determined to be 2.1 ± 0.1 s^{-1}, while the growth (k_i) was 2.2 s^{-1}. The half-life ($t_{1/2}$) of **81b** was estimated to be ca. 410 ms, while the lifetime based on k_i was determined to be 455 ms. Similar measurements were done for the carbenes **81a** and **c**, and the values of k_i and $t_{1/2}$ are summarized in Table 36. Thus, triplet di(2,4,6-trimethylphenyl)carbene (**81a**) is shown to be some 5 orders of magnitude longer-lived than the parent diphenylcarbene. As more methyl groups are introduced to the aromatic rings, the carbenic center is more tightly blocked by the four ortho methyl groups toward external reagents. Thus, in di(2,3,5,6-tetramethylphenyl)carbene (**81b**), each of the four ortho methyl groups around the carbene center is buttressed by four additional *m*-methyl groups and hence **81b** is shown to be longer-lived than **81a**. On the other hand, the steady increase in k_i in going from **81a** to **81c** clearly suggests that, as the ortho methyl groups are brought much closer to the carbenic center by the buttressing methyl groups, the carbenic center comes to interact more easily with the ortho methyl groups. Thus, di(pentamethylphenyl)carbene (**81c**) comes to be trapped by the ortho methyl groups to generate the *o*-quinodimethane more efficiently and hence becomes shorter-lived again.

The rate constants of those carbenes with typical triplet quenchers (Table 36) suggest that the rate constants with oxygen and CHD are approximately 1 and 5 orders of magnitude smaller than that observed with the parent diphenylcarbene (**8a**), respectively.[139]

(b) Deuterium Isotope Effects. The above study reveals that polymethylated diphenylcarbenes **81** are exceptionally long-lived for arylcarbenes, although they are still not persistent enough to be isolated. The buttressing effects are shown to be effective in strengthening the ortho effect that protects the reactive center. However, in the case of a methyl group, which is potentially reactive toward carbenes, those in the ortho position become more efficient intramolecular quenchers of the carbene as a result of the buttressing group, thus making the carbene less persistent again.

One of the best ways to quench this process is to replace the hydrogens at the ortho methyl groups with deuterium. The desired diazomethanes (**81c**-d_{12}-N_2 and **81c**-d_8-N_2) were prepared, and product analysis as well as kinetic studies was carried out. Irradiation of **81c**-d_{12}-N_2 in benzene at 15 °C produced the carbenic dimer (**82c**-d_{24}, 73%) as a main product at the expense of the cyclobutene (**83c**-d_{12}, 27%) (Scheme 14). This is in sharp contrast with that observed for **81c**, which produced the cyclobutene almost exclusively. Similar irradiation of **81c**-d_8-N_2 also gave the dimer (**82c**-d_{16}) but only in 35% yield, and the butene (**83c**) was still a main product in this case. The butene is composed of two isotopomers (**83c**-d_8 and **83c′**-d_8) as a result of C−H and C−D insertion, and from the ratio (58/7), the kinetic deuterium isotope effect (KDIE, k_H/k_D) is estimated to be 8.0 (Scheme 15).[139]

LFP of **81c**-d_{12}-N_2 in degassed benzene at 20 °C resulted in essentially the same transient absorption bands as those observed for the protio analogue (**81c**); a transient showing a strong absorption at 340 nm due to the deuterated triplet carbene (**81c**-d_{12}) and a second transient at 377 nm due to the deuterated *o*-quinodimethane (**84c**-d_{12}) appeared as the initial absorption decayed. However, the kinetic behaviors are distinctly different between these two carbenes. Thus, the growth rate and optical yield of the deuterated quinodimethane were very small compared to those of the protio analogue, and the decay of **81c**-d_{12} was found not to be fit by a single exponential, as opposed to the almost completely unimolecular decay of **81c** (Table 36). The half-life was estimated from the decay curve to be 1.1 s in benzene at 20 °C. The KDIE based on the absolute rate constants is calculated to be 4.76. In order to gain more insight into the nature of 1,4 hydrogen migration, the rate was measured as a function of temperature (15−75 °C).[139] A differential activation energy and a ratio of pre-exponential factors (Table 37) are consistent with a classical atom transfer reaction[142] and reported[143] for H abstraction by a triplet carbene as well.

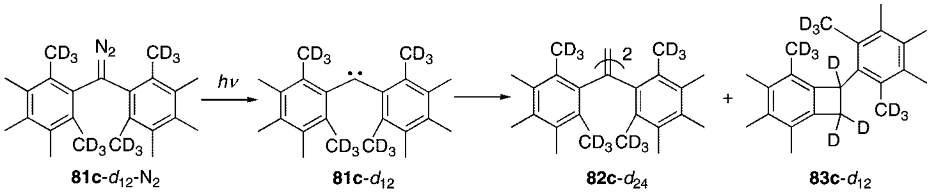
KDIE obtained byproduct analysis is significantly larger than that obtained by LFP. There may be several reasons for this, with the most likely being simple experimental variability in the measurement and imperfect deuteration of the substrates. Moreover, while LFP measures the real absolute rate of H migration from the triplet carbene, the product ratio results from all possible reactions that lead to the butene. The most important possibility that must be taken into account is the involvement of the excited-state of the diazo compounds.[86,109]

(c) p-Substituent Effect. It has been shown that the ZFS parameters of diphenylcarbenes are changed by para substituents in an interesting manner. An especially important finding is that substitution generally causes a decrease in *D* values over that in the parent molecule regardless of the nature of the substituents. This means that π-delocalization of spin density is extended and hence thermodynamic stabilization is increased by para substituents.

Thus, it is expected to make di(2,6-dimethylphenyl)carbenes more persistent by introducing appropriate substituents at the para position. A series of bis(2,6-dimethylphenyl)carbenes bearing symmetrical para disubstituents have been generated and studied.[141]

Product analysis studies on the irradiation of **81e**−**k**-N_2 in degassed benzene showed that carbenes **81** decayed mainly either by dimerization to form tetra(aryl)ethene **82** or by attack at an ortho methyl group to afford benzocyclobutenes **83** by way of *o*-quinodimethanes **84** in solution (Scheme 16). The photolysis of **81f**-N_2 (X = F) and **81i**-N_2 (X = OMe) gave an additional product, dihydroanthracene derivatives **85**, presumably formed from *o*-quinodimethanes **84** as a result of intramolecular cyclization. Comparison of the product distributions observed suggests that the distributions are somewhat sensitive to substituents at the para positions, although steric crowdedness around the carbene center (the distance between the carbene center and migrating hydrogen) is not expected to be altered by the para groups. The ratio of **82**/[**83** + **85**], for example, increased in the order of *p*-OMe < *p*-F < *p*-H < *p*-^{t}Bu < *p*-Me ≪ *p*-Cl ∼ *p*-Br. The enhanced yield of the intramolecular reaction products (**83** + **85**) from para-fluoro and methoxy derivatives **81f**,**i** may indicate that the butene can also be formed from the singlet state of **81**, since those groups are known as strong π-donor

Scheme 14



Scheme 15

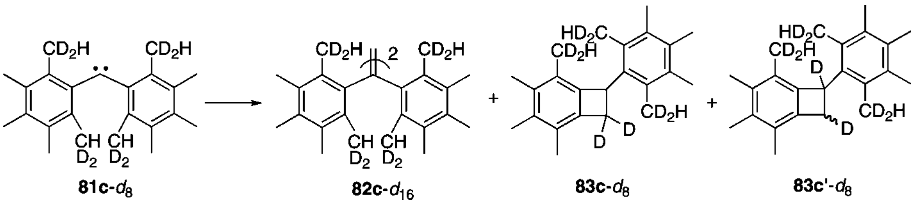
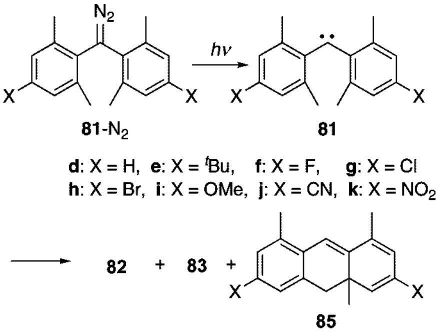


Table 37. Arrhenius Parameters for H (D) Transfer in Triplet Carbenes 81c[139]

Carbene	Temp (K)	E_a (kcal/mol)	A (s^{-1})	k_H/k_D	$[\Delta E_a]_D^H$	A_H/A_D
81c	288-338	9.9	9.8×10^7	4.76	1.0	0.9
81c-d_{12}	290-338	10.9	1.1×10^7			

Scheme 16



	yield(%)		
a	63	8	<1
d	60	15	<1
e	67	9	<1
f	70	17	9
g	87	5	<1
h	80	5	<1
i	27	7	27

substituents which stabilize the singlet state as a result of conjugative interaction with the formally vacant p orbital of the singlet state.

ESR measurements were made both in MTHF and in a 1,2,3-propanetriol triacetate (PT) matrix, and the ZFS parameters are reported in Table 38. The decreases in the ZFS parameters upon warming the matrix were observed in both the matrices. It is worth examining quantitatively how the para substituents affect the electronic structure of ^{3}**81**. To estimate the relative abilities of substituents to delocalize the spin, sigma-dot substituent constants (σ•) have been proposed.[144] Among the various approaches to the definition of a σ• scale, Arnold's σ_α• scale[145] is the most suitable for the analysis of the substituent effect on the *D* values of ^{3}**8**, since this scale is a nonkinetic measure of radical stabilizing effects based on hyperfine coupling constants in the benzylic radical.[146]

Attempts to correlate the *D* values of **81** with σ_α• show that correlations are sensitive to the geometric structures of the carbenes. Thus, the *D* values observed for nascent carbenes in rigid matrices at low temperature, i.e., those obtained in MTHF at 77 K and in PT at 110 K, where carbenes retain their metastable geometries, gave a highly scattered ($r < 0.5$) plot when correlated against σ_α•. Improved correlations are found when the *D* values observed for the carbenes in their minimum-energy geometries, attained upon annealing, are employed. Thus, the *D* values in PT at 200 K correlate relatively well ($\rho = 0.589$, $r = 0.9$) with σ_α•.[147] The *D* values reported for di-para-substituted diphenylcar-

Table 38. ESR Data of Di(2,6-dimethylphenyl)carbenes[141]

Carbene 81	X	Matrix	T (K)	$\|D/hc\|$ (cm^{-1})	$\|E/hc\|$ (cm^{-1})	E/D	T_d (K)
d	H	MTHF	77	0.377	0.0101	0.0268	140
		MP	77	0.349	0.0049	0.0140	
		PT	77	0.354	0.0093	0.0263	240
			77[a]	0.335	2.8×10^{-6}	8.4×10^{-6}	
e	^{t}Bu	MTHF	77	0.373	0.0134	0.0359	170
		MP	77	0.347	0.0061	0.0176	
		PT	77	0.371	0.0128	0.0345	210
			77[a]	0.328	2.6×10^{-6}	7.9×10^{-6}	
f	F	MTHF	77	0.377	0.0129	0.0342	120
		MP	77	0.361	0.0081	0.0224	
		PT	77	0.377	0.0116	0.0308	220
			77[a]	0.344	2.8×10^{-6}	8.1×10^{-6}	
g	Cl	MTHF	77	0.354	0.0144	0.0407	120
		MP	77	0.337	0.0052	0.0154	
		PT	77	0.354	0.0120	0.0339	220
			77[a]	0.326	2.5×10^{-6}	7.7×10^{-6}	
h	Br	MTHF	77	0.353	0.0117	0.0331	120
		MP	77	0.333	0.0054	0.0162	
		PT	77	0.348	0.0118	0.0339	220
			77[a]	0.327	2.5×10^{-6}	7.6×10^{-6}	
i	OMe	MTHF	77	0.368	0.0134	0.0364	120
		MP	77	0.343	0.0087	0.0254	
		PT	77	0.370	0.0129	0.0349	200
			77[a]	b	b	b	
j	CN	MTHF	77	0.340	0.0093	0.0274	180
		MP	77	c	c	c	
		PT	77	0.344	0.0093	0.0270	230
			77[a]	0.283	2.7×10^{-6}	9.5×10^{-6}	
k	NO_2	MTHF	77	0.335	0.0081	0.0242	170
		MP	77	c	c	c	
		PT	77	0.330	0.0078	0.0236	220
			77[a]	0.259	2.7×10^{-6}	1.0×10^{-5}	

[a] After annealing. [b] The triplet signals disappeared before the relaxation. [c] ESR signal intensity was too weak to assign ZFS parameters.

Table 39. UV−Vis Spectroscopic Data of Di(2,6-dimethylphenyl)carbenes[141]

Carbene **81**	X	λ_{max} (nm)	T_d (K)
d	H	318, 327, 435, 446, 472	115
e	^{t}Bu	316, 327, 438, 448, 460, 470	150
f	F	311, 323, 431, 441, 452, 466	110
g	Cl	330, 432, 441, 455, 466	110
h	Br	341, 432, 443, 455, 466	110
i	OMe	321, 333, 439, 450, 460, 473	110
j	CN	331, 488	160

Table 40. Kinetic Data of Di(2,6-dimethylphenyl)carbenes[141]

Carbene **81**	X	λ_{max} (nm)	$2k/\varepsilon l$ (s^{-1})	k_i (s^{-1})	$t_{1/2}$ (ms)	k_{O2} ($M^{-1}s^{-1}$)	k_{CHD} ($M^{-1}s^{-1}$)
d	H	–	1.4×10	3.3	180	1.5×10^8	9.4×10
e	^{t}Bu	–	5.8	0.62	500	1.8×10^8	3.0×10^2
f	F	–	5.8×10	2.1	60	1.7×10^8	4.4×10^2
g	Cl	–	4.0×10	-	100	1.1×10^8	1.8×10^2
h	Br	–	2.2×10	-	50	9.7×10^7	1.4×10^2
i	OMe	–	1.3×10^2	-	20	3.1×10^8	1.2×10^3
j	CN	480	1.8×10	1.0×10	590	3.1×10^7	1.3×10^2

Scheme 17

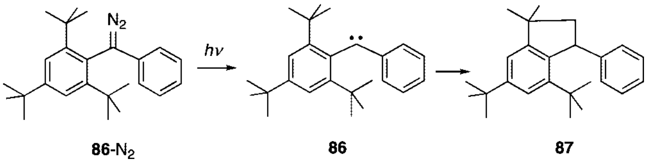


Table 41. ESR Data of Polyalkylated Diphenylcarbenes

Carbene	Matrix	T (K)	|D/hc| (cm^{-1})	|E/hc| (cm^{-1})	E/D	ref
86	MTHF	77	0.3408	~0	~0	150
	MP	77	0.3390	~0	~0	150
88	MTHF	77	0.4076	0.01495	0.03668	150
	MP	77	0.3749	0.00935	0.02494	150
91	MTHF	77	0.332	0.001	0.003	151
	MP	77	0.333	0.001	0.003	151

Table 42. UV−Vis Spectroscopic Data of Polyalkylated Diphenylcarbenes[a]

Carbene	λ_{max} (nm)	T_d (K)	ref
86	340	110	149
88	316, 389, 414, 428, 446	100	150
91	281, 321, 338	145	151

[a] Measured in MTHF at 77 K.

benes **8** (Table 14) also correlate well with ($\rho = 0.264$, $r = 0.977$) with σ_α•. The magnitude of ρ for **81** is larger than that for ortho-unsubstituted ones **8**. This is reasonable, since carbenes **81** have a more linear and perpendicular geometry than **8**, as evidenced by the large decrease in *D* and *E* values relative to **8**, and hence the unpaired electron can be delocalized more effectively in the π-system of aromatic rings including substituents.[147]

The effect of the para substituents on the thermal stability (T_d) is to be noted. The data in PT appear to level off to some extent, because T_d values (determined by ESR) in PT are close to the limit of the inherent stability of the carbene ^{3}**81**. Inspection of the data in THF (Table 38) indicates that the 4-cyano and 4-nitro groups exhibit significantly higher T_d (180 K) compared to the others, thus indicating significant stabilizing effects on ^{3}**8**. Taking into account the increased ability of the substituent to delocalize the unpaired electron, one may conclude that triplet carbenes kinetically stabilized by the ortho substituents can be further stabilized thermodynamically by spin-delocalizing para substituents. However, the 4-Bu group is found to exert an equally significant effect on T_d (170 K). Since σ• of this group is not large, the effect cannot be explained in terms of spin delocalization.

The absorption maxima observed for **81** and the temperature (T_d) (determined by UV) due to **81** are summarized in Table 39. Again, rather high T_d is noted for **81e** and **81j** compared to other carbenes.

LFP of **81e**-N_2 in a degassed benzene solution at room temperature produced triplet carbene **81e**, showing a maximum at 328 nm. The decay of the absorption due to **81e** can be fit to a second order decay ($2k/\varepsilon l = 5.8\ s^{-1}$), and a half-life ($t_{1/2}$) was estimated to be ca. 500 ms from the decay curve. On the other hand, the growth rate of *o*-quinodimethane **84e** was determined to be $k_i = 0.62\ s^{-1}$. Similar measurements were done for the carbenes **81**, and kinetic data are reported in Table 40. In accordance with the product analysis data and low temperature UV−vis spectroscopic studies, the growth of *o*-quinodimethane **84** was not observed in LFP of **81g**-N_2 and **81h**-N_2. On the other hand, the half-life of **81** ranges from 20 (**81i**) to 590 ms (**81j**) depending on the para substituents. A significantly large $t_{1/2}$ is noted for **81e** and **81j** compared to that of other carbenes.

Thus, the stability as judged by T_d and $t_{1/2}$ as a function of *D* value indicates that those data are not correlated to each other. The half-life ($t_{1/2}$) is just a measure of lifetime and cannot be regarded as a quantitative scale for reactivity. T_d is also not taken as such a scale unless the decay process is demonstrated to be essentially the same over the carbenes studied. In this respect, the rate constant of the triplet carbene with a typical quencher can be employed as a more quantitative measure of the reactivity. However, neither k_{O_2} nor k_{CHD} appreciably correlate with the *D* value.

The reason for this rather unexpectedly poor correlation is not clear. Effects of substituents on the energy difference between the singlet and triplet states and spin−orbit coupling efficiencies are taken into account in this case.

5.3.1.4. 2,4,6-Tri-*tert*-butylphenyl(phenyl)carbene.

The *tert*-butyl group has been recognized as one of the most effective protecting groups and successfully employed to protect many reactive centers in organic molecules. For instance, the divalent centers of silylenes and germylenes, heavy atom analogues of carbenes, are shown to be blocked by *tert*-butyl groups.[148]

2,4,6-Tri*tert*-butylphenyl(phenyl)carbene (**86**) was generated by photolysis of the corresponding diazo compound (**86**-N_2) (Scheme 17).[139,149] The ZFS parameters[150] and the absorption bands[139] of **86** in a rigid matrix at 77 K are listed in Tables 41 and 42, respectively. An essentially zero *E* value even in MTHF at 77 K suggests that this carbene has a linear structure regardless of the rigidity of the matrix. The absorption band (340 nm) of **86** in MTHF disappeared at 110 K irreversibly. Transient absorption bands due to triplet carbene **86** were observed by LFP only in the presence of benzophenone (BP). In this case, the triplet excited-state of BP was observed at 340 and 350 nm, which was quenched

Table 43. Kinetic Data of Polyalkylated Diphenylcarbenes[a]

Carbene	T (°C)	λ_{max} (nm)	k (s^{-1})	τ (μs)	k_{O2} ($M^{-1}s^{-1}$)	ref
86	rt	340		120	$(1.2 \pm 0.2) \times 10^8$	139
	20	340	7.97×10^3	125		
86-d_{27}	20	340	6.87×10^3	146		139
88	20	320	7.74×10^3	129		150
91	rt	335	4.3×10^3	233		151

[a] Measured in benzene at room temperature.

Scheme 18

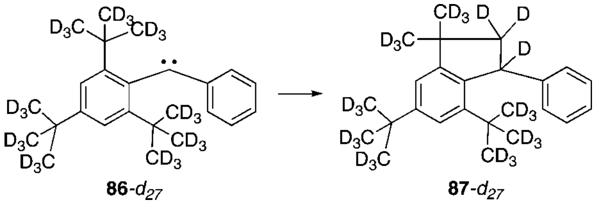


Table 44. Arrhenius Parameters for H (D) Transfer in Triplet 2,4,6-Tri-*tert*-butylphenyl(phenyl)carbene (87)[a,139]

Carbene	Temp (K)	E_a (kcal/mol)	A (s^{-1})	k_H/k_D	$[\Delta E_a]^H_D$	A_H/A_D
87	280-298	11.0	1.1×10^{12}	1.16	0.3	0.7
87-d_{27}	280-298	11.3	1.6×10^{12}			

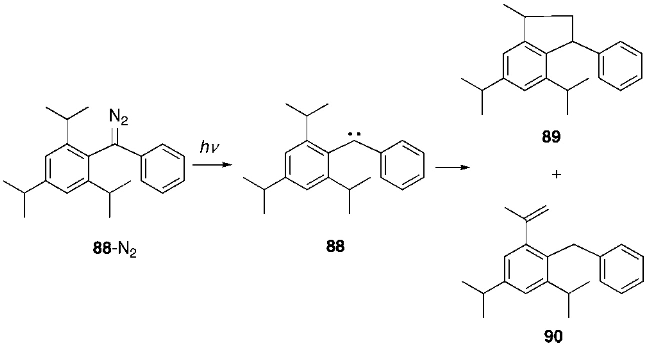
[a] Measured in benzene.

by **86**-N_2 with the nearly diffusion-controlled rate constant of $k = (4.7 \pm 0.8) \times 10^9$ M^{-1} s^{-1}. The residual spectrum at 340 nm is similar with that obtained in the MTHF matrix at low temperature. The transient band due to the carbene **86** decayed in first-order ($k_i = 7.97 \times 10^3$ s^{-1}) with the lifetime of 125 μs, which is only 60 times longer than that of the parent diphenylcarbene (**8a**). The quenching rate constant with oxygen was determined to be $(1.2 \pm 0.2) \times 10^8$ M^{-1} s^{-1} (Table 43). Irradiation of a degassed benzene solution of **86**-N_2 at room temperature afforded 4,6-di-*tert*-butyl-1,1-dimethyl-3-phenylindan (**87**) almost exclusively (Scheme 17). The formation of **87** was not quenched by methanol. Thus, the carbene **86** decays almost exclusively by abstracting a hydrogen from the ortho *tert*-butyl group.[139,149]

In order to hinder the hydrogen abstraction process by using the kinetic deuterium isotope effect, deuterated diazo compound **86**-d_{27}-N_2 was prepared (Scheme 18). Product analysis and sensitized LFP studies (Table 43) showed that deuterated carbene **86**-d_{27} also gave indan almost exclusively and decayed unimolecularly with the rate constant of $k_i = 6.87 \times 10^3$ s^{-1} ($\tau = 146$ μs). The kinetic deuterium isotope effect (KDIE) estimated for intramolecular hydrogen abstraction is only 1.16.[139] This is extremely small compared to that observed for the similar hydrogen abstraction by triplet carbene.[143]

The Arrhenius parameters for hydrogen and deuterium abstraction were obtained from the rate measurements as a function of temperature and are summarized in Table 44 and compared with that obtained for carbene **81c** (Table 37). Although the nature of hydrogens being abstracted is very different between the two carbenes, there is only a small difference in E_a values. This is interpreted as suggesting that the transferring hydrogen in **81c** is in-plane with the aromatic ring, where little benzylic stabilization is expected. On the other hand, a very large A value for **86** over that of **81c** can be understood in terms of a large difference in numbers of the transferring hydrogens and distance between the hydrogens and carbenic center, and this is responsible for the large difference in k_H between the two systems despite nearly equal E_a values. Significant differences in k_H/k_D and $[E_a]^H_D$ are also discussed.[139]

Scheme 19



Thus, the *tert*-butyl group, which has been successfully employed to protect many unstable species, turns out to be useless to stabilize triplet carbene, which makes this project very difficult.

5.3.1.5. 2,4,6-Triisopropylphenyl(phenyl)carbene. The isopropyl group appears to be a more attractive kinetic protector than the *tert*-butyl group, since there is not expected to be too much close contact with the carbene center when introduced at the ortho position of diphenylcarbene, but is still able to block the center from external reagents.

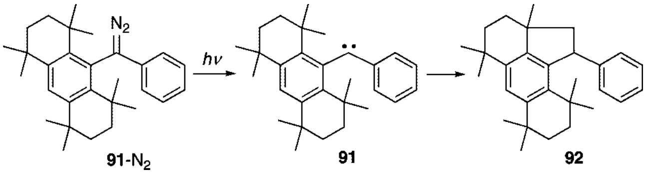
Irradiation of a degassed benzene solution of (2,4,6-triisopropylphenyl)phenyldiazomethane (**88**-N_2) at room temperature afforded phenylindan (**89**) and diphenylmethane (**90**) in a 10:1 ratio (Scheme 19). However, the formation of **89** and **90** was completely quenched when the carbene was generated in methanol in this case.[150]

Irradiation of **88**-N_2 in a MTHF matrix at 77 K gave stable triplet signals with the ZFS parameters of $D/hc = 0.4076$ cm^{-1} and $E/hc = 0.01495$ cm^{-1}. Similar photolysis in a soft matrix, 3-methylpentane, gave markedly smaller ZFS parameters ($D/hc = 0.3749$ cm^{-1}, $E/hc = 0.00935$ cm^{-1}) (Table 41). This suggests that, in soft matrices, the carbene relaxes to a structure with an expanded central C−C−C angle, presumably to gain relief from steric compression. A nonzero E value suggests that this carbene still has a bent structure even in its relaxed geometry.[150]

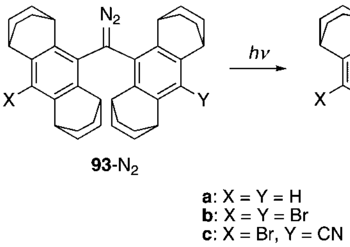
Irradiation of **88**-N_2 under identical conditions produced the absorption bands of **88**, which disappeared irreversibly when the matrix was allowed to warm to 100 K (Table 42). The lifetime of **88** in degassed benzene was determined to be 129 μs (Table 43), which is essentially the same as that of **86** ($\tau = 125$ μs). The observations reveal that ortho isopropyl groups act as a kinetic protector comparable to the sterically more bulky *tert*-butyl group, although it cannot protect the carbenic center from efficient trapping reagents such as methanol.

5.3.1.6. 9-(1,1,4,4,5,5,8,8-Octamethyl-1,2,3,4,5,6,7,8-octahydroanthryl)phenylcarbene. One way to retard intramolecular hydrogen transfer is to adjust the distance between hydrogen and the carbene center. We thus prepared precursor (**91**-N_2) of hindered DPC, in which the two ortho *tert*-butyl groups had been "tied back" by incorporation into a six membered ring (Scheme 20).[151] If the diphenylcarbene

Scheme 20



Scheme 21



91 were to decay intramolecularly, a primary hydrogen would have to move in a different manner than that in **86** and the carbene is expected to be more persistent than **86**.

Irradiation of **91**-N$_2$ in a degassed benzene solution gave indan derivatives **92** as a mixture of stereoisomers. The formation of **92** is explained in terms of insertion of the carbene into the C−H bonds of the methyl groups at the 1 and/or 8 positions. The observation is essentially the same as that reported for **86**. However, spectroscopic studies reveal a somewhat different nature between the two carbenes.[151]

The ESR signals of triplet carbene **91** were observed in a MTHF matrix at 77 K (Table 41). The absorption bands due to **91** in the same matrix started to decompose at around 145 K (Table 42). The greater thermal stability of **91** relative to that of **86** is noted. The decay of the transient band due to **91** was found to be first order ($k = 4.3 \times 10^3$ s^{-1}), in accordance with the product analysis study, indicating that intramolecular hydrogen atom abstraction is the main decay pathway for **91**, and the lifetime was determined to be 233 μs (Table 43).[151]

An appreciable increase in the stability of triplet carbene is thus achieved by tuning the distance between the ortho hydrogens and the carbene center. The effect is however not so large. All bond lengths and angles in **92** are within the expected limits for this type of compounds,[152] but a slight distortion of the fused five-membered ring is noted. These observations mean that there might be a slight steric strain in a cyclic transition state for the hydorgen atom abstraction of carbene **91** leading to **92**. Presumably, the stability of carbene will be further increased if ortho *tert*-butyl groups are tied back by incorporation into a smaller ring.

5.3.1.7. Di[1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)-anthryl]carbenes. Bicycloalkyl groups are very attractive, since bridgehead C−H bonds are less susceptible to hydrogen abstraction, although not entirely inert, and the bridging chains will act as protectors. Triplet di[1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthryl]carbene (**93**) has been generated and studied by spectroscopic means with the product analysis (Scheme 21),[153] and results are compared with those obtained for di(2,3,5,6-tetramethylphenyl)carbene (**81b**), an open-chain "counterpart" of **93a**. A comparison of the ZFS parameters suggests that ^{3}**93a** exhibits larger *E*/*D* values than ^{3}**81c**, especially in the relaxed geometries, indicating that ^{3}**93a** has a less expanded geometry than ^{3}**81c** (Tables 34 and 45). The ESR signals of ^{3}**93a** were persistent even at 150 K, while the signals of ^{3}**81c** disappeared at around 110 K. LFP studies show that the transient bands due to ^{3}**93a** decay in second-order fashion with the rate constant of $2k/\varepsilon l = 8.4$ s^{-1} ($t_{1/2} = 1.5 \pm 0.0.1$ s), which is to be compared with that of ^{3}**81c** ($t_{1/2} = 0.42$ s). However, the rate constants for the reactions of ^{3}**93a** with typical triplet quenchers, oxygen and CHD, suggest that ^{3}**93a** is more reactive than ^{3}**81c** (Tables 36 and 47**)**.[153]

Table 45. ESR Data of Di[1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthryl]carbenes[153]

Carbene	Matrix	*T* (K)	|*D*/*hc*| (cm^{-1})	|*E*/*hc*| (cm^{-1})	*E*/*D*	T_d (K)
93a	MTHF	77	0.400	0.0106	0.0265	150
	MP	110	0.376	0.0080	0.0213	
93b	MTHF	77	0.404	0.0098	0.0242	200
	MP	110	0.381	0.0084	0.0220	
93c	MTHF	77	0.372	0.0087	0.0233	180
	MP	110	0.359	0.0060	0.0168	

ZFS parameters indicate that **81c** has a more opened geometry than **93a**, at least in the relaxed, minimum energy one. 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. This suggests that **93a** is subject to the attack of a small particle such as hydrogen more easily than **81c**. In accordance with this observation, the reactivity of **93a** toward typical triplet quenchers, i.e., oxygen and 1,4-cyclohexadiene, is higher than that of **81c** (Tables 36 and 47).[153]

The half-life of **93a** in degassed benzene in the absence of proper trapping reagents is however slightly longer than that of **81c**. This is probably ascribable to the difference in the decay pathway between the two carbenes.

Spectroscopic observations suggest that the hydrogen migration is one of prominent decay pathways for **81c** but that this is the less prominent decay pathway for **93a**. It has been shown that intramolecular hydrogen migration is rather sensitive to the distance between the migrating hydrogen and the carbene center. The diradical centers of the 1,4-diradical generated as a result of the hydrogen migration in **81c**, on the other hand, would be stabilized by benzylic resonance, while in the 1,4-diradical from **93a**, the radical center on the bridgehead carbon atom undergoes little resonance stabilization. These considerations suggest that the hydrogen migration is not likely to be a prominent decay pathway for **93a**, at least compared with the open-chain counterpart, **81c**.

Dimerization of **93a** seems to be the more likely decay process, as the decay kinetics of **93a** cleanly follows second-order kinetics. Therefore, the second factor which may be taken into account is the difference in steric restriction during the dimerization between **93a** and **81c**. Inspection of the optimized geometry indicates that dimerization of the carbene center of **81c** is hindered but still attained, as the facing methyl groups can rotate around one another in order to minimize the interaction potential during dimerization. On the other hand, in **93a**, the flexible motion of the bulky and rigid "three-dimensional" bicyclic substituents during the dimerization is not attained.

It is intriguing that while the decay kinetics of **93a** cleanly follows second-order kinetics, all attempts to isolate and/or detect the expected dimer of **93a** have been unsuccessful.[153]

The thermal stability (T_d in Tables 45 and 46) and half-life ($t_{1/2}$ in Table 47) of **93** are sensitive to the para-

Table 46. UV−Vis Spectroscopic Data of Di[1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthryl]carbenes[a],153

Carbene	λ_{max} (nm)	T_d (K)
93a	318, 333, 483	140
93b	322, 336, 474	180
93c	336, 463, 502	160

[a] Measured in MTHF at 77 K.

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.

It is more useful to compare the rate constants of **93** with those of oxygen (k_{O_2}) and 1,4-cyclohexadiene (k_{CHD}). Inspection of the data in Table 50 clearly shows that the reactivity of ^{3}**93** decreases as more spin-delocalizing groups are introduced. The quenching rate constant (k_{MeOH}) by methanol also decreases in the same order. A similar ongoing decrease in k_{MeOH} by methanol from *p*-H to *p*-Br to *p*-CN is also observed for ortho unsubstituted diphenylcarbene systems.[130] 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.[89,154,155] In other words, the data in Table 47 suggest that the free-energy difference between the ground triplet and singlet states increases on going from **93a** to **93b** to **93c**.

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.

5.3.1.8. Di(pentafluorophenyl)carbene. Di(pentafluoropheny1)carbene (**94**) was generated and investigated by product analysis and spectroscopically.[156] The reaction pattern exhibited by **94** is somewhat different from that observed for ordinary DPCs (Scheme 22). Photolysis of **94**-N_2 in benzene gave norcaradiene **95** (79%), most probably from the singlet state, along with a small amount of the triplet product, the ethane (**96**, 8%). This is rather surprising, since most diphenylcarbenes are unreactive to benzene (vide supra). Reaction with (*E*)-1,2-dichloroethene, which is know to give cyclopropane from stereospecific addition of singlet carbenes but dichloropropene as a result of rearrangement from addition of triplet carbenes, is intriguing. Thus, generation of **94** in the presence of (*E*)-1,2-dichloroethene resulted in the formation of both the cyclopropane (**97**, 33%) and the propene (**98**, 5%), with the ratio of **97** to **98** being 6.70. This ratio is considerably higher than that reported for DPC (0.25)[157] and even higher than that for fluorenylidene (1.51),[158] which has a smaller S−T gap and hence tends to react in the singlet state compared to diphenylcarbene. These observations suggest that **94** tends to react in its singlet state.

However, photolysis of **94**-N_2 in cyclohexane gives tetrakis(pentafluorophenyl)ethane (**96**, 90%) as a main product along with a small amount of di(pentafluorophenyl-)methane (6%). These products are also observed in the reaction of nonfluorinated diphenylcarbene with cyclohexane and are most likely formed from the triplet state.[124]

Thus, **94** tends to react in the singlet state with benzene and alkene, while it reacts in the triplet state with alkane. This is explained in terms of the enhanced electrophilicity as well as increased steric crowdedness of the carbenic center in light of the Hammett σ value ($\sigma_m = 0.43$, $\sigma_p = 0.06$) as well as van der Waals radii ($F = 1.35$ Å, $H = 1.20$ Å) and bond lengths (C−F = 1.32 Å, C−H = 1.08 Å). Thus, **94** reacts with those having moderate reactivities toward carbene, e.g., benzene and alkene, mostly in the singlet state, owing to the increased electrophilicity. However, the electrophilicity of **94** is not so increased as to react with the σ electrons of the alkane C−H bonds. Moreover, the singlet carbene C−H insertion is considered to be sensitive to steric factors. Thus, the carbene **94** is forced to react in the triplet state.

Photolysis of **94**-N_2 in an Ar matrix at 10 K produced **94**, which was observed by IR (1506, 1484, 1475, 1050, 992, 983, and 660 cm^{-1}) and UV ($\lambda_{max} = 300$ nm) and was shown to react with doped O_2 to produce ultimately perfluorobenzoate (**99**) by way of the carbonyl oxide (**94**-O_2) and the dioxirane (**94**-O_2'), with both intermediates being characterized by IR and UV−vis spectroscopy. LFP of **94**-N_2 in acetonitrile solution produced a transient absorption ($\lambda = 320$ nm) due to di(pentafluorophenyl)methyl radical (**94**-H), obviously produced by hydrogen atom abstraction of the triplet **94**. The transient band due to the triplet **94** was not observed due to overlapping with the precursor diazomethane, and hence, the lifetime was estimated by an indirect method. LFP of **94**-N_2 in the presence of 1,4-cyclohexadiene (CHD) produced the methyl radical (**94**-H). The apparent built-up rate constant of the radical was plotted as a function of [CHD], which is linear. From the plot, the rate constant of **94** with CHD and the lifetime of the triplet **94** are estimated to be 1.1×10^7 M^{-1} s^{-1} and ~1 μs, respectively. Although **94** shows very different reaction patterns from that of nonfluorinated diphenylcarbene, its lifetime is essentially the same.

5.3.1.9. Polychlorinated Diphenylcarbenes. Di(2,4,6-trichlorophenyl)carbene (**100a**) was first generated by Zimmerman and Peskovich in 1964 in their attempts to prepare a hindered divalent species completely unreactive toward external species.[12] Although this carbene was not stable enough to be isolated, it again exhibited unusual chemical properties. Thus, in solution at room temperature, this carbene also dimerized to give tetrakis(2,4,6-trichlorophenyl)ethene (**101a**) in 70−80% yield (Scheme 23), which suggests that the hindered triplet carbene concentration builds up to the point where dimerization occurs.

The stability of triplet di(trichlorophenyl)carbene (**100a**) was investigated by spectroscopic means and flash photolysis techniques.[159] Irradiation of **100a**-N_2 in a MTHF glass at 77 K exhibited stable ESR (Table 48), and UV−vis absorption bands (Table 49) ascribable to ^{3}**100a** are observed. Variable temperature ESR study shows that the signals ($D/hc = 0.371$ cm^{-1} and $E/hc = 0.0133$ cm^{-1}) of ^{3}**100a** immediately generated by photolysis of **100a**-N_2 gradually change upon warming the matrix eventually to give a new signal with $D/hc = 0.360$ cm^{-1} and $E/hc = 0.0106$ cm^{-1}, indicating the structural relaxation due to steric strain around the carbene center.

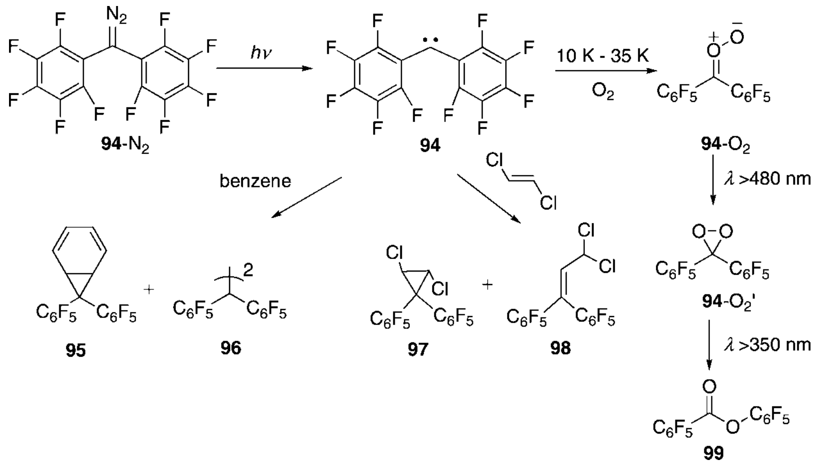
Flash photolysis of a degassed benzene solution of **100a**-N_2 at room temperature produced triplet **100a** at 344 nm, which decayed with a second-order kinetics with $2k/\varepsilon l$ being 8.9×10^2 s^{-1} and $t_{1/2} = 18$ ms (Table 50). Thus, **100a** is shown to be 4 orders of magnitude longer-lived than the parent diphenylcarbene (**8a**). The triplet carbene **100a** was trapped by oxygen to generate the corresponding benzophenone oxide **100a**-O_2 with the rate constant of 7.4×10^7 M^{-1} s^{-1} and also by 1,4-cyclohexadiene to produce di(trichloro-

Table 47. Kinetic Data of Di[1,2,3,4,5,6,7,8-octahydro-1,4:5,8-di(ethano)anthryl]carbenes[a],[152]

Carbene	T (°C)	λ_{max} (nm)	$2k/\varepsilon l$ (s^{-1})	τ [or $t_{1/2}$] (ms)	k_{O2} ($M^{-1}s^{-1}$)	k_{CHD} ($M^{-1}s^{-1}$)	k_{MeOH} ($M^{-2}s^{-1}$)
93a	20	318, 333, 483	8.4	[1.5 ± 0.1]	2.3×10^8	3.6×10^2	4.3×10^4
93b	20			2.8	1.7×10^8	1.8×10^2	6.9×10^3
93c	20			1.4	1.2×10^8	6.7×10	2.9×10^2

[a] Measured in benzene at room temperature.

Scheme 22



Scheme 23

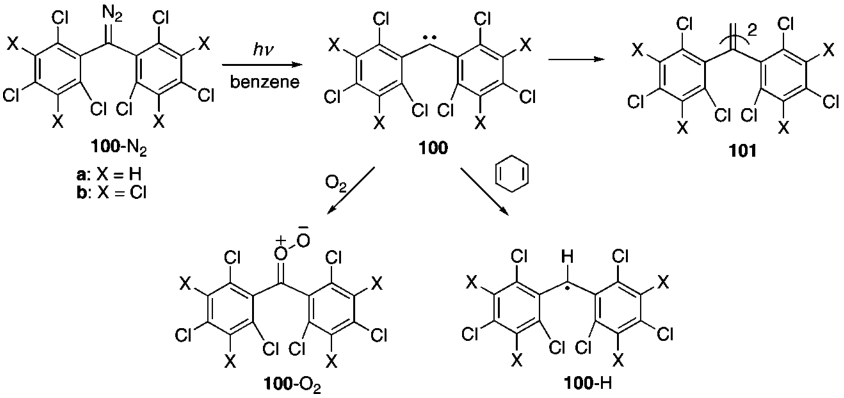


Table 48. ESR Data of Di(2,4,6-trichlorophenyl)carbene (100a)[159]

Matrix	T (K)	$\|D/hc\|$ (cm^{-1})	$\|E/hc\|$ (cm^{-1})	E/D	T_d (K)
MTHF	77	0.371	0.0133	0.0358	120
VPI-5[a]	77	0.370	0.0012	0.0324	220

[a] VPI-5: molecular sieve VPI-5.

Table 49. UV−Vis Spectroscopic Data of Polychlorinated Diphenylcarbenes[159]

Carbene	Matrix	T (K)	λ_{max} (nm)
100a	MTHF	77	338, 450 - 500
100b	MTHF	77	356, 493, 525

pheny1)methyl radical (**100a**-H, $\lambda_{max} = 365$ nm) with the rate constant of $(3.5 \pm 0.1) \times 10^3\ M^{-1}\ s^{-1}$ (Table 50). Note that those rate constants are some 2 to 3 orders of magnitude smaller than that obtained for the parent diphenylcarbene.

The triplet carbene has also been shown to be trapped by tetramethylpiperidine *N*-oxide (TEMPO) to give the corresponding benzophenone as a major product along with tetramethylpiperidine.[130] The quenching rate constant was determined to be $2.1 \times 10^6\ M^{-1}\ s^{-1}$ for **100a** (Table 50), which is again 2 orders of magnitude smaller than that ($2.7 \times 10^8\ M^{-1}\ s^{-1}$) for **8a**.[160]

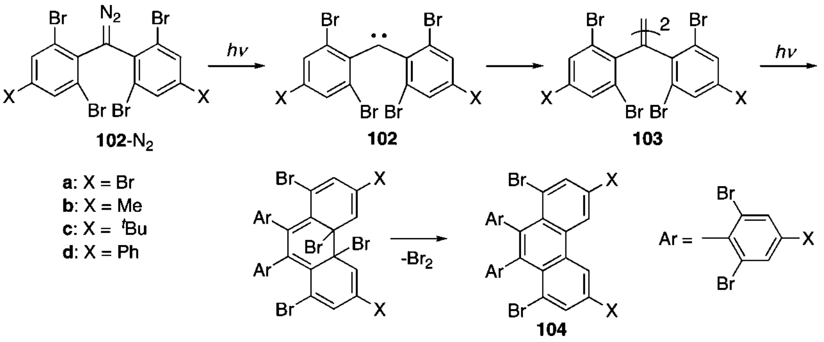
In order to strengthen the effect of the chlorine group on the stability of triplet diphenylcarbenes, the reactivities of perchlorodiphenylcarbene (**100b**) generated by photolysis of **100b**-N_2 were investigated (Scheme 23).[159] The reaction found for **100b** in benzene is essentially similar to that observed for **100a**. However, when generated in cyclohexane, **100b** still gave the dimer (**101b**) in 80% yield, while **100a** gave a large amount of products arising from hydrogen abstraction and the formation of the dimer was decreased to 26%. The difference in the product distribution can be interpreted as reflecting the difference in the extent of steric crowdedness around the carbenic center between these two carbenes. Thus, in **100b**, each of four chlorine groups around the carbene center is buttressed by one of the four meta

Table 50. Kinetic Data of Polychlorinated Diphenylcarbenes[a,159,160]

Carbene	T (°C)	λ_{max} (nm)	$2k/\varepsilon l$ (s^{-1})	$t_{1/2}$ (ms)	k_{O2} ($M^{-1}s^{-1}$)	k_{CHD} ($M^{-1}s^{-1}$)	k_{TEMPO} ($M^{-1}s^{-1}$)
100a	rt	344	8.9×10^2	18	7.4×10^7	$(3.5 \pm 0.1) \times 10^3$	2.1×10^6
100b	rt	357	4.2×10^2	28		$(6.2 \pm 0.1) \times 10^3$	

[a] Measured in benzene at room temperature.

Scheme 24



chloro groups, and therefore, the carbene center is more rigidly protected than that in **100a**.

Irradiation of **100b**-N_2 in a MTHF glass at 77 K resulted in the appearance of the absorption due to triplet **100b** at 356, 493, and 525 nm (Table 49). Flash photolysis of **100b**-N_2 in a degassed benzene solution produced a transient absorption due to **100b** at 357 nm, which decayed with a second-order kinetics with $2k/\varepsilon l$ being 4.2×10^2 s^{-1} and $t_{1/2}$ = 28 ms. The dimerization rate is significantly decreased as four additional chloro groups are introduced at the meta position, obviously due to the buttressing effects. Thus, the lifetime is increased from 18 to 28 ms with the aid of the buttressing effect.[159]

5.3.1.10. Polybrominated Diphenylcarbenes. Bromine atom appears to be more promising as a protecting group toward the triplet carbene center than chlorine because the van der Waals radius (Br = 1.95 Å) is bigger than that of chlorine atom and the C−Br bond length (1.85 Å) is longer than the C−Cl bond length. In other words, the ortho bromo groups are expected to overhang the reactive site more effectively.

A series of di(2,6-dibromophenyl)carbenes (**102**) having different substituents at the 4 positions were generated by irradiation of the corresponding precursor diazomethanes (**102**-N_2), and their reactivities are investigated (Scheme 24).[161]

Photolysis of **102**-N_2 in benzene gave a rather complex mixture, from which a dimer was isolated, but the structure and yield of the dimer were notably different from those observed for the chlorinated diphenylcarbenes. The dimer obtained from **102c** (R = ^{t}Bu) is not a simple carbene dimer but a phenanthrene derivative (**104c**), most probably derived from a simple carbene dimer (**103**) by photocyclization, followed by oxidation. This assumption is verified when a phenyl group is introduced at the para position. In this case, not only the phenanthrene derivative but also the simple carbene dimer were isolated in 8 and 58% yields, respectively, when generated in benzene, and the dimer (**103d**) was converted to **104d** upon further irradiation (Scheme 24).

The yields of the dimeric products are highly dependent upon the nature of para substituents. Thus, the yields decreased rather sharply from 66 to 60 to 40% as the para substituents are changed from Ph to ^{t}Bu to Br. Only an unidentifiable tarry mixture was obtained from **102b** (R = Me).

Table 51. UV−Vis Spectroscopic Data of Polybrominated Diphenylcarbenes[161]

Carbene	Matrix	T (K)	λ_{max} (nm)	T_d (K)
102a	MTHF	77	337, 349, ~480	
	MTHF	77	339, 353	
102b	MTHF	77	335, 350	
102c	MTHF	77	335, 349	170
102d	MTHF	77	352, 497	170
102e	MTHF	77	343, 357	170

The lifetime of triplet ortho-tetrabrominated diphenylcarbenes in benzene is found to be affected by the substituents at the para positions in a striking manner. LFP of **102a**-N_2 in a degassed benzene solution at room temperature produced triplet carbene **102a**, showing a strong absorption at 353 nm and a weak absorption extending from 420 to 500 nm. Triplet carbene **102a** was shown to decay by undergoing dimerization ($2k/\varepsilon l$ = 8.9 s^{-1}) and to have a half-life of 1 s in a degassed benzene solution at room temperature, some 6 orders of magnitude longer-lived than the parent diphenylcarbene (**8a**) (Table 53).[161]

The half-life of the triplet state was decreased when the substituents at para positions are changed from bromo (**102a**, $t_{1/2}$ = 1.0 s) to methyl groups (**102b**, $t_{1/2}$ = 0.22 s), but it was increased rather dramatically when more bulky groups such as *tert*-butyl groups are introduced. Thus, in the case of di(2,6-dibromo-4-*tert*-butylphenyl)carbene (**102c**), the transient absorption survived over several minutes in degassed benzene at room temperature and the half-life was estimated to be 16 s. Di(2,6-dibromo-4-phenylphenyl)carbene (**102d**) also showed the half-life of 12 s.[161]

Anomalous effects of para substituents on the reactivities of ^{3}**102** were shown by monitoring the UV−vis spectra of ^{3}**102** at low temperature as a function of temperature (Table 51). Irradiation (λ > 350 nm) of **102c**-N_2 in a MTHF glass at 77 K resulted in the appearance of new bands with maxima at 331 and 344 nm attributable to ^{3}**102c**. The stability of carbene was examined then by slowly warming the matrix

Table 52. ESR Data of Polybrominated Diphenylcarbenes[161]

Carbene	Matrix	T (K)	$\lvert D/hc \rvert$ (cm^{-1})	$\lvert E/hc \rvert$ (cm^{-1})	E/D	T_d (K)
102a	MTHF	4	0.3598	0.0295	0.0820	130
		77	0.396	0.0295	0.0745	
	MP	77	0.368	0.00026	0.0007	
102b	MTHF	77	0.396	0.0275	0.0695	
102c	MTHF	77	0.397	0.0311	0.0784	
	MP	77	0.442	~0	~0	
102d	MTHF	77	0.359	0.0301	0.0838	170
		100	0.402	0.0044	0.0109	
102e	MTHF	77	0.484	0.0151	0.0311	
	MP	77	0.600	0.0119	0.020	

containing ^{3}**102c** (5 °C/15 min) from 77 K. No appreciable changes were observed for the absorption bands due to ^{3}**102c** in MTHF up to 160 K. Significant decomposition began only at 170 K, where the "first-order" half-life was approximately 48 min, which should be compared with that observed for ^{3}**102a**, whose $t_{1/2}$ was 40 min already at 120 K. In marked contrast, the introduction of a methyl group at the para positions caused a significant destabilization in ^{3}**102**. Thus, in a MTHF matrix, ^{3}**102b** decayed very fast even below 100 K.

The results clearly suggest that the lifetime of triplet polybrominated diphenylcarbenes ^{3}**102** is dramatically affected by the remote para substituents, which are not expected to exert a significant effect on the steric congestion around the carbenic center.

The ESR ZFS parameters of ^{3}**102a**−**c** reported in Table 52 indicate that there are no significant changes in E/D values as one changes the para substituents. These observations indicate that the para substituents exhibit little effect on the geometries of ^{3}**102**.[161]

The reactivities of **102** toward typical triplet quenchers (Table 53) indicate that the rate constants are some 2 to 3 orders of magnitude smaller than that obtained for the parent triplet diphenylcarbene. However, inspection of the data summarized in table suggests that the reactivities of ^{3}**102** toward those triplet quenchers are again not significantly affected by the para substituents.

Most of the persistent triplet diphenylcarbenes undergo dimerization in benzene to form tetra(aryl)ethenes as an almost exclusive isolable product. Carbene ^{3}**102** also underwent dimerization, as evidenced by the second-order decay kinetics in benzene. However, product analysis of the spent solution showed that the carbenic dimers were formed in a surprisingly smaller amount (vide infra), as opposed to the yield of carbene dimer from other sterically congested diphenylcarbenes, e.g., polychlorinated diphenylcarbene.[159] This suggests that simple dimerization of ^{3}**102** at the carbene center must suffer from severe steric repulsion and hence the carbene is forced to react at the other positions. The most probable reactive sites are the aromatic rings, where spin can be delocalized.

In this light, it is important to note that trityl radicals are known to undergo either methyl−para or para−para coupling depending on the substitution patterns.[1,162] Thus, it is likely that the brominated diphenylcarbenes (^{3}**102**) also undergo similar coupling. The coupling reactions of trityl radicals are not suppressed by "reactive" substituents. The anomalous reactivity of halogen at the para position is noted. For instance, (*p*-bromophenyl)diphenylmethyl undergoes methyl−para coupling.[1,162] On the other hand, tri(*p*-tolyl)methyl undergoes rapid disproportionation to yield tri(*p*-tolyl)methane and a quinoid compound which rapidly polymerizes.[163] However, the coupling at the para positions is retarded by a *tert*-butyl group at this position.[164]

Thus, rather large stabilizing effects of *tert*-butyl and phenyl groups at the para positions on the lifetime of ^{3}**102** compared to those of bromo and methyl groups are compatible with the effect of substituents observed in the coupling reaction of trityl radicals. In other words, when those bulky groups are introduced at the para positions, the decay pathways from aromatic rings are suppressed and the carbenes are forced to decay at the carbene centers, which are highly congested. Thus, the yield of the dimers and the lifetime are both increased.

The complexity of the products observed in the reaction of ^{3}**102** may be partly due to the complexity associated with the coupling reactions. The α-para coupling of triplet diphenylcarbenes, for instance, unlike that of trityls, does not lead to a final stable product and gives rise to intermediate open-shell molecules whose subsequent reactions will be complicated by possible ambient reactivity.

Significant stability of brominated diphenylcarbene is noted by ESR studies of the crystal state. Photolysis of single crystals of **102a**-N_2 at liquid helium temperature generated fine structure ESR spectra due to a typical triplet diarylcarbene with a large D value. The signals survived up to room temperature without loss of intensity for months. This is the first stable triplet carbene in the crystal state at room temperature.[161a]

Since the 3-substituents "buttress" the 2-substituents in 1,2-disubstituted benzene derivatives,[136] one would assume then that protection of the carbenic center by ortho substituents will be greatly strengthened by introduction of another group at the 3-position and that the lifetime of such carbenes must be prolonged.

Di(2,3,6-tribromo-4-*tert*-butylphenyl)carbene (**102e**) was generated and investigated, but the results are somewhat contrary to that expected (Scheme 25).[161c] Monitoring of the spectral change of **102e** in a MTHF matrix as a function of temperature indicated that the absorption ascribable to ^{3}**102e** was also persistent up to 170 K, which is essentially the same as that observed for ^{3}**102c**. The half-life of ^{3}**102e** in a degassed benzene solution is 16 s, which is identical with that of ^{3}**102c**. Quenching rate constants of ^{3}**102e** by oxygen and CHD are reported in Table 53, which also indicate that the reactivities of ^{3}**102e** are not significantly changed compared to ^{3}**102c**.

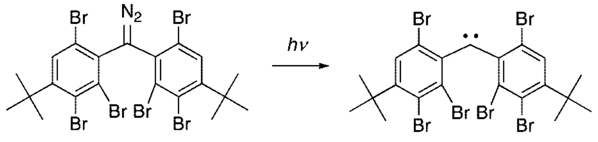
The observations suggest that the buttressing effect, which exerted a significant effect on the reactivity of triplet polymethylated diphenylcarbenes ^{3}**81**, shows little influence on the reactivity of triplet polybrominated diphenylcarbenes ^{3}**102**. The zero-field splitting parameters observed for ^{3}**102e** in MTHF at 77 K were similar with those obtained for ^{3}**102c** under the same conditions. Since MTHF is known to be a hard matrix, it is evident that these data do not reflect the thermodynamically stable geometry of the carbene (vide supra). In a soft matrix, i.e., MP, where carbenes can relax to a stabler geometry even at 77 K, the D and E values are distinctly different between ^{3}**102c** and ^{3}**102e**. Thus, the E value of ^{3}**102c** was estimated to be essentially zero, while, in ^{3}**102e**, E was still significant (Table 52). This is exactly the reverse of that observed with ^{3}**81a**−**c**, where E values decrease as more methyl groups are introduced (Table 34).

Table 53. Kinetic Data of Polybrominated Diphenylcarbenes[a,160,161]

Carbene	T (°C)	λ_{max} (nm)	$2k/\varepsilon l$ (s^{-1})	k_i (s^{-1})	$t_{1/2}$ (ms)	k_{O2} ($M^{-1}s^{-1}$)	k_{CHD} ($M^{-1}s^{-1}$)	k_{TEMPO} ($M^{-1}s^{-1}$)
102a	rt	353, 420 - 500	8.9	-	1000	1.1×10^7	7.4×10^2	9.8×10^3
102b	rt		-	4.7	220	2.3×10^7	3.2×10^2	
102c	rt	340, 380 - 420	0.35	-	16000	2.1×10^7	5.3×10^2	1.7×10^3
102d	rt	338, 355	0.35	-	12000	7.5×10^6	2.8×10^2	
102e	rt		0.35	-	16000	4.6×10^6	2.5×10^2	

[a] Measured in benzene at room temperature.

Scheme 25



102e-N_2 **102e**

The difference can be ascribable to the difference in more specific natures between methyl and bromine groups. Bromine groups are spherically symmetrical and therefore interact with each other with little directional factor. Therefore, the benzene ring is forced to be distorted when two bromine groups are introduced at adjacent positions. On the other hand, in the case of a methyl group, a hydrogen atom, bound to carbon, is only conically symmetrical and the interaction potential of this hydrogen atom with another atom will depend on the particular point on the carbon−hydrogen bond to which the other atom approaches. Therefore, the two methyl groups at adjacent positions can be accepted on the benzene ring without causing severe distortion by simply rotating each other to minimize the interaction potential.[165] This will result in the restraint of free rotation of the ortho methyl group and bring the methyl group closer and tighter around the carbenic center. Electronic repulsion between the two adjacent substituents should also be more significant for electronegative bromine groups than for neutral methyl groups.[161c]

5.3.1.11. Possible Synergetic Effects of Bromine and Methyl Groups. The results show that bromine and methyl groups can both serve as equally effective kinetic protectors toward triplet carbene but they seem to shield the center in different fashion, as expected from the difference in shape and size. It is very intriguing to generate triplet diphenylcarbene protected by both the substituents and investigate reactivities in order to examine possible synergetic effects of the two kinetic protectors on the stability of triplet diphenylcarbene.[161c]

Irradiation of (2,6-dibromo-4-*tert*-butylphenyl)(2,6-dimethyl-4-*tert*-butylphenyl)diazomethane (**105a**-N_2) in a MTHF glass at 77 K gave typical ESR signals ascribable to triplet carbene ^{3}**105a** (Scheme 26, Table 54). It is interesting to note that the value of ^{3}**105a** is not intermediate between the two but is very much like those of ^{3}**102c**, indicating that the geometry of ^{3}**105a** is dominantly influenced by the bromophenyl side of the two groups. Monitoring UV−vis spectral changes as a function of temperature showed that absorption bands ascribable to ^{3}**105a** started to disappear significantly only at 170 K in MTHF (Table 55). Thus, the thermal stability of ^{3}**105a** is comparable to that of ^{3}**102c** but is much higher than that of ^{3}**81e**, which decomposed significantly already at 130 K.

In spite of these notable similarities of the properties of ^{3}**105a** to that of ^{3}**102c** in low temperature matrices, the behaviors of ^{3}**105a** in solution at room temperature were found to be more or less comparable to that of ^{3}**81e** (Table 56). LFP of **105a**-N_2 in degassed benzene generated transient absorption due to ^{3}**105a**, which decayed within 10 s, considerably faster than ^{3}**102c**. A rough lifetime was estimated in the form of a half-life, $t_{1/2}$, to be 1.8 s. This is 1 order of magnitude smaller than that of ^{3}**102c** and comparable to that of ^{3}**81e** ($t_{1/2} = 0.5$ s). The decay kinetics of ^{3}**105a** indicated that a new species with an absorption maximum at 370 nm assignable to *o*-quinodimethane was formed as the carbene absorption at 340 nm decayed. The growth rate (k_i) of *o*-quinodimethane was estimated to be 0.58 s^{-1}. This value is also comparable to that observed with ^{3}**81e** ($k_i = 0.62\ s^{-1}$). Thus, ^{3}**102a** is shown to decay, at least in part, by abstracting hydrogen from the ortho methyl group while the main decay pathway for ^{3}**102c** is dimerization. This intramolecular reaction channel available for ^{3}**105a** explains the difference in lifetime between the two carbenes.

Product analysis of the spent solution indicates that the phenanthrene-type dimer (**106**, 25%) was again obtained, but an anthracene derivative (**108**, 16%), which is not observed in the reaction of **102a**−**d**, was also formed. The formation of **108** is interpreted in terms of intramolecular hydrogen migration in triplet carbene ^{3}**105a**, from an ortho methyl group to the carbenic center, to generate *o*-quinodimethane **109**, followed by subsequent cyclization and dehydrobromination (Scheme 26). The formation of **108** is in accord with the spectroscopic observation. The structure of phenanthrene **106** suggests that debromination is crucial for the formation of **106** under these conditions.[161c]

The results suggest that DPC protected by unsymmetrical groups of a different nature undergoes little extra stabilization as a result of possible synergetic effects of the two groups, but exhibits a hybrid character depending on the conditions.

5.3.1.12. *o*-Trifluoromethylated Diphenylcarbenes. The fluoro group is especially interesting in carbene chemistry because it can play key roles either intramolecularly or intermolecularly. For instance, phenyl(trifluoromethyl)carbene gives no intramolecular rearrangement product while phenyl(methyl)carbene decays almost exclusively by 1,2-H shift to give styrene.[108] On the other hand, C−F bonds are known to be almost the only type of bond unreactive toward carbenic centers.

Flash vacuum pyrolysis (FVP) of di(2-trifluoromethylphenyl)diazomethane (**110a**-N_2) and [2,6-di(trifluoromethyl)phenyl](phenyl)diazomethane (**110b**-N_2) at 350 °C/10^{-4} Torr gave the same two products **111** (38%) and **112** (8%) as volatile products (Scheme 27).[166] Control experiments showed that FVP of **111** under similar conditions gave **112**, suggesting that **112** can be produced by a secondary reaction of **111** as a result of HF elimination. The results are explained in terms

Scheme 26

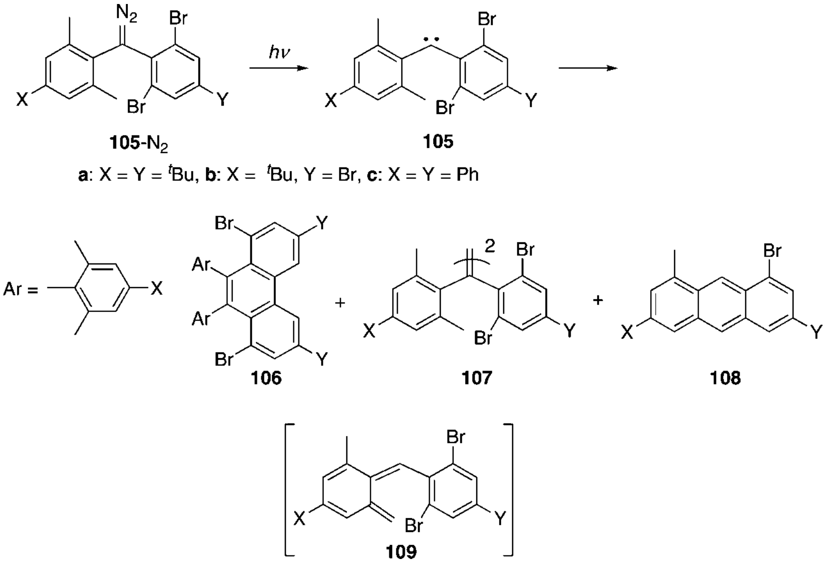


Table 54. ESR Data of (2,6-Dibromophenyl)(2,6-dimethylphenyl)carbenes

Carbene	Matrix	T (K)	$\|D/hc\|$ (cm^{-1})	$\|E/hc\|$ (cm^{-1})	E/D	T_d (K)
105a	MTHF	77	0.423	0.0324	0.0765	
105b	MTHF	77	0.423	0.0326	0.0771	160
105c	MTHF	77	0.348	0.0326	0.0937	

Table 55. UV–Vis Spectroscopic Data of (2,6-Dibromophenyl)(2,6-dimethylphenyl)carbenes[a]

Carbene	Matrix	T (K)	λ_{max} (nm)	T_d (K)
105a	MTHF	-	-	170
105b	MTHF	77	327, 348	160
105c	MTHF	77	315, 349, 391	170

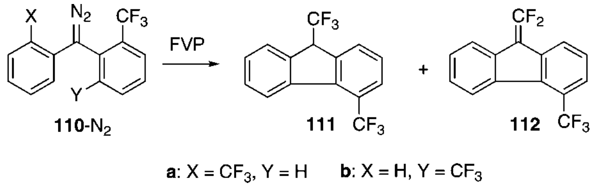
[a] Measured in MTHF at 77 K.

Table 56. Kinetic Data of (2,6-Dibromophenyl)(2,6-dimethylphenyl)carbenes[a]

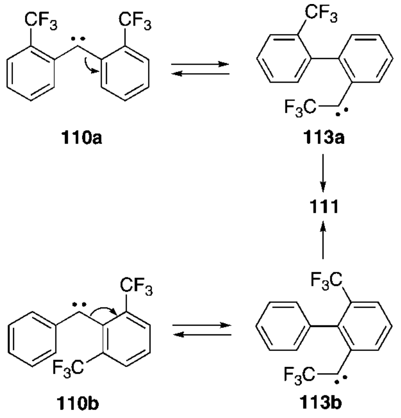
Carbene	T (°C)	λ_{max} (nm)	$2k/\varepsilon l$ (s^{-1})	k_i (s^{-1})	$t_{1/2}$ (ms)	k_{O2} (M^{-1}s^{-1})	k_{CHD} (M^{-1}s^{-1})
105a	rt	370	2.4	0.58	1800	-	-
105b	rt		9.7	-	550	3.1×10^7	3.6×10^2
105c	rt	365	1.7	-	500	2.1×10^7	1.2×10^2

[a] Measured in benzene at room temperature.

Scheme 27



Scheme 28



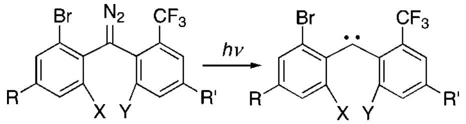
of carbene–carbene rearrangement; the carbene center migrates through the aromatic ring until the center comes to a position where proximate groups can trap the carbene center to give final stable compounds.[14] Thus, carbene **110a** generated by thermolysis of the diazo compound rearranges to give carbene **113a**, which reacts with a phenyl ring to produce **111**, while **110b** rearranges to give **113b**, which eventually produces **111** (Scheme 28). These observations clearly indicate that neither 1,2-fluorine migration nor C–F bond insertion is observed even at this high temperature, demonstrating the unreactive nature of the C–F bonds in carbene chemistry.[166]

Ideally stable triplet DPC may be realized if one can generate diphenylcarbene having four CF_3 groups at all the ortho positions. However, it is synthetically almost impossible to prepare the precursor diphenyldiazomethane. A precursor which we are able to prepare is the one having two CF_3 in addition to two bromine groups at all the ortho positions, e.g., (2,6-dibromo-4-*tert*-butylphenyl)[4-isopropyl-2,6-di(trifluoromethyl)phenyl]diazomethane (**28**-N_2) (Scheme 29).[167]

The carbene generated from **28**-N_2 turned out to be very stable. The ESR signals of **28** were stable and started to decay only at 210 K. In more viscous media, PT, no appreciable changes were observed even at 230 K and measurable decay was observed only at 273 K (0 °C), where the "first-order" half-life ($t_{1/2}$) is approximately 10 min (Table 57).[167]

The lifetime of **28** in degassed benzene at room temperature was too long to be monitored by an LFP system, and a conventional UV–vis spectroscopic method is more conveniently employed in this case (Table 58). The UV–vis spectrum obtained just after photolysis of the diazomethane in benzene at room temperature exhibited characteristic

Scheme 29



28-N_2 **28**
X = Br, Y = CF_3, R = ^{t}Bu, R' = ^{i}Pr

114-N_2 **114**
a: X = Br, Y = CF_3, R = R' = Ph
b: X = CF_3, Y = Br, R = R' = Ph

Table 57. ESR and UV−Vis Spectroscopic Data of Trifluoromethylated Diphenylcarbenes[167]

Carbene	$\|D/hc\|$ (cm^{-1})	$\|E/hc\|$ (cm^{-1})	E/D	λ_{max} (nm)	T_d (K)
28	0.383	0.0247	0.0645	318, 329, 343	210
114a	0.358	0.0281	0.079	357, 506	240
114b	[a]	[a]	[a]	358, 494	260

[a] ZFS parameters could not be determined.

Table 58. Kinetic Data of Trifluoromethylated Diphenylcarbenes[a,167]

Carbene	$2k/\varepsilon l$ (s^{-1})	$t_{1/2}$ (min)	k_{O2} ($M^{-1}s^{-1}$)	k_{CHD} ($M^{-1}s^{-1}$)
28	1.70×10^{-3}	16	8.6×10^5	1.0×10
114a	3.26×10^{-3}	11	4.6×10^5	6.7
114b	2.88×10^{-4}	40	5.4×10^5	6.7

[a] Measured in benzene at room temperature.

features of ^{3}**28**. The transient bands did not disappear completely even after 1 h under these conditions. The deacy was found to be second-order ($2k/\varepsilon l = 1.7 \times 10^{-3}$ s^{-1}), and the approximate half-life ($t_{1/2}$) of **28** was estimated to be 16 min. The rate constant (k_{O_2}) for the quenching of **28** by O_2 was determined to be 8.6×10^5 M^{-1} s^{-1}, and the rate constant (k_{CHD}) of hydrogen abstraction of **28** from CHD was determined to be 1.0×10 M^{-1} s^{-1} (Table 58), which are some 3 and 6 orders of magnitude smaller than those of the parent diphenylcarbene, respectively (Table 58).[167]

We also find that the lifetime is unexpectedly increased simply by changing the position of two protecting groups, CF_3 and Br. Two types of diphenyldiazomethanes having two trifluoromethyl and two bromine groups at the ortho positions, either in unsymmetrical or in symmetrical fashion, that is, (2,6-dibromo-4-phenylphenyl)[4-phenyl-2,6-di(trifluoromethyl)phenyl]diazomethane (**114a**-N_2) and di(2-bromo-4-phenyl-6-trifluoromethylphenyl)diazomethane (**114b**-N_2), were prepared.

UV−vis spectral data for **114a** and **114b** obtained in MTHF at 77 K are listed in Table 57. The absorption bands of **114a** started to decay slowly at 120 K, decayed rather sharply at around 200 K, and were observable up to 240 K. Similar absorption but increased stabilities was noted for **114b**. Thus, the bands of **114b** started to decay slowly at around 140 K, decayed rather sharply at 220 K, but were observable up to 260 K (Table 57). These observations clearly demonstrate anomalous stability of **28** and **114** for a triplet diphenylcarbene, where **114b** is appreciably more stable than **114a**.

Brief irradiation of **114a**-N_2 in degassed benzene at 20 °C produced transient absorption bands of **114a**, showing a strong maximum at 340 nm. The absorption bands decayed very slowly, and the transient bands did not disappear completely even after 2 h under these conditions. The decay was found to be second order ($2k/\varepsilon l = 3.26 \times 10^{-3}$ s^{-1}). The approximate half-life ($t_{1/2}$) of **114a** was estimated to be 11 min. Similar irradiation of **114b** also produced transient bands at 344 nm. The spectrum attributable to **114b** decayed much slower than that of **114a** and did not disappear completely even after standing a day. Triplet diphenylcarbene surviving a day in solution at room temperature is realized for the first time. The decay was also found to be second order ($2k/\varepsilon l = 2.88 \times 10^{-4}$ s^{-1}). The approximate half-life ($t_{1/2}$) of **114b** was estimated to be 40 min.

The rate constants (k_{O_2} and k_{CHD}) measured for **114a** and **114b** are summarized in Table 58. The rate constant (k_{O_2}) for the quenching of ^{3}**114a** by O_2 was determined to be 4.6×10^5 M^{-1} s^{-1}, which is some 4 orders of magnitude smaller than that observed with the "parent" diphenylcarbene ($k_{O_2} = 5.0 \times 10^9$ M^{-1} s^{-1}) and 1 order of magnitude smaller than that observed with the most stable triplet diphenylcarbene thus far mentioned, i.e., di(2,6-dibromo-4-phenylphenyl)carbene (**102d**). The absolute rate constant for the reaction of ^{3}**114a** with the diene, $k_{CHD} = 6.7$ M^{-1} s^{-1}, is approximately 6 orders of magnitude smaller than that observed with the "parent" diphenylcarbene ($k_{CHD} = 1.0 \times 10^7$ M^{-1} s^{-1}).

It is interesting to note here that another carbene (^{3}**114b**) showed essentially identical reactivities toward those typical triplet quenchers, i.e., oxygen and CHD, even though the stability of ^{3}**114b** estimated in degassed benzene and in MTHF is significantly larger than that of its positional isomer ^{3}**114a**.

Photolysis of **114a**-N_2 and **114b**-N_2 in degassed benzene gave a complex mixture. ^{1}H NMR spectra of the irradiation mixtures were too complicated to further characterize the structure. However, some of the fractions obtained by GPC of the photomixture showed a mass peak corresponding to the dimer of carbene **114**.

It is interesting to note here that ^{3}**114b**, having bromine and trifluoromethyl groups at the ortho positions of each of two phenyl rings, showed significantly greater stability than ^{3}**114a**, having two bromine groups at the ortho positions of one phenyl ring and two trifluoromethyl groups at the ortho positions of the other phenyl ring in degassed benzene solution. This indicates that, even if the same two kinds of ortho substituents are introduced, the effect on the stability of triplet diphenylcarbenes depends on how those groups are introduced.[167]

Inspection of the optimized geometries at the UB3LYP/6-31G* level of theory of ^{3}**114a** and ^{3}**114b** indicates that there is only a very slight difference between the two carbenes. This is in accord with the observation that both carbenes showed essentially identical reactivities toward oxygen and CHD. A significant difference in the stability observed in benzene is ascribable to the difference in the decay pathway under these conditions. In the absence of proper trapping reagents, triplet carbenes decay mainly by dimerization. So the difference in the stability is due to that in the rate of dimerization. If one assumes ^{3}**114** has a nearly perpendicular geometry, in ^{3}**114a**, the two carbon atoms of most effective kinetic protector, CF_3 groups, are fixed in the same plane, while, in ^{3}**114b**, they are located in a perpendicular manner. Presumably, the perpendicular alignment of the two most bulky groups is a more effective way to shield

Scheme 30

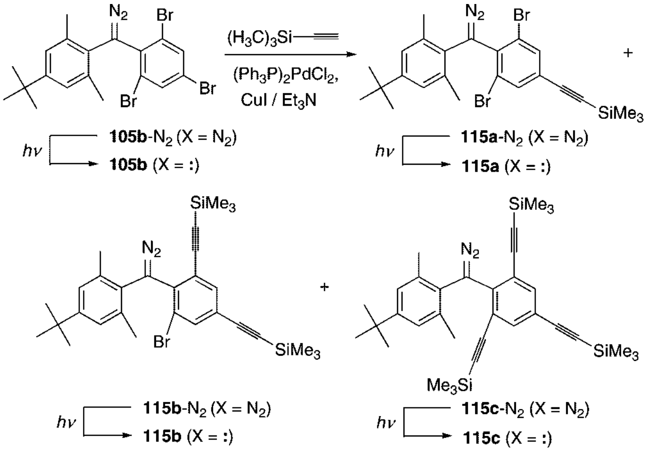


Table 59. ESR and UV−Vis Spectroscopic Data of Diphenylcarbenes[a,170]

Carbene	$\lvert D/hc\rvert$ (cm^{-1})	$\lvert E/hc\rvert$ (cm^{-1})	E/D	λ_{max} (nm)	T_d (K)
105b	0.423	0.0326	0.0771	327, 348	160
115a	0.419	0.0317	0.0756	308, 330	160
115b	0.328	0.0093	0.0285	315, 390	160
115c	0.348	0.011	0.0316	416, 405	160

[a] Measured in MTHF at 77 K.

Table 60. Kinetic Data of Diphenylcarbenes[a,170]

Carbene	k (s^{-1})	τ (s)	k_{O2} ($M^{-1}s^{-1}$)	k_{CHD} ($M^{-1}s^{-1}$)
105b	[9.7][b]	[0.55][c]	3.1×10^7	3.6×10^2
115a	[1.27][b]	[1.3][c]	1.8×10^7	1.7×10^2
115b	0.33	3.0	3.5×10^7	1.0×10^2
115c	3.95	0.25	1.4×10^8	3.4×10^2

[a] Measured in benzene at 20 °C. [b] In $2k/\varepsilon l$. [c] Half-life.

the carbenic center than the planar one from the dimerization. This change in the alignment may not be important for the attack of a smaller and reactive reagent such as oxygen and 1,4-cyclohexadiene.

5.3.1.13. *o*-Ethynylated Diphenylcarbenes. In the procedure employed to prepare those sterically congested diphenyldiazomethanes, diazo functional groups are introduced at the last step of synthesis, since these groups are generally labile and do not survive under chemical procedures for further modification. In other words, kinetic protectors are introduced in the main framework before diazo groups are constructed. This approach has a serious pitfall, since the procedure automatically requires that the kinetic protectors should not be large enough to prevent a subsequent chemical procedure for constructing the diazo group. In other words, the carbene generated from such a diazo precursor should also have a space to be quenched by accepting a reagent externally. This synthetic dilemma needs to be overcome so that a stable triplet carbene can be realized.

We found that a precursory diphenyldiazomethane for a persistent triplet carbene is also persistent for a diazo compound and, hence, can be further modified to a more complicated diazo compound with the diazo group intact. For instance, di(2,4,6-tribromophenyl)diazomethane (**102a**) survives under Sonogashira coupling reaction[168] conditions and undergoes substitution with trimethylsilylacetylene at the para positions, leading to di(2,6-dibromo-4-trimethylsilylethynylphenyl)diazomethane (**102f**).[169] This is obviously due to the fact that the kinetic protectors introduced to protect the carbene center from an external reagent are also able to protect the diazo carbon.

If the bromine group at the ortho position can also be replaced by a substituent with the diazo group intact, it might be possible to introduce a new (possibly more effective) kinetic protector *after* the diazo group is introduced. In order to test this idea, we have attempted exhaustive ethynylation of polybrominated diphenyldiazomethane.[170]

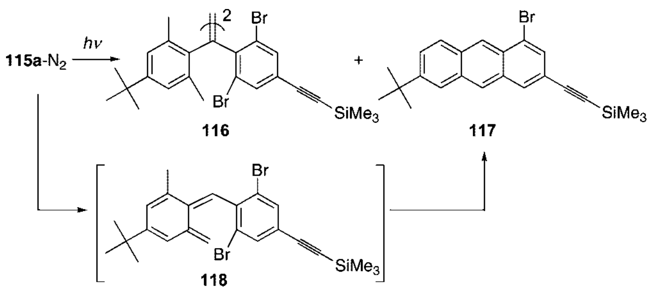
The substrate chosen for the attempt was (2,4,6-tribromophenyl)(4-*tert*-butyl-2,6-dimethylphenyl)diazomethane (**105b**-N_2), in which bromine groups on one side of the phenyl ring are replaced with alkyl groups in order to decrease the possible complexity due to multisubstitution (Scheme 30). The reaction of the diazomethane with 2 equiv of trimethylsilylacetylene in the presence of $(PPh_3)_2PdCl_2$/CuI in NEt_3 at room temperature gave a para-monosubstituted product, (4-trimethysilyethynyl-2,6-dibromophenyl)(4-*tert*-butyl-2,6-dimethylphenyl)diazomethane (**115a**), in 90% yield, along with a small amount of a disubstituted one, [2,4-di(trimethylsilylethynyl)-6-bromophenyl](4-*tert*-butyl-2,6-dimethylphenyl)diazomethane (**115b**), with no trisubstituted product being isolated. When **115a** was treated with 7 equiv of the acetylene at 45 °C for 1 day, **115b** was formed in 30% yield along with a small amount of trisubstituted product, [2,4,6-tris(trimethylsilylethynyl)phenyl](4-*tert*-butyl-2,6-dimethylphenyl)diazomethane (**115c**). On the other hand, when **115b** was reacted with 10 equiv of the acetylene at 45 °C for 1 day, **115c** was obtained in 17% yield. Reactions at a temperature higher than this resulted in a significant loss of the diazo functional group (Scheme 30).

Spectroscopic data (ZFS parameters and UV−vis absorption along with T_d) and kinetic data (k, k_{O_2}, k_{CHD}) are collected in Tables 59 and 60, respectively, which also include the data for triplet diphenylcarbene (^{3}**105b**) before ethynylation for the sake of comparison.

The slight decrease in D values on going from ^{3}**105b** to ^{3}**115a** is interpreted as indicating that unpaired electrons are delocalized into the ethynyl group at the para position. A significant decrease in both D and E/D values on going from ^{3}**115a** to ^{3}**115b** then suggests that, as one more ethynyl group is introduced at the ortho position, unpaired electrons are more delocalized into the substituents simply because of the increasing number of accepting groups. This may also indicate that the central bond angle is expanded due to an increased ortho interaction induced by the trimethylsilylethynyl group. However, the D and E/D values increased slightly on going from ^{3}**115b** to ^{3}**115c**, which was not expected in this interpretation. It is interesting to note here in this connection that significant changes were observed in UV−vis spectra on going from ^{3}**115b** to ^{3}**115c**. It may be, then, that the additional effect of the ortho ethynyl group is not large enough to affect the ZFS parameters. The spectroscopic features provided no evidence for significant through-space interaction between carbene centers and ortho ethynyl substituents.

Optimized geometries calculated for three model triplet (2-X-6-Y-phenyl)(2,6-dimethylphenyl)carbene systems, where the substituents X/Y are varied from Br/Br (**105b′**) to Br/ethynyl (**115b′**) to ethynyl/ethynyl (**115c′**), by DFT(UB3LYP/6-31G(d)) suggest that the angle of the carbene center (α)

Scheme 31



decreases as the substituents X/Y are changed from Br/Br ($\alpha = 171.5°$) to Br/ethynyl ($\alpha = 163.2°$) to ethynyl/ethynyl ($\alpha = 160.6°$). This indicates that the steric interaction decreases as the ortho bromine group is replaced with the ortho ethynyl group. The bond distance between the aromatic ortho carbon and the ortho bromine atom in **105b′** is 1.905−1.906 Å, while that between the ortho carbon and ortho ethynyl carbon in **115c′** is 1.423−1.424 Å, indicating that the ortho ethynyl carbon is located closer to the carbenic carbon than the ortho bromine group. However, the van der Waals radius of Br is larger than that of C. These differences result in the observed difference in the geometrical parameters between **105b′** and **115c′**.

Inspection of the data in Tables 59 and 60 suggests that replacement of the ortho bromine group with the trimethylsilylethynyl group would not result in a significant change in the stability of triplet DPCs. Thus, neither the thermal stability in the matrix at low temperature (T_d in Table 59) nor the half-life and/or lifetime in solution at room temperature (τ or $t_{1/2}$ in Table 60) show a particular trend as the bromine substituent is successively replaced with ethynyl groups. It is important to note here that the decay mode of the triplet carbene changed from second order to first order once an ethynyl group was introduced at the ortho position.

This suggests that carbenes ^{3}**115b** and ^{3}**115c** most likely decayed by reacting with the *o*-ethynyl group. Photolysis of **115a**-N$_2$ (having no ortho ethynyl groups) in degassed benzene gave a dimer, tetra(aryl)ethene (**116**), along with anthracene **117** (Scheme 31).[170] These observations indicate that the decay pattern is not affected by a change in the substituent at the para position.

In marked contrast, similar irradiation of **115b**-N$_2$ and **115c**-N$_2$ (having ethynyl groups at ortho positions) resulted in the formation of a tarry matter.[170]

It has been reported that triplet carbenes react with a carbon−carbon triple bond quite efficiently. For instance, triplet DPC reacts with acetylenes in a stepwise fashion to give a triplet diradical, which eventually results in the formation of indene derivatives.[171] Triplet fluorenylidene reacts with phenylacetylene and other terminal acetylenes even at 77 K to give the corresponding triplet vinylcarbenes.[172]

Therefore, it is likely that the triplet carbene center in ^{3}**115b** and ^{3}**115c** can be trapped by the ethynyl bond at the ortho position to generate a triplet diradical. Probably, the diradical cannot give a stable final product in a simple step, unlike in the case of intermolecular reaction, and hence leads to a complex reaction mixture. 2-(2-Ethynylphenyl)phenylcarbene undergoes intramolecular addition to the ethynyl group to give a cyclopropene derivative.[173] In the present case, an indenylidene in its triplet state may be formed, as the cyclopropene from **115b** and **115c** would be highly strained.

As it is clear that there is a significant difference in the decay pathways between DPC having ortho bromine groups and that having ortho ethynyl groups, it is more useful to compare the reactivity toward typical triplet quenchers in order to examine the role of a kinetic protector on the reactivity of triplet DPC. Inspection of the data in Table 60 again indicated that there are no clear trends in the quenching rate constant to evaluate the effect of the ethynyl group on the reactivity of triplet DPC, as opposed to the bromine group.

5.3.1.14. Phenylated Diphenylcarbenes. The phenyl group is an attractive protector, since, although a singlet carbene is known to add benzene with the formation of norcaradienes and/or cycloheptatrienes,[14] triplet states are usually unreactive toward benzene.[87] The formation of norcaradiene and/or cycloheptatriene in the singlet state may also be prohibited by strain if the phenyl group is introduced at the ortho position, thus making this reaction also inefficient.

However, diphenylcarbene **119** bearing a phenoxy group at the 2 position in cyclohexane gave intramolecular benzene adduct **120**. The reaction was found to be sensitive to the irradiation wavelength; irradiation with a Pyrex filter (>300 nm) afforded a mixture of the isomers (**121**−**123**) at the expense of the norcaradiene **120** (Scheme 32). Control experiments showed that the initial adduct **120** was photolabile and produced these new adducts (**121**−**123**) quite efficiently upon irradiation with light of wavelength >300 nm.[174]

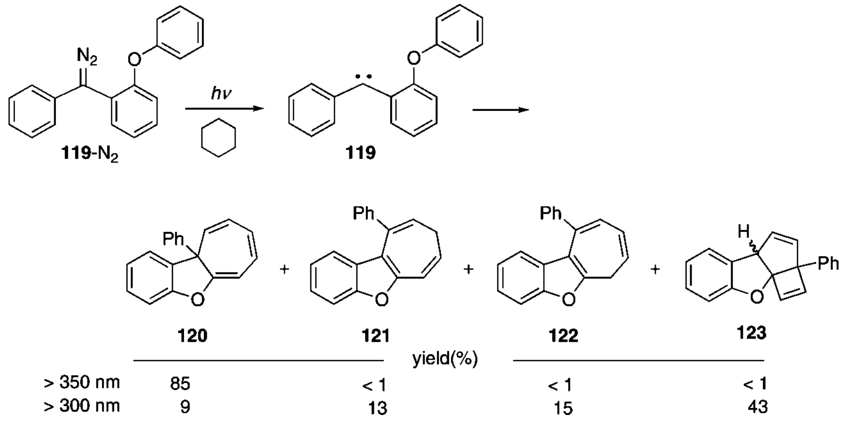
The results indicate that the phenyl group of the ortho phenoxy group locates in a position which allows singlet carbene to react in a normal fashion. Moreover, oxygen atom makes the phenyl ring electron rich and enhances the intramolecular attack of the carbene center.

Introduction of a phenyl group directly at the ortho position should be more attractive, since the location of the phenyl group in this case is less favorable for the intramolecular addition of the carbene than that of **119**. Photolysis of (biphenyl-2-yl)phenyldiazomethane (**124**-N$_2$) in acetonitrile gave 9-phenylfluorene (**127**) as the only product (Scheme 33).[175] Since formation of norcaradiene and/or cycloheptatriene may be prohibited by strain in the intramolecular interaction of the singlet carbene with a phenyl ring at the ortho position, cyclization to give a diradical or *o*-xylylene **125** is proposed for the formation of **127**. In the presence of methanol, the methyl ether (**126**) was formed competitively with **127**, indicating that the cyclization is about as fast as the intermolecular O−H insertion with methanol. The formation of **127** was not significantly affected by triplet sensitization. LFP of **124**-N$_2$ in acetonitrile generated a transient band at 370 nm whose rates of decay ($k = 3.4 \times 10^5$ M^{-1} s^{-1}) are nearly independent of solvents. The 370 nm band was assigned to triplet **127**, since the same absorption was generated by laser excitation of **127**. Thus, **127** must thus be formed during the laser pulse (20 ns) in order for its $T_0 \rightarrow T_n$ absorption to be observed.[175]

Reaction of phenyl(2′,4′,6′-trimethylbiphenyl-2-yl)carbene (**128**) gave, when generated in acetonitrile, the dihydrophenanthrene (**131**) as a result of insertion into C−H bonds of the ortho methyl groups along with a small amount of **132**, while **128** was almost exclusively trapped in methanol (Scheme 34).[175]

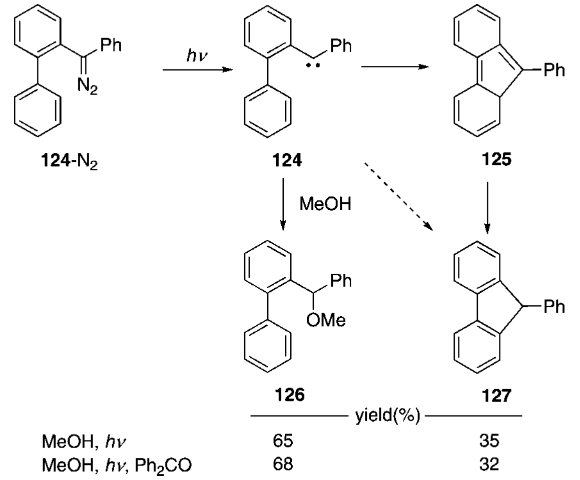
In order to know the effect of the ortho phenyl group as opposed to that of the ortho bromo group on the reactivities of triplet diphenylcarbenes, the chemistries of (2,4,6-triphen-

Scheme 32



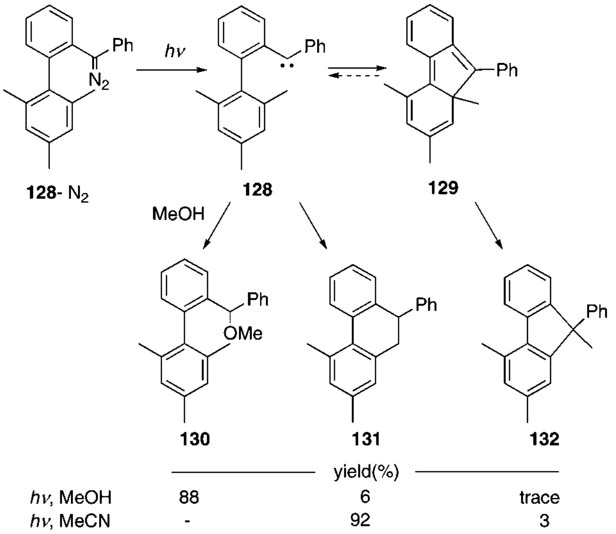
	120	121	122	123
	yield(%)			
> 350 nm	85	< 1	< 1	< 1
> 300 nm	9	13	15	43

Scheme 33



	126	127
	yield(%)	
MeOH, *hν*	65	35
MeOH, *hν*, Ph_2CO	68	32

Scheme 34

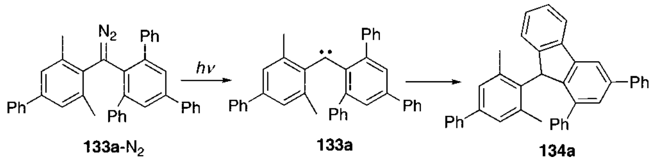


	130	131	132
	yield(%)		
hν, MeOH	88	6	trace
hν, MeCN	-	92	3

ylphenyl)(4-phenyl-2,6-dimethylphenyl)carbene (**133a**) and its unphenylated derivative (2,6-dibromo-4-phenylphenyl)(4-phenyl-2,6-dimethylphenyl)carbene (**105c**) are investigated and compared.[176]

Irradiation of **133a**-N_2 in degassed benzene gave fluorene derivative **134a** as a sole isolable product, with neither dimeric products nor anthracene derivatives being detected (Scheme 35), while similar irradiation of **105c**-N_2 under identical conditions gave a dimeric compound (Scheme 26).[176]

Scheme 35



Spectroscopic data of the triplet state of **133a** (ZFS parameters and UV−vis absorption along with T_d) are collected in Table 61, which also includes the data for ^{3}**105c** before phenylation for the sake of comparison.

A significant decrease in both *E* and *E*/*D* values on going from ^{3}**133a** to ^{3}**105c** suggests that, as phenyl groups are introduced at the ortho position, the central bond angle is expanded due to increased ortho interaction induced by the phenyl group. A slight decrease in *D* values on going from ^{3}**133a** to ^{3}**105c** can then be interpreted as indicating that unpaired electrons are delocalized into phenyl groups at the ortho positions not only because of the increasing number of accepting groups but also because of the expansion of the central bond angle. However, the extent of the increase is rather small when taking into account the increase of the number of phenyl rings. This indicates that ortho phenyl rings are not coplanar with the carbenic phenyl ring (vide infra).[176]

The UV−vis spectrum obtained by photolysis of **133a**-N_2 in MTHF at 77 K showed rather strong and broad absorption bands centered at 356 nm along with apparent maxima at 326 and 387 nm. Since ESR signals ascribable to triplet carbene are observed under identical conditions, the absorption spectrum can be attributable to triplet carbene ^{3}**133a**. The bands are to be compared with those observed for **105c**, which exhibited a strong band at 349 nm along with weak bands at 315 and 391 nm.. The bands disappeared irreversibly at around 130 K. This temperature is to be compared with that observed for ^{3}**105c**, which is shown to survive up to 170 K. A marked decrease in the thermal stability upon replacement of the ortho bromine group with a phenyl group is thus noted.

LFP of **133a**-N_2 in a degassed benzene solution at room temperature produced a transient species showing a broad band with apparent maxima at 420 nm, which decayed in a first-order fashion with the rate constant $k = 7.6 \times 10^4$ s^{-1}, with the lifetime being 13 μs (Table 62). However, the transient species are significantly different from that observed for ^{3}**133a** in a matrix at low temperature and hence are not assignable to ^{3}**133a**. The spectroscopic features and decay profile are in good agreement with that observed in LFP of

Table 61. ESR and UV−Vis Spectroscopic Data of Ortho-Arylated Diphenylcarbenes[a,176]

Carbene	$\lvert D/hc \rvert$ (cm^{-1})	$\lvert E/hc \rvert$ (cm^{-1})	E/D	λ_{max} (nm)	T_d (K)	k_{O2} ($M^{-1}s^{-1}$)	τ
105c	0.348	0.0326	0.0937	315, 349, 391	170	2.1×10^7	500 ms
133a	0.300	0.00486	0.0162	326, 356, 387	130	1.7×10^7	16 μs
133b	0.304	0.00454	0.0149	323, 353, 390	130		
133c	0.308	0.00557	0.0181	316, 341, 376	140		
133d	0.324	0.00873	0.0269	320, 357, 400	130		
133e	0.335	0.00586	0.0175	320, 351, 380	140		

[a] Measured in MTHF at 77 K.

Table 62. Kinetic Data Obtained in LFP of Ortho-Arylated Diphenyldiazomethanes (133-N_2)[a,176]

Diazo Compd. **133**-N_2	λ_{max} (nm)	k (s^{-1})	τ (μs)
a	410	7.6×10^4	13
b	420	7.6×10^4	13
c	480	6.9×10^4	15
d	400	7.1×10^4	14
e	420	8.7×10^4	12

[a] Measured in benzene at room temperature.

134a under the identical conditions. It is thus likely that the transient band observed in LFP of **133a**-N_2 is ascribable to triplet **134a**, which is formed during the laser pulse (20 ns).[176]

When LFP was carried out on a nondegassed benzene solution of **133a**-N_2, transient bands showing apparent maximum at 390 nm that are quite different from that observed in LFP under degassed conditions were observed. The bands are obviously shifted to a shorter wavelength than that observed in LFP of **133a**-N_2 in degassed benzene and can be regarded as the tail part of the absorption bands due to triplet carbene ^{3}**133a**.

This assignment was actually supported by monitoring the decay of the band more carefully. As the band decayed, a new band appeared at 440 nm. The growth rate of the new band was essentially identical with that of the decay rate, indicating that the transient product was trapped by oxygen to generate a new transient product, which is most likely carbonyl oxide **133a**-O_2. Moreover, analysis of the spent solution showed the presence of ketone **133a**-O in 10% yield along with fluorene **134a**.

A plot of the observed pseudo-first-order rate constant of the formation of the oxide against [O_2] is linear. From the slope of this plot, k_{O_2} was determined to be 1.9×10^7 M^{-1} s^{-1}. The intercept gave k_0, the rate of decay of ^{3}**133a** in the absence of oxygen, to be 6.3×10^4 s^{-1} ($\tau = 16$ μs). Essentially the same data are obtained by monitoring the decay of the band at 390 nm ($k_{O_2} = 1.7 \times 10^7$ M^{-1} s^{-1} and $k_0 = 6.0 \times 10^4$ s^{-1}).

LFP of **133a**-N_2 in degassed benzene in the presence of a large excess of CHD resulted in the formation of the same transient bands observed in LFP of **133a**-N_2 in the absence of oxygen, with no other bands being detected. Product analysis studies also indicated that fluorene **134a** was formed almost exclusively even in the presence of a large excess of CHD. Triplet carbene ^{3}**133a**, which is efficiently trapped by oxygen, is not trapped by a less efficient trapping reagent, CHD.

The crucial difference between the present system and (biphenyl-2-yl)phenylcarbene (**124**) is found in the reactivity toward methanol. While a significant amount of O−H insertion product was formed in the reaction of **124**, **134a** was not quenched by methanol at all. This suggests that the singlet state is also protected from external reagent in **134a**.

How well is the carbene center in the triplet state protected by the ortho phenyl groups? The lifetime of 16 μs is unexpectedly small. It is interesting to note here that the quenching rate constant of ^{3}**133a** by oxygen is essentially identical with that observed for ^{3}**105c** ($k_{O_2} = 2.1 \times 10^7$ M^{-1} s^{-1}), whose lifetime under ambient conditions is ca. 1 s. Moreover, ^{3}**105c** was shown to abstract hydrogen from CHD with a rate constant of $k = 1.2 \times 10^2$ M^{-1} s^{-1}, while ^{3}**133a** was not quenched by CHD. This means that the carbenic center in ^{3}**133a** is equally well shielded by the ortho phenyl groups from external reagents, as in ^{3}**105c**. An extremely shorter lifetime of ^{3}**133a** ($\tau = 16$ μs) as opposed to ^{3}**105c** ($\tau = 1$ s) is then interpreted only in terms of reaction of the triplet state with the ortho phenyl groups. This is in accordance with the product study showing that ketone is produced only in 10% yield even in the irradiation in the presence of oxygen (vide supra).[176]

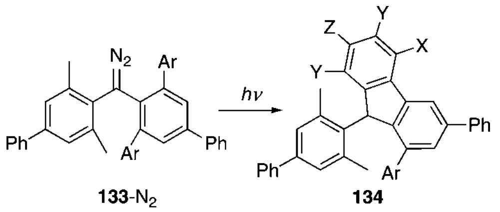
Reaction of sterically congested triplet carbenes with benzene is usually considered to be very slow. Indeed, almost no products from such a reaction have been detected in the photolysis of sterically congested diphenyldiazomethanes. However, methylene is shown to react with benzene both in singlet and triplet states.[177] In the triplet reaction, C−H abstraction is proposed from kinetic studies, but C−C bond formation to generate a diradical intermediate is suggested by theoretical calculations. It is then possible that triplet states can interact with the adjacent ortho carbon of the ortho phenyl group which is in close vicinity. Such an interaction will eventually lead to fluorene by way of isofluorene.

The finding that the carbenic center is almost completely shielded by an ortho aryl group from external reagents indicates that once one can introduce an aryl less reactive toward carbene at the ortho carbon, one will be able to generate a fairly stable triplet carbene. Diphenylcarbenes **133b**−**e**-N_2, bearing a series of substituents (4-Ph, 3,5-$(CF_3)_2$, and 2-F) on the ortho phenyl rings, gave essentially identical results (Scheme 36, Tables 61 and 62), indicating that those substituents exhibit little effect on the overall reaction pathway.[176] The perfluorophenyl group is an attractive candidate in this respect, since C−F bonds are the only bond utterly unreactive toward carbene.[166]

5.3.2. Fluorenylidenes

Although fluorenylidene (FL, **135a**) and diphenylcarbene (DPC) appear similar, their chemistry is quite different. FL

Scheme 36



b: Ar = C_6D_5, X = Y = Z = D
c: Ar = 4-Ph-C_6H_4, X = Y = H, Z = Ph
d: Ar = 3,5-$(CF_3)_2C_6H_3$, X = Z = H, Y = CF_3
e: Ar = 2-F-C_6H_4, X = F, Y = Z = H

Table 63. Bimolecular Quenching Rate Constants for Triplet Fluorenylidene

Quencher	k_q ($M^{-1}s^{-1}$)	ref
MeOH	$(1.2 - 8.6) \times 10^8$	181
Cyclohexane	$(7.7 - 8.3) \times 10^7$	181a
Oxygen	$(1.4 \pm 0.2) \times 10^9$	182

reacts with (*E*)-2-butene to give quite a high yield of cyclopropane in a stereospecific manner.[178] In the reaction of cyclohexane, 9-cyclohexylfluorene is formed as a main product (65%) along with a small amount of escaped products, fluorene (8%) and 9,9′-bifluorenyl (10%). There is no crossover product present in the FL−cyclohexane adduct when generated in an equimolecular mixture of cyclohexane and cyclohexane-d_{12}.[124] FL reacts with benzene to give the equilibrating norcaradiene−cycloheptatriene mixture.[179]

All of those behaviors are completely different from that observed for DPC (vide supra). FL is necessarily planar, but DPC being both bent and twisted may experience severe steric interaction in the transition state of the reaction.

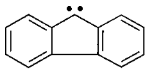
The lifetime of triplet FL is 1 μs in cyclohexane,[180] which is 3 orders of magnitude smaller than that of ^{3}DPC. The observed rate of carbene decay would be a composite of both singlet and triplet elementary reactions. Thus, the lifetime is dependent on an equilibrium concentration of singlet carbene.[50]

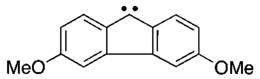
The S−T gaps, ΔG_{ST} (298 K), calculated for FL by B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) using the PCM model are 4.24, 2.36, and −1.05 kcal/mol in the gas phase, cyclohexane, and acetonitrile, respectively. The high level calculation (CBS-QB3) predicts a smaller S−T gap (2.21 kcal/mol) for FL in the gas phase.[50]

Singlet and triplet FL have bands centered at 415 and 470 nm, respectively. The lifetime of ^{1}FL in cyclohexane and cyclohexane-d_{12} is 88 ± 11 and 90 ± 9 ps, respectively, thus suggesting that ^{1}FL does not react with cyclohexane before undergoing intersystem crossing to ^{3}FL. In cyclohexane, 500 ps after the pulse, fluorenyl radical (FLH) begins to appear in the spectra. This indicates that shortly after the singlet−triplet equilibrium mixture of FL is fully established, ^{3}FL begins to react with the solvent.[50] Bimolecular quenching constants for ^{3}FL are listed in Table 63.[181,182]

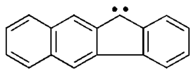
In acetonitrile, the absorption of ^{1}FL at 2 ns is ∼40% of its maximum absorption determined 75 ps after the laser pulse. Thus, it can be deduced that, in the equilibrium mixture, there is ∼60% of ^{3}FL and ∼40% of ^{1}FL, which corresponds to an equilibrium constant $K_{eq} = [^3FL]/[^1FL] = 1.5$ and $\Delta G_{ST} = 0.2$ kcal/mol.[50]

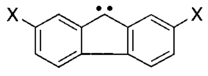
Effects of substituents on the nature of FL have been investigated. 3,6-Dimethoxyfluorenylidene (**135b**) is shown to have a singlet ground state with ΔG_{ST} of ≤ −2 kcal/mol. It is expected that the electron-donating ability of oxygen will raise the energy of the aromatic orbital in relation to that of the nonbonding carbene orbitals. Thus, the perturbation of the nonbonding p type orbital on the carbene carbon by interaction with the occupied orbitals of the fluorenyl residue is expected to be greater for **135b** than it is for **135a**.[143b]


135a
$\Delta G_{ST} \leq 1.9$ kcal/mol



135b
$\Delta G_{ST} \leq -2$ kcal/mol


135c
$\Delta G_{ST} \leq 1.0$ kcal/mol



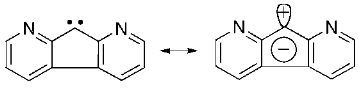
135d
$\Delta G_{ST} \leq 4.2 \pm 0.5$ kcal/mol

On the other hand, ΔG_{ST} of 2,3-benzofluorenylidene (**135c**) is estimated to be less than or equal to 1.0 kcal/mol, about half of what it is for the parent **135a**. One clear difference between **135a** and **135c** is the relative energy of the occupied and unoccupied aromatic orbital that mixes with the p orbital of carbene. The energy of singlet **135c** is predicted to be lowered relative to the triplet by this mixing more than for **135a**.[183]

On the other hand, the energy gap between the triplet and singlet for the three 2,7-dihalofluorenylidenes (**135d**), where X = Cl, Br, and I, is estimated to be 4.2 ± 0.5 kcal/mol, about twice the value of **135a**, regardless of the nature of the halogens. Since the electron-withdrawing abilities of Cl, Br, and I in the meta positions are virtually identical, the properties of **135d** are predicted to be essentially independent of the identity of X.[184]

The effect of substituents on ΔG_{ST} of DPC has been shown to be not so prominent as that for FL. For instance, 4,4′-methoxy substituents do not reverse the normal order of triplet below singlet.[69] The more dramatic effect of substituents for FL is likely to be a consequence of both the smaller energy difference in the parent carbene and a more powerful substituent effect due to the more planar structure of the fluorenyl nucleus.

1,8-Diazafluorenylidene (**136**) has a triplet ground state but reacts primarily from its singlet state. For instance, it inserts into the C−H bonds of cyclohexane and adds to benzene. The rates of these reactions are found to be ∼10^{10} M^{-1} s^{-1}, which is essentially the diffusion encounter limit, and several hundred times greater than the corresponding value measured for **135a**. The nonbonding electrons of the ring nitrogen atoms of **136** are in orbitals with proper symmetry to interact with the in-plain σ-orbital of the carbene. Simultaneously, the ring nitrogen atoms will stabilize the p^2 electronic configuration due to their increased electronegativity and their direct conjugation with the carbene carbon. Due to these two factors, the major contribution to this carbene is suggested to be from the p^2 configuration, which leaves the carbene with a nearly vacant σ-orbital. Thus, the increased electrophilicity is a direct consequence of the higher reactivity of a vacant σ orbital rather than that of a π orbital.[185]



136 p^2

5.3.2.1. 1-Alkylfluorenylidenes. 9-Diazofluorenes **137**-N_2 bearing a series of alkyl (R) groups from Me to ^{t}Bu at the 1-position were prepared and photolyzed to generate the corresponding fluorenylidenes (**137**) (Schemes 37 and 38).[186] In cyclohexane, the ratio of C−H insertion product **138** from singlet fluorenylidenes ^{1}**137** to fluorene **137**-H_2 and 9,9′-bifluorenyl **139** from the triplet state decreased smoothly from 3.26 to 1.84 as the 2-substituent was changed from Me to *i*-Pr. This is interpreted as indicating that the direct insertion of the singlet carbene into the C−H bond of the solvent is subjected to steric repulsion as more bulky groups are introduced and consequently the hydrogen abstraction from the triplet state becomes important. Similar trends were observed in the reaction of **137** with α-methylstyrene and benzene. In benzene, a considerable amount of benzocycloheptatrienes **142** were obtained even in the reaction of **137c** (R = ^{i}Pr). This is in sharp contrast to (2,4,6-triisopropylphenyl)(phenyl)carbene (**88**), which decays almost exclusively by reacting with the C−H bonds of ortho isopropyl groups in benzene.[150] Also, in this case, an appreciable amount of 9,9′-bifluorenyl **139** (17%) was produced while the formation of bifluorenylidene **143** was only <4%. This is in contrast with that observed for sterically congested diphenylcarbenes, which usually decay by dimerization when generated in benzene. Dominant formation of **139** over **143** suggests that the dimerization process becomes energetically less favorable for **137** due to steric repulsion caused by the 1-R group, and the triplet carbene is forced to abstract hydrogen even from the solvent benzene.

The chemistry of **137d** (R = ^{t}Bu) is completely different from that observed for the others. Thus, the carbene decayed mainly by intramolecular interaction with the *tert*-butyl group at the 1-position to give 1,9-ethanofluorene **140** (58%) and 1-(2-methyl-3-propenyl)fluorene **141** (33%), with the solvent adduct formation being a minor process. While the formation of **141** was quenched by CHD, that of **140** was little affected, suggesting that **141** is formed from the triplet state by intramolecular H abstraction, followed by a neophyl-type rearrangement. Again, this is in sharp contrast to the case of (2,4,6-tri-*tert*-butylphenyl)(phenyl)carbene (**86**), which decays almost exclusively by insertion into the C−H bonds of the ortho *tert*-butyl groups.[149]

Direct intramolecular C−H insertion forming **140** is not an energetically favorable reaction, since the approach of the carbene center to the *tert*-butyl C−H bonds is restricted due to the rigidity of the fluorenyl structure. The X-ray structure of 1,2-dihydrocyclopentafluorene indicates that strain causes deformation of one of the aromatic rings to a flat unsymmetrical boat structure.[187]

LFP of **137b**-N_2 (R = Et) and **137c**-N_2 (R = ^{i}Pr) in acetonitrile generated a transient band at 400 and 520 nm, which were assigned to acetonitrile ylide and the radical FLH, respectively. Although a transient band ascribable to the triplet fluorenylidenes (**137b**,**c**) was not observed, their lifetimes were estimated from the first-order growth rate of the ylide at 400 nm to be 38 and 33 ns, respectively. LFP of **137d**-N_2 (R = ^{t}Bu) gave completely different results. Thus, the photolysis resulted in the formation of a transient band at 370 nm, with no other transient bands being observed. The formation of this band followed a first-order kinetics, with a lifetime of 49 ns, and the decay was also found to be first-order ($k = 9.2 \times 10^3\ s^{-1}$). The transient absorption is ascribable to neither the ylide nor the radical and is likely to be an intermediate generated from **137d** as a result of hydrogen abstraction from the *tert*-butyl group. LFP in the presence of CHD resulted in the generation of a transient band at 520 nm at the expense of the 370 nm transient. Accepting that the 520 nm band is ascribable to **137d**-H radical, this observation is in accord with the results of product studies, which indicate that **137d** is quenched by the diene by hydrogen abstraction to form **137d**-H_2 by way of **137d**-H. The rate constant for the reaction of ^{3}**137d** with CHD was estimated to be $k_{CHD} = 1.2 \times 10^8\ M^{-1}\ s^{-1}$. LFP of **137d**-$N_2$ in the presence of oxygen produced a transient band at 450 nm attributable to carbonyl oxide (**137d**-O_2), and the rate constant for the reaction of **137d** with oxygen was determined to be $k_{O_2} = (6.3 \pm 0.3) \times 10^9\ M^{-1}\ s^{-1}$.

Irradiation of **137a**-N_2 in an Ar matrix at 10 K afforded the absorption bands due to ^{3}**137a**. Analogous irradiation of **137b**-N_2 and **137c**-N_2 also resulted in the formation of similar absorption bands due to the corresponding triplet carbenes ^{3}**137b** and ^{3}**137c**, respectively (Table 64). Irradiation of **137d**-N_2, however, produced completely different absorption spectra, which showed no absorption bands due to carbene **137d**. Thus, **137d** is not stable under these conditions.

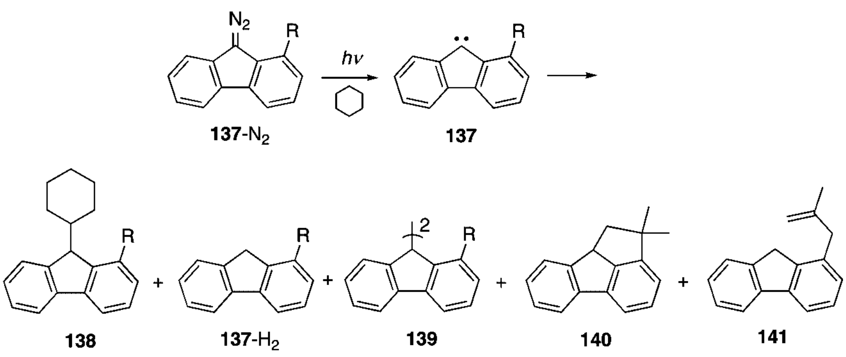
5.3.3. Heteroarylcarbenes

Pyridines having a triplet carbene unit have been successfully employed to generate high heterospin polycarbenes with 2D- and/or 3D-spin networks.[188,189] The strategy is based on the supramolecular chemistry exhibited by pyridine- and polypyridine-metal ions.[190] For instance, magnetic interaction between radical centers and metal ions can be realized through a pyridyl ligand to generate a high spin unit. This system allows us to extend the dimension of the spin network from one (1D) to two (2D) and three (3D) by simple self-assembly between pyridyl groups and metal ions.[191] However, the chemical stability of the triplet carbene in these systems is ignored. In this respect, it is desirable to design and prepare a persistent triplet pyridylcarbene. Triplet di(4-pyridyl)carbenes ^{3}**144a** and **b** having two and four chlorine groups at the ortho positions as a kinetic protector were generated and characterized (Scheme 39).[192]

The ZFS parameters and UV−vis spectral data of **144** are summarized in Table 65. Both *D* and *E*/*D* values decrease from triplet di(4-pyridyl)carbene (^{3}DPyC) to ^{3}**144a** to ^{3}**144b**. The observed decrease in the *D* and *E*/*D* values is then explained as indicating that the carbene bond angle expands as more chlorine groups are introduced at the ortho positions, as a result of steric repulsion between the ortho substituents and increased delocalization of the electrons. The ortho chlorine groups are also expected to stabilize triplet **144** kinetically, by protecting the carbenic center from external reagents.[159] In accord with this interpretation, the thermal stability of triplet **144** increased significantly in this order, as judged from the temperature at which ESR signals and UV−vis absorption bands disappear (T_d).

LFP of **144b**-N_2 in a degassed benzene solution at room temperature produced no apparent new transient absorption band (Table 66). This is obviously because of the inherent weak nature of the absorption band due to ^{3}**144b** (vide supra). However, when LFP was carried out on a nondegassed benzene solution containing **144b**-N_2, a new broad absorption

Scheme 37



	138	137-H2	139	140	141
	yield(%)				
a: R = Me	63.9	2.2	17.4	-	-
b: R = Et	71.3	1.1	25.9	-	-
c: R = ^{i}Pr	63.5	2.9	31.6	-	-
d: R = ^{t}Bu	5.2	0	0	58.0	32.4

Scheme 38

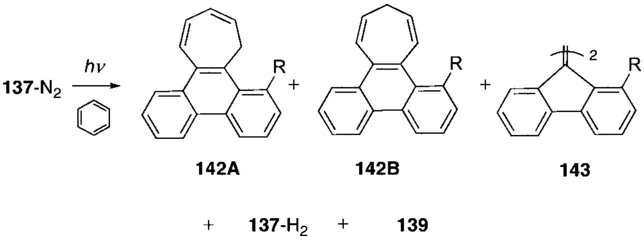


Table 64. UV–Vis Spectroscopic and Kinetic Data of Alkylfluorenylidenes 137[186]

Carbene 137	λ_{max}[a] (nm)	k_{O2}[b] ($M^{-1}s^{-1}$)	k_{CHD}[b] ($M^{-1}s^{-1}$)	τ (ns)
a	252.0, 256.0, 257.0, 260.5 324.0, 438.0, 464.0			1
b	259.0, 324.5, 449.5, 477.5			38
c	255.5, 324.5, 446.5, 479.0			33
d	c	$(6.3 \pm 0.3) \times 10^9$	1.2×10^8	49

[a] Measured in an Ar matrix at 10 K. [b] Measured in acetonitrile at room temperature. [c] Not observed.

Scheme 39

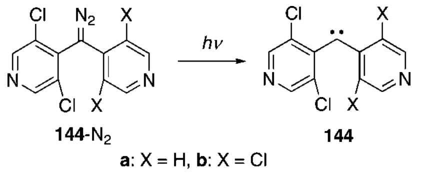


Table 65. ESR and UV–Vis Spectroscopic Data of Chlorinated Di(4-pyridyl)carbenes 144[a,192]

Carbene 144	$\|D/hc\|$ (cm^{-1})	$\|E/hc\|$ (cm^{-1})	E/D	T_d (K)	λ_{max} (nm)
a	0.421	0.019	0.043	180	512, 467
b	0.409	0.013	0.032	200	360, 500

[a] Measured in PT.

Table 66. Kinetic Data of Chlorinated Di(4-pyridyl)carbenes 144[a,192]

Carbene 144	k (s^{-1})	τ (μs)	k_{O2} ($M^{-1}s^{-1}$)
a	7.9×10^5	1.3	6.6×10^8
b	1.7×10^4	60	6.5×10^7

[a] Measured in benzene at 20 °C.

band at 370 nm appeared ascribable to the carbonyl oxide. The spent solution was found to contain di(2,6-dichloro-4-pyridyl) ketone (**144b**-O) as the main product.

From the plot of the apparent build-up rate constant, k_{obs}, of the carbonyl oxide versus the concentration of oxygen, the rate constant for the quenching of ^{3}**144b** by oxygen was determined to be 6.5×10^7 M^{-1} s^{-1}. The intercept of the slope (k_0) was determined to be 1.7×10^4 s^{-1}. The lifetime of ^{3}**144b** was thus estimated to be 60.0 μs.[99] A similar measurement was carried out with another di(4-pyridyl)diazomethane, **144a**-N_2, and the kinetic data are summarized in Table 66.

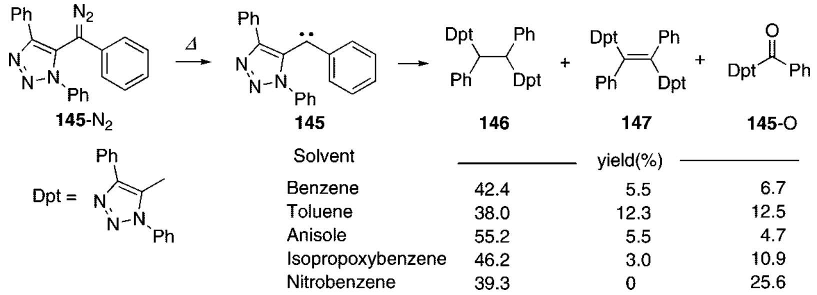
Inspection of the data in Table 66 indicates that chlorine groups at the ortho positions effectively stabilize **144** only when they are introduced at all the ortho positions. The half-life is increased only slightly when two chlorine groups are introduced, but it is increased by 2 orders of magnitude when all the ortho hydrogens are replaced with chlorine groups. The reaction with the most efficient quencher of triplet carbene, i.e., oxygen, is also significantly retarded when four ortho chlorine groups are introduced.

It is interesting to compare the effect of chlorine groups on triplet **144** with that on triplet diphenylcarbenes (DPCs).[159] It has been shown that the lifetime of triplet di(2,4,6-trichlorophenyl)carbene (**100a**) is 18 ms,[159] which is some 4 orders of magnitude greater than that of the "parent" triplet diphenylcarbene ($\tau = 1$ μs). Thus, the effect of ortho Cl on ^{3}**144** is notably smaller than that on ^{3}DPCs.

The ZFS parameter of parent ^{3}DPC ($D = 0.4055$ cm^{-1}) is smaller than that of parent triplet di(4-pyridyl)carbene ($D = 0.437$ cm^{-1}). In addition, the rate of the decrease in D values on introduction of four ortho Cl groups in ^{3}**144**, i.e., on going from ^{3}DPyC ($D = 0.437$ cm^{-1}) to ^{3}**144b** ($D = 0.409$ cm^{-1}), is ca. 6%, which is apparently smaller than the corresponding decrease in DPC, i.e., on going from ^{3}DPC ($D = 0.4055$ cm^{-1}) to chlorinated ^{3}DPC ($D = 0.364$ cm^{-1})[159] (ca. 10%). These results suggest that, in ^{3}**144**, unpaired electrons are more localized on the carbene center than in ^{3}DPCs and are not effectively delocalized to the aromatic ring, even on introduction of ortho Cl groups.

Heteroarylcarbene **145** generated by thermolysis of 5-(α-diazobenzyl)-1,4-diphenyltriazole (**145**-N_2) was studied only

Scheme 40



Solvent	146	147	145-O
	yield(%)		
Benzene	42.4	5.5	6.7
Toluene	38.0	12.3	12.5
Anisole	55.2	5.5	4.7
Isopropoxybenzene	46.2	3.0	10.9
Nitrobenzene	39.3	0	25.6

Scheme 41

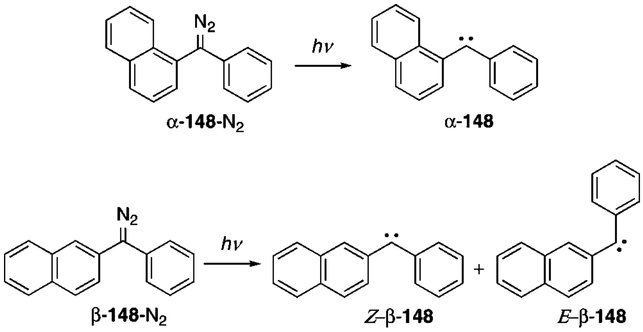


Table 67. ESR and UV−Vis Spectroscopic Data of Naphthyl(phenyl)carbenes[a]

Carbene	*|D/hc|* (cm^{-1})	*|E/hc|* (cm^{-1})	*E/D*	λ_{max} (nm)	ref
α-**148**	0.353	0.016	0.0453	262, 370, ~600	194
β-**148**	0.384	0.020	0.0521	380	194
(*E*)	0.3898	0.0195	0.0500		195
(*Z*)	0.4044	0.0168	0.0415		195

[a] Measured in MTHF at 77 K.

by product analysis. Thermolysis of **145**-N_2 in aromatic solvent at 70 °C afforded the symmetrically tetrasubstituted ethane **146**, the corresponding ethene **147**, and 5-benzoyl-1,4-diphenyltriazole (**145**-O) (Scheme 40). These products, the result of abstraction of hydrogen, dimerization, and reaction with O_2, are those typical of triplet carbenes, and products attributable to singlet carbenes such as ketazine were evidently not formed in significant quantities.[193] Spectroscopic studies and further modification of this type of carbene are desired.

5.4. Naphthyl(aryl)carbenes

5.4.1. Naphthyl(phenyl)carbenes

Two isomers of naphthyl(phenyl)carbenes **148** are investigated and compared (Scheme 41).[194] The ZFS parameters are listed in Table 67. From the *E*/*D* ratio, it is suggested that α-**148** has a less bent geometry than *β*-**148**. In the case of *β*-**148**, the two rotation isomers with $D/hc = 0.3898$ cm^{-1}, $E/hc = 0.0195$ cm^{-1} and $D/hc = 0.4044$ cm^{-1}, $E/hc = 0.0168$ cm^{-1} were observed in a frozen MTHF matrix.[195] The rotation isomers of carbene **148** can be assigned readily from a simple inspection of the nearest spin densities.[195b]

In LFP of **148**-N_2 in deaerated hexane at room temperature, the transient absorption band of triplet α-**148** monitored at 360 nm showed a clean second-order decay ($k/\varepsilon = 1.8 \times 10^5$ s^{-1} cm), while that of triplet *β*-**148** showed a pseudo-first-order decay ($k = 1.9 \times 10^5$ s^{-1} at 380 nm, $\tau = 5.2$ μs) (Table 68).[194] The quenching rate constants of **148** by oxygen and 1,4-cyclohexadiene (Table 68) indicate that the carbene center in α-**148** is better protected against the external reagents than that in *β*-**148**.

Table 68. Kinetic Data of Naphthyl(phenyl)carbenes[a,194]

Carbene	λ_{max} (nm)	k/ε [or k] (s^{-1}cm) (s^{-1})	τ (μs)	k_{O2} (M^{-1}s^{-1})	k_{CHD} (M^{-1}s^{-1})
α-**148**	360, ~600	1.8×10^5	–	$(2.1 \pm 0.1) \times 10^9$	$(1.1 \pm 0.9) \times 10^6$
β-**148**	380, ~600	[1.9×10^5]	5.2	$(3.8 \pm 0.3) \times 10^9$	$(4.6 \pm 0.3) \times 10^6$

[a] Measured in benzene at room temperature.

The absorption (from T_1 to T_0, $\lambda_{max} = 380$ nm) and fluorescence (from T_1 to T_0, $\lambda_{max} = 380$ nm) spectra of triplet were observed by photolysis of **148**-N_2 at room temperature as well as at 77 K.[194] The two-step laser-induced fluorescence lifetime of the excited state (T_1) was consistent with that obtained by transient absorption spectroscopy (from T_1 to T_n, $\lambda_{max} = 450$ nm) at room temperature. From the temperature dependence (77−150 K) of the fluorescence lifetime, the relaxation process of the excited state (T_1) of **148** was examined. The barriers for the nonradiative process were estimated to be 1.72 and 0.6 kcal/mol for α- and *β*-**148**, respectively. This difference is interpreted in terms of the difference in steric crowdedness between the two carbenes.[194]

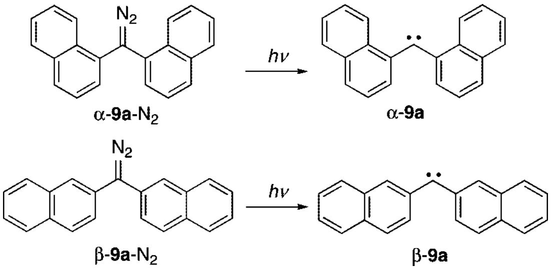
The reactivities of *β*-**148** are compared with those of DPC (**8a**) and *β*-naphthylcarbene (*β*-**6a**). Carbene *β*-**148** reacted with cyclohexane to give naphthyl(phenyl)methylcyclohexane and naphthyl(phenyl)methane. When generated in a 1:1 mixture of cyclohexane−cyclohexane-d_{12}, considerable amounts of crossover products (the methylcyclohexane-d_1 and -d_{11}) were formed, indicating that the carbene−cyclohexane adduct arises via a triplet pathway. Such crossover products are formed in the reaction of **8a**, but not in the reaction of *β*-**6a**. In this regard, *β*-**148** resembles **8a** rather than *β*-**6a**, which reacts primarily through its low lying singlet state. Carbene ^{3}*β*-**148** reacts faster with methanol than does either ^{3}**8a** or ^{3}*β*-**6a**. This indicates that the singlet−triplet energy gap in *β*-**148** is smaller than that in **8a** and *β*-**6a**. Despite the small S−T gap in *β*-**148**, this carbene reacts primarily through its ground triplet state in cyclohexane.[195]

5.4.2. Di(naphthyl)carbenes

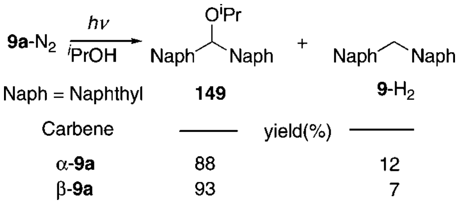
α-Naphthylcarbene (α-**6a**) exhibits lower reactivity and a higher singlet character and possesses a smaller singlet−triplet energy gap (ΔG_{ST}) than *β*-**6a**. In order to examine how these two factors influence the reactivity of sterically more congested diaryl systems, α- and *β*-isomers of di(naphthyl)carbenes (**9**) were generated and their reactivity was examined (Scheme 42).[63]

The reaction of **9a** in 2-propanol gave propyl ether **149a** as a major product along with a small amount of dinaph-

Scheme 42



Scheme 43



Scheme 44

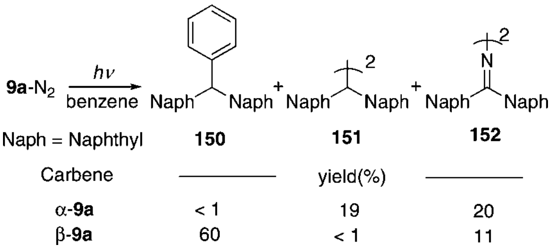


Table 69. ESR and UV−Vis Spectroscopic Data of Di(naphthyl)carbenes[a,63]

Carbene	$\|D/hc\|$ (cm^{-1})	$\|E/hc\|$ (cm^{-1})	E/D	λ_{max} (nm)	T_d (K)
α-**9a**	0.3232	0.0105	0.0325	330, 350, 362, 375, 412	100
β-**9a**	0.3832 0.3971	0.0182 0.0158	0.0475 0.0398	325, 360, 398	80

[a] Measured in MTHF at 77 K.

Table 70. Kinetic Data of Di(naphthyl)carbenes[a,63]

Carbene	$2k/\varepsilon l$ [or k] (s^{-1})	$t_{1/2}$ [or τ] (μs)	k_{O2} ($M^{-1}s^{-1}$)	k_{CHD} ($M^{-1}s^{-1}$)	k_{MeOH}/K ($M^{-2}s^{-1}$)
α-**9a**	7.4×10^4	70	1.7×10^9	1.2×10^4	3.1×10^5
β-**9a**	[1.2×10^6]	[0.83]	$> 10^{10}$	5.0×10^6	$> 10^{10}$

[a] Measured in benzene at 20 °C.

thylmethane **9a**-H_2, with the ratio of **149a**/**9a**-H_2 being increased on going from α- to β-**9a** (Scheme 43). The results indicate that the reaction from the triplet becomes more appreciable in the reaction of α-**9a** than that of β-**9a**.

The reaction with benzene resulted in the formation of products that were much more dramatically affected by the change in the carbene structure (Scheme 44). The reaction of β-**9a** with benzene afforded di(2-naphthyl)phenylmethane (β-**150a**) as the major product along with a small amount of radical dimer β-**151a** and azine β-**152**, whereas similar reaction of α-**9a** resulted in the formation of a small amount of the dimer (α-**151a**) and the azine (α-**152a**) along with a large amount of intractable oil, with no α-**150a** being detected. The formation of a formal insertion product (β-**150a**) into the C−H bonds of benzene in the reaction of β-**9a** is rather unusual, since carbenes react with benzene by the initial attack on the π electrons on the aromatic ring in the singlet state to result in the formation of a norcaradiene and/or cycloheptatriene.[14] The deuterium distributions in the product β-**150a** obtained in the irradiation of β-**9a**-N_2 in a 1:1 mixture of C_6H_6 and C_6D_6 showed that direct insertion products, i.e., β-**150a**-h_6 and -d_6, were formed almost exclusively (>98%), while the yield of scrambled products detected was less than 2%. The results indicate that the C−H insertion product is formed almost exclusively from the singlet carbene β-**9a**. Direct attack of the singlet β-**9a** at the C−H bond of benzene is rather unlikely in light of the decreased electrophilicity as well as increased steric crowdedness. Presumably, as the carbenic center of β-**9a** approaches the π-electrons on the aromatic ring so as to form the norcaradiene, it will experience severe steric hindrance due to the two aromatic rings, and the carbene will thus be forced to follow the pathway to generate a π-complex or a neutral zwitterionic species that will ultimately cascade to **150**. Almost complete absence of the solvent adduct (e.g., α-**150a**) in the reaction of α-**9a** is in sharp contrast with that observed for β-**9a** and can also be explained in terms of the steric effect.

Two sets of signals were observed for β-**9a**, as in the ESR spectra of other triplet naphthylcarbenes, presumably due to the presence of rotational isomers. Inspection of the data in the table indicates that E/D values decrease on going from the β- to α-isomer of **9a**, suggesting that the carbene becomes less bent due to increased steric interaction.

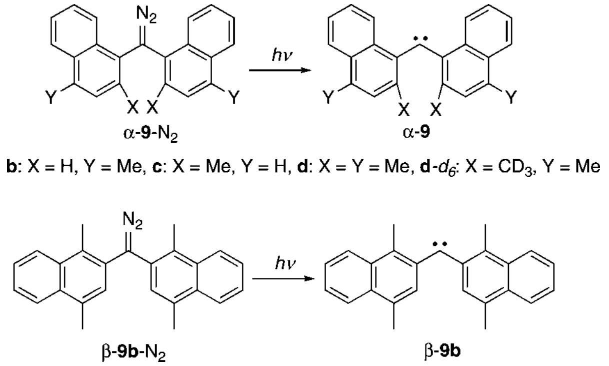
Optical spectroscopy in the frozen medium gave analogous but more intriguing results (Table 69). Careful monitoring of the spectral changes as a function of the temperature revealed a significant difference in thermal stability between the two isomers. Thus, no appreciable changes were observed for the absorption bands ascribable to α-**9a** in MTHF up to 100 K, while the absorption band observed for β-**9a** started to disappear already at 80 K.

LFP of α-**9a**-N_2 in a degassed benzene solution at room temperature produced a transient species showing a strong absorption at 377 nm due to triplet α-**9a**. The decay was found to be second-order, and $2k/\varepsilon l$ was determined to be 7.4×10^4 s^{-1} (Table 70). The rough lifetime of α-**9a** was estimated in the form of half-life, $t_{1/2}$, to be 70 μs. LFP of β-**9a**-N_2 also generated a transient band due to triplet β-**9a**, which decayed in a first-order kinetics ($k = 1.2 \times 10^6$ s^{-1}, $\tau = 0.83$ μs) (Table 70).

Unimolecular vs bimolecular decay kinetics for β- and α-isomers in benzene must reflect the difference in the reaction patterns between the two carbenes. Unimolecular decay of triplet β-**9a** can be interpreted as indicating that the triplet states are trapped by the solvent benzene. However, the product studies clearly suggest that the singlet state is responsible for the final product (**150**). The fact that the optical density of ^{3}β-**9a** is not decreased significantly compared to that of ^{3}α-**9a** under identical conditions, i.e., in degassed benzene at 20 °C, indicates that not all of **150** is produced from the nascent singlet. Thus, monitored ^{3}β-**9a** also leads to the final product either by the pre-equilibrium mechanism or by surface crossing.

The second-order decay kinetics of ^{3}α-**9a**, on the other hand, suggests that the triplet states decay by undergoing dimerization. Product analysis did not support the spectroscopic observation, although the absence of the solvent adducts implies that α-**9a** is unreactive toward benzene.

Scheme 45



Presumably the complexity of the products observed in the reaction of **9a** must be partly due to the complexity associated with the coupling reactions.

Comparison of the lifetime in the form of the half-life of the two carbenes in benzene showed that α-**9a** is some 2 orders of magnitude longer-lived than the *β*-isomer. Since the decay processes are not the same for both carbenes, the stability cannot be discussed simply based on the kinetic data. Nevertheless, the stability order is consistent with that of steric congestion.

The kinetic data obtained in typical triplet quenchers should be more informative in order to estimate differences in the reactivity between the two carbenes in the triplet states (Table 70). The quenching rate constant of $^3\beta$-**9a** with oxygen was too high to be monitored and significantly higher than that of $^3\alpha$-**9a**. The rate constants for hydrogen abstraction from CHD observed with $^3\beta$-**9a** are 2 orders of magnitude greater than that of $^3\alpha$-**9a**. These results suggest that $^3\alpha$-**9a** is considerably less reactive than $^3\beta$-**9a** and can be interpreted in terms of better steric shielding in $^3\alpha$-**9a** than in the corresponding *β*-isomer.[63]

5.4.3. Methylated Di(naphthyl)carbenes

5.4.3.1. Effect of Methyl Groups. The above study reveals that triplet di(naphthyl)carbenes are significantly longer-lived than triplet DPC, confirming the expectation from the structural studies based on the ESR measurement in low-temperature matrices. Thus, triplet di(α-naphthyl)carbene is more than 2 orders of magnitude longer-lived than triplet DPC ($t_{1/2} \sim 2\ \mu$s). This suggests that di(naphthyl)carbene can serve as a more promising prototype diarylcarbene for persistent triplet carbene than DPC. Naturally, one would expect that the lifetime of di(naphthyl)carbene could be elongated by introducing appropriate substituents around the carbene centers. As has been shown in persistent diphenylcarbenes, methyl groups can serve as an exceptionally good protecting group for triplet carbene. Thus, a series of di(naphthyl)diazomethanes (α-**9b**−**d**-N_2 and *β*-**1b**-N_2, Scheme 45) bearing methyl groups on aromatic rings were prepared and the effect of methyl groups on the reactivities of di(naphthyl)carbenes **9** photolytically generated from them was investigated.

Irradiation of methylated **9** in 2-propanol also gave the propyl ether **149** along with dinaphthylmethane **9**-H_2. The product distributions are rather sensitive to the substituents, especially in the case of the α-isomers. Thus, as methyl groups are introduced at the ortho positions of the carbene center, the product from the triplet carbenes, i.e., **9**-H_2, increases rather significantly.

Scheme 46

$$\mathbf{9}\text{-}N_2 \xrightarrow[\text{benzene}]{h\nu} \mathbf{150} + \mathbf{151} + \mathbf{152}$$

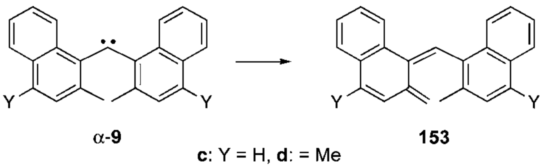
Carbene	150	151	152
	yield(%)		
α-**9b**	< 1	< 1	74
α-**9c**	0	0	0
α-**9d**	0	0	0
β-**9b**	0	0	0

Table 71. ESR and UV Spectroscopic Data of Polymethylated Dinaphthylcarbenes[a,63]

Carbene	|*D/hc*| (cm^{-1})	|*E/hc*| (cm^{-1})	*E/D*	λ_{max} (nm)	T_d (K)
α-**9b**	0.3197	0.0108	0.0337	380	90
α-**9c**	0.3256	0.0089	0.0273	379	110
α-**9d**	0.2490	0.0053	0.0215	384	105
α-**9d**-d_6	0.3265	0.0099	0.0303	383	
β-**9b**	0.3466	0.0173	0.0500	375, 398	95
	0.3484	0.0141	0.0405		

[a] Measured in MTHF at 77 K.

Scheme 47



More dramatic changes in the product distributions are observed in the reactions with other substrates. The photolysis of α-**9c**-N_2 and α-**9d**-N_2 in benzene resulted in a large amount of intractable oil, with almost no meaningful products obtained in the reaction with the “parent” α-**9a** being isolated. A similar but less significant change of the product distributions upon the methyl substitution is also observed in the reaction of the *β*-isomers (Scheme 46).

The zero-field splitting parameters, *D* and *E*, reported in Table 71 indicate that *E*/*D* values steadily decrease as one introduces more methyl groups on the aromatic rings, suggesting that the carbene becomes less bent due to increased steric interaction between the methyl groups.

Optical spectroscopy in the frozen medium gave essentially the same spectral changes observed with the “parent” carbenes. However, the thermal stability and the decay pathway are sensitive to the substitution patterns (Table 71). First, in the case of α-**9**, T_d increases by about 10 K upon ortho methyl substitution (compare T_d between α-**9a** in Table 69 and α-**9c** in Table 71). This is obviously due to increased stability by the protecting ortho methyl groups.

Second, upon thawing the matrix, a new broad absorption appeared around 440−450 nm attributable to *o*-quinodimethanes **153** (Scheme 47), as carbene absorption bands decreased in the case of the $^3\alpha$-**9c** and **d** bearing the methyl group at the ortho position, while all other carbene bands decayed monotonously without showing secondary transient absorption bands.

The LFP of the methylated **9**-N_2 in a degassed benzene solution produced similar transient absorption bands to those observed for “parent” **9a**, although their decay modes and kinetics are sensitive to the substitution patterns (Table 72). Judging from the half-life in benzene, $^3\alpha$-**9** becomes destabilized slightly by the para-methyl groups ($t_{1/2}$ decreases

Table 72. Kinetic Data of Polymethylated Dinaphthylcarbenes[a,63]

Carbene	$2k/\varepsilon l$ (s^{-1})	$t_{1/2}$ (μs)	k_i (s^{-1})	k_{O2} ($M^{-1}s^{-1}$)	k_{CHD} ($M^{-1}s^{-1}$)	k_{MeOH}/K ($M^{-2}s^{-1}$)
α-**9b**	1.1×10^5	28		1.9×10^9	6.6×10^4	~ 10^6
α-**9c**	1.0×10^4	1400		6.5×10^8	2.8×10^3	1.1×10^4
α-**9d**		100000	10.5	1.0×10^8	3.6×10	1.2×10^3
α-**9d**-d_6	3.6×10^3	265000	< 1			
β-**9b**	5.2×10^4	58		1.7×10^9	1.8×10^5	

[a] Measured in benzene at 20 °C.

slightly on going from α-**9a** to α-**9b**) but is stabilized significantly by the ortho methyl groups ($t_{1/2}$ increases significantly on going from α-**9a** to α-**9c**). This can be interpreted in terms of electronic effects, which cause the upper-lying singlet state to be close to the triplet ground states, and steric effects, which stabilize the triplet states kinetically. The introduction of two more methyl groups at the para positions (α-**9c**) resulted in an increase in the lifetime by some 2 orders of magnitude, which can be ascribable to the suppression of the coupling reaction at this position.

However, the reactivities of α-**9** toward typical triplet quenchers, i.e., oxygen and CHD, are also decreased in this order (Table 72). This suggests that the increased stability of α-**9d** in benzene cannot be simply ascribable to the decrease in the reaction sites in its dimerization reaction but to the inherent decrease of the reactivities of the carbene center. It should be noted here that LFP of α-**9d**-N_2 in degassed benzene gave a secondary transient species exhibiting a broad band assignable to *o*-quinodimethane **153d** and that the decay of ^{3}α-**9d** was found not to fit the first-order kinetics and to be slower by half than the growth of **153d**. This suggests that not all of ^{3}α-**9d** decays by intramolecular hydrogen abstraction. In marked contrast, 2,2′-dimethylated carbene α-**9c** decayed rather monotonously without showing any sign of formation of *o*-quinodimethane **153c**. These observations suggest that, while both α-**9c** and α-**9d** carry methyl groups at the ortho positions, ^{3}α-**9d** can decay by abstracting a hydrogen from the ortho methyl groups, whereas this process is not involved in the decay pathway for ^{3}α-**9c**.

A simple explanation for this difference is to invoke the distance between the carbene center and hydrogen on the ortho methyl group. The ortho methyl groups in α-**9d** are brought closer to the carbenic center than those in α-**9c**.[196]

Similar effects of the methyl groups are also observed for the kinetics of the *β*-isomer of the carbene. Thus, on going from *β*-**9a** to *β*-**9b**, the lifetime increased by 2 orders of magnitude, and k_{CHD} decreased by 1 order of magnitude. The kinetic data for *β*-**9b** and α-**9c**, both having protecting ortho methyl groups, should be compared here. Thus, the significantly shorter lifetime in benzene and the larger reactivities toward triplet quenchers of *β*-**9b** as opposed to α-**9c** again suggest the important steric role of peri-hydrogen in the reaction of di(naphthyl)carbenes.[63]

5.4.3.2. Deuterium Isotope Effects. The kinetic deuterium isotope effects (KDIEs) on the intramolecular hydrogen transfer reactions were studied. Irradiation of di[1-(2-trideuteriomethyl-6-methyl)naphthyl]diazomethane (α-**9d**-d_6-N_2) in MTHF at 77 K gave essentially the same transient absorption bands as those observed in the photolysis of the protio analogue (α-**9d**), ascribable to the triplet carbene (α-**9d**-d_6). The bands ascribable to α-**9d**-d_6 decayed monotonously without showing any sign of formation of secondary transient species, i.e., *o*-quinodimethane **153**.

The transient absorption ascribable to α-**9d**-d_6 disappeared monotonously in this case. The decay of ^{3}α-**9d**-d_6 followed a second-order kinetics, and the lifetime of ^{3}α-**9d**-d_6 in the form of half-life was estimated to be 265 ms, which is some three times greater than that of the protio analogue. No new absorption band ascribable to *o*-quinodimethane **153** was detected to the limit of our LFP time scale and detection. Therefore, we could only estimate the highest limit for k_i as $<1\ s^{-1}$. The KDIE on the intramolecular hydrogen transfer reaction was then roughly estimated to be ~10 (Table 72).

5.5. Anthryl(aryl)carbenes

A unique role of the anthryl group on the structure and chemistry of triplet carbenes has been noted. An anthryl ring can be used as a reservoir of the unpaired electrons as well as a steric protector for the carbenic center. In spite of its highly useful nature, the anthryl group has not been employed as a building block for persistent triplet carbenes. A part of the reason for this lies mainly in the difficulty in preparing the nitrogenous precursors. The 10 position is usually attacked when 9-substituted anthracenes are subjected to the procedure necessary to prepare diazo compounds.

5.5.1. Anthryl(phenyl)carbenes

This difficulty is overcome simply by introducing a phenyl group at the 10 position, which enabled us to prepare a series of anthryl(aryl)diazomethanes (**154**-N_2). Anthryl(aryl)carbenes **154**, where aryl groups are phenyl, 2,4,6-trimethylphenyl, and octahydro-1,4:5,8-di(ethano)anthryl, were generated by irradiation of the corresponding diazo precursors (**154**-N_2) and fully characterized by ESR in a rigid matrix at low temperature (Scheme 48 and Table 73).[197]

The ZFS parameters observed for **154** are reported in Table 73. The *D* values of typical diarylcarbenes are in the range of 0.41−0.32 cm^{-1}.[54,79] With the exception of di(9-anthryl)carbene,[198] the *D* values of ^{3}**154** are the smallest ever reported.

The fact that the *D* value of ^{3}**154b** is significantly smaller than that of the "parent" 10-phenyl-9-anthrylcarbene (^{3}**154a**) indicates that the unpaired electrons are extensively delocalized not only onto anthryl but also on phenyl rings.

It is intriguing to examine the effect of the aryl group on the structure of triplet anthrylcarbenes ^{3}**154**. The data in Table 73 clearly indicate that the aryl groups exert considerable effects on the *E* value but little effect on the *D* value. Consequently, the *E*/*D* value decreases rather significantly as more bulky groups are introduced on the phenyl group, suggesting that the central bond angle of ^{3}**154** expands as expected. Little changes in the *D* value on going from ^{3}**154b** to ^{3}**154c** to ^{3}**154d** may mean that the value of *D* is already too small to show a possible change or that delocalizing abilities of aryl groups also vary.

When a MTHF glass containing carbene ^{3}**154b** was warmed gradually in 10 K increments, the ESR signals started to disappear at around 120 K. Since the ESR signals of most triplet diarylcarbenes disappear below 90 K, this means that ^{3}**154b** is thermally fairly stable. The ESR signals of ^{3}**154c** are persistent until 130 K, and those of ^{3}**154d** survive even up to 175 K, where the sample is fluid.[197]

The anomalous thermal stability of ^{3}**154d** is obviously ascribable to the synergetic effects of thermodynanic and kinetic stabilization. Thus, the unpaired electrons are extensively delocalized onto the anthryl group while the carbenic

Scheme 48

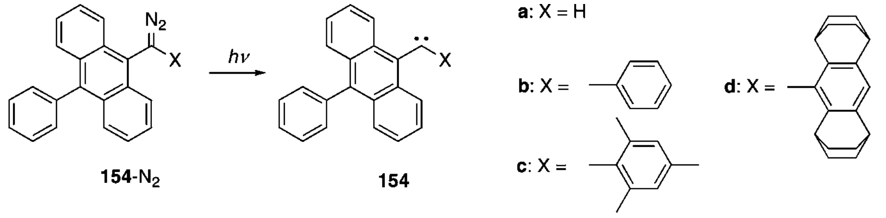


Table 73. ESR Data of 10-Phenyl-9-anthrylcarbenes[a,197]

Carbene **154**	|D/hc| (cm^{-1})	|E/hc| (cm^{-1})	E/D	T_d (K)
a	0.298	0.0133	0.0446	–
b	0.216	0.00632	0.0292	120
c	0.201	0.00348	0.0173	130
d	0.217	0.00289	0.0133	175

[a] Measured in MTHF at 77 K.

Table 74. ESR Data of Di(9-anthryl)carbene

Carbene	Matrix	T (K)	|D/hc| (cm^{-1})	|E/hc| (cm^{-1})	E/D	ref
10a	DAK[a]	4 - 480	0.133	0.0011	0.0083	198
	MTHF	77	0.1038	0.0000	0.0000	20
		110	0.089	0.0000	0.0000	20

[a] Di(9-anthryl) ketone.

center is effectively shielded by bicyclohexyl groups along with the two peri hydrogens.[197]

5.5.2. Di(9-anthryl)carbene

Among the many triplet arylcarbenes, triplet di(9-anthryl-)carbene (**10a**) 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.

Triplet di(9-anthryl)carbene (^{3}**10a**) was first generated in 1971 by photolysis of the corresponding diazo precursor (**10a**-N$_2$) and characterized by ESR spectroscopy in a dianthryl ketone matrix, which revealed small values for both E and D, i.e., 0.0011 and 0.113 cm^{-1}, respectively, at 4 K (Table 74).[198] Annealing the matrix allows the carbene to adopt its minimum energy structure, which is almost completely linear. It has been reported that the half-life of ^{3}**10a** 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 due to an intrinsic lack of reactivity. A solid solution of ^{3}**10a** in viscous glass matrices such as MTHF was stable at 77 K, but, upon warming with a consequent thawing of the matrix, ^{3}**10a** disappeared irreversibly (Tables 74 and 75).[3]

The reactivity of ^{3}**10a** in solution at ambient temperatures was first studied in 1988 in more detail.[199] It was found that ^{3}**10a** underwent a bimolecular self-reaction at the diffusion-controlled limit. Singlet carbene ^{1}**10a** 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 5 × 10^5 M^{-1} s^{-1}, nearly 4 orders of magnitude smaller than the rate constants for many other triplet carbenes (Table 76). Product studies showed that ^{3}**10a** 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.[199]

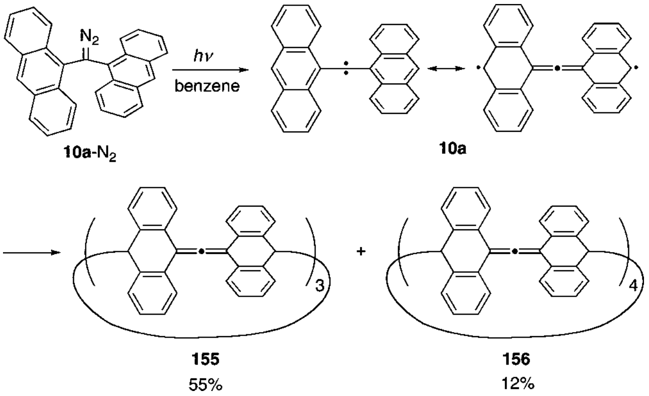
Table 75. UV−Vis Spectroscopic Data of Di(9-anthryl)carbene[20]

Carbene	Matrix	T (K)	λ_{max} (nm)	T_d (K)
10a	MTHF	77	359, 450	-
		85	359, 448	
		115	361, 433	
	PT	77	357, 449	230
		190	357, 445	
		220	359, 430	

Table 76. Kinetic Data of Di(9-anthryl)carbene

Carbene	Solvent	T (°C)	λ_{max} (nm)	k (M^{-1}s^{-1})	τ (μs)	k_{O2} (M^{-1}s^{-1})	ref
10a	MeCN	25	355, 445	7×10^9	-	5×10^5	199
	Benzene	rt	362, 435	-	0.56	4.0×10^8	20

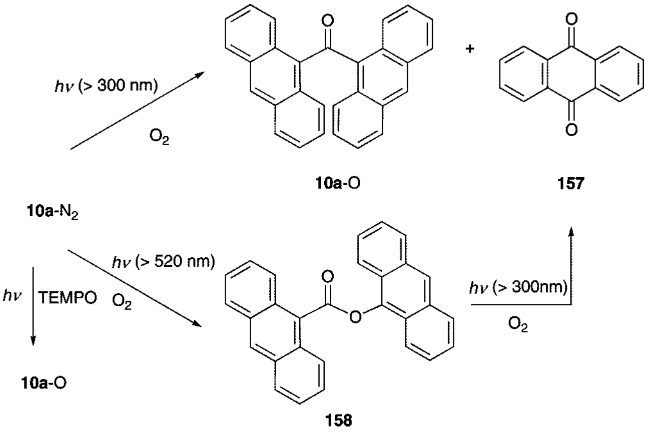
Scheme 49



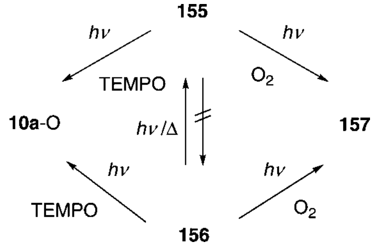
A more detailed study was made in 2002, which revealed that the reaction is very complicated.[20,200] Product analysis study showed that the main product formed by irradiation (λ > 300 nm) of di(9-anthryl)diazomethane (**10a**-N$_2$) in degassed benzene is the trimer of di(9-anthryl)carbene rather than a dimer, as suspected earlier.[199] The structure of the trimer was characterized by X-ray crystallographic analysis to be the one (**155**) formed as a result of 3-fold coupling at the 10 and 10′ positions of di(9-anthryl)carbenes.[200] The tetramer (**156**), formed as a result of 4-fold coupling at the 10 and 10′ positions of **10a**, was also obtained (Scheme 49).

The formation of the oligomers (**155** and **156**) was not quenched even in the presence of typical carbene trapping agents such as methanol and 1,4-cyclohexadiene.

Scheme 50



Scheme 51



However, when the irradiation ($\lambda > 300$ nm) was carried out in a nondegassed benzene solution, two oxidation products, i.e., dianthryl ketone (**10a**-O) and anthraquinone (**157**), were formed at the almost complete expense of oligomer formation (Scheme 50). When the irradiation of **10a**-N_2 was carried out with longer wavelength light ($\lambda >$ 520 nm), 9-anthryl 9-anthracenecarboxylate (**158**) was isolated, which decomposed to give **157** upon further irradiation with shorter wavelength light ($\lambda > 300$ nm) (Scheme 50). It has been shown that carbonyl oxides undergo rearrangement to give dioxiranes and then esters (e.g., **158**) in competition with the oxygen transfer to form ketones.[201] Thus, **158** is proposed to be the most likely precursor for quinone **157**.

The irradiation of **10a**-N_2 in degassed benzene containing 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO) gave dianthryl ketone (**10a**-O) and tetramethylpiperidine in equimolar amounts (Scheme 50).[20]

The oligomers were found to exhibit interesting behaviors, some of which are similar to that of carbene. The trimer (**155**) remained unchanged upon irradiation in degassed C_6D_6 but decomposed in the presence of oxygen to give **157** as the main product. **155** also reacted with TEMPO under irradiation ($\lambda > 300$ nm) to form **10a**-O exclusively (Scheme 51). Irradiation of **156** in degassed C_6D_6 produced **155** almost exclusively. The tetramer exhibited essentially the same reactivity as that of **155** (Scheme 51).

LFP of **10a**-N_2 in a degassed benzene solution at room temperature produced a transient species showing strong, rather sharp bands at 362 and 435 nm. LFP of a nondegassed solution of **10a**-N_2 again produced essentially the same transient species as observed in the LFP of the degassed solution of **10a**-N_2. However, 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 is linear. From the slope and the intercept of this plot, a quenching rate constant by oxygen, $k_{O_2} = 4.0 \times 10^8$ M^{-1} s^{-1}, and $k_0 = 4.1 \times 10^5$ s^{-1} are obtained, respectively. 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 and it is likely that the precursor to the observed species is triplet carbene ^{3}**10a**. However, all attempts to detect the oxide **10a**-O_2 were unsuccessful.

The transient species were not trapped at all by 1,4-cyclohexadiene and methanol, suggesting that the transient species is not a triplet carbene but is likely an intermediate leading to the final products, **155** and **156**.

Although we are not able to detect triplet carbene ^{3}**10a** itself by LFP in solution at room temperature, we can estimate a rough lifetime of the carbene by the Stern−Volmer treatment of trapping experiments with oxygen, assuming that the precursor leading to the species observed is a triplet carbene (either ^{3}**10a**-n or ^{3}**10a**-r). A plot of $\Delta OD^0/\Delta OD$ versus the concentration of oxygen is linear, and the slope is equal to $k_{O_2}\tau$ ($= 5.6 \times 10^3$ M^{-1}). Assuming that k_{O_2} is a diffusion rate constant ($=10^{10}$ M^{-1} s^{-1} in benzene at 20 °C),[111,182] one can estimate k_d to be 1.8×10^6 s^{-1}, $\tau = 0.56$ μs (Table 76).

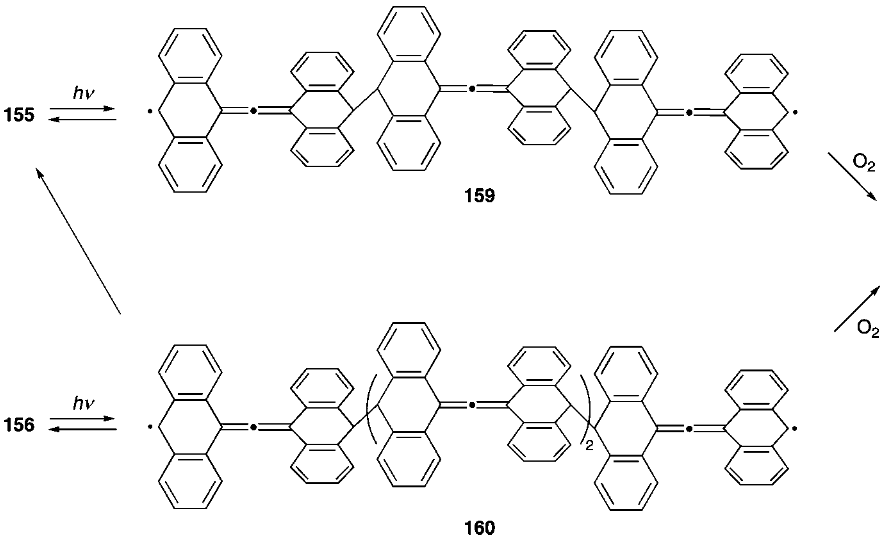
LFP studies indicate that the trimer diradical (**159**) is generated as a main initial product in the photolysis of diazo precursor **10a**-N_2 (Scheme 52). A convenient way to explain the formation of the diradical **159** as a major product is to assume that a monomeric species **10a**-d, formed from **10a**, is in equilibrium with the dimer diradical (**10a**-d)$_2$ and that the mixture decays rapidly to form the trimer diradical **159**, which eventually leads to the trimer **155**. As the trimer diradical was observed as the major transient product at the initial stage of the LFP of **10a**-N_2, this decay pathway is assumed to be very rapid and efficient. The formation of the tetramer **156** from the triplet carbene can then be explained in terms of the dimerization of the dimer diradical, which is in equilibrium with **10a**-d. As the tetramer diradical (**160**) could not be detected by LFP of either **10a**-N_2 or **156**, and given that the dimer diradical decays by a second-order kinetics (to form **156**), it is likely that the dimer diradical undergoes coupling directly to form **156** without recourse to the tetramer diradical **160**. Thus, the apparently puzzling reactions involved in the photolysis of **10a**-N_2, **155**, and **156** can be explained by the pathway shown in Scheme 53, at least qualitatively.

5.5.3. Di(10-aryl-9-anthryl)carbenes

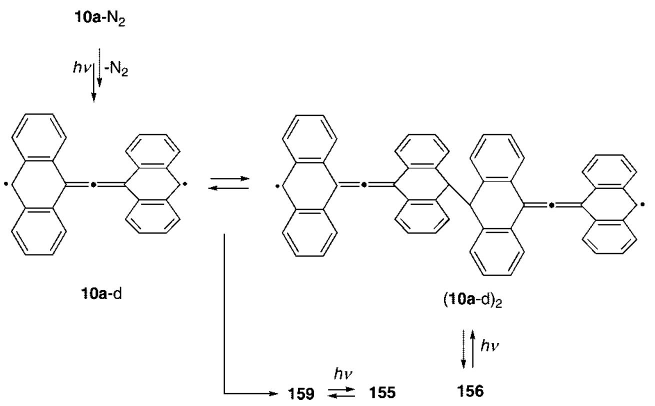
Although di(9-anthryl)carbene (**10a**) seemed ideal for the formation of a stable triplet carbene, it was found to be very ephemeral; its lifetime in a degassed benzene solution at room temperature is 0.5 μs, shorter even than that of triplet diphenylcarbene. This is obviously because it decays by reacting at position 10, where significant spin density builds up for the oligomerization to take place. At the same time, the lack of formation of the olefin-type dimer by coupling two units of ^{3}**10a** at their carbene centers indicates that the carbene center is indeed well shielded and stabilized as mentioned above. It can be inferred that the stability of ^{3}**10a** would increase if the path to its oligomers were somehow quenched. One way to achieve this is introducing a substituent at position C_{10} in order to block the reactivity there.

Di(anthryl)carbene having a phenyl group at position 10 was generated by irradiation of di(10-phenyl-9-anthryl)di-

Scheme 52



Scheme 53



azomethane ($\mathbf{10b}$-N$_2$) in MTHF at 77 K (Scheme 54, Table 77). Di(10-phenyl-9-anthryl)carbene (**10b**) exhibited ESR signals essentially the same as those observed for dianthrylcarbene ^{3}**10a**, indicating that the phenyl groups are not in the same plane with the anthryl rings due to the repulsion between ortho and peri hydrogens. The only difference of the signals between ^{3}**10a** and ^{3}**10b** is the thermal stability. When the MTHF glass containing ^{3}**10a** was warmed gradually, the signals due to ^{3}**10a** started to disappear at around 90 K, while no significant decay of the signals of ^{3}**10b** was observed even at 240 K. A significant decay of the signal of ^{3}**10b** started only at around 270 K (~0 °C), and the signals did not decompose completely even at 300 K (~27 °C) (Table 77).

Irradiation of $\mathbf{10b}$-N$_2$ in a MTHF matrix at 77 K resulted in the appearance of new absorption bands (343, 362, and 475 nm) assignable to ^{3}**10b** (Table 78). When the temperature of the matrix containing ^{3}**10b** was raised gradually, a broad absorption maximum at 475 nm became sharp and shifted to 454 nm at 110 K. Since this is the temperature where the ESR signals shifted due to geometrical relaxation of ^{3}**10b**, these new bands were assigned to the relaxed ^{3}**10b**. They were observed even at 270 K and did not disappear completely even at 300 K. Product analysis of the spent solution showed the presence of a simple carbene dimer (**161b**) as a main product.

LFP of $\mathbf{10b}$-N$_2$ in degassed benzene at room temperature produced transient absorption bands identical to those observed for the relaxed ^{3}**10b** in the low temperature matrix. The bands due to ^{3}**10b** persisted for more than 3 h before disappearing completely. Fitting the decay curve with a second-order kinetics ($2k/\varepsilon l = 5.2 \times 10^{-4}$ s^{-1}), a half-life for ^{3}**10b** of 19 min was estimated (Table 79).

The carbene ^{3}**10b** formed the dimer **161b**, but the product was always accompanied by a significant amount of an unidentifiable tarry component. This suggests that not all the carbene decayed by undergoing dimerization at the carbenic center. It is possible that some of the triplet state still finds a route to react at position 10, since it is obvious that sufficient spin density is localized at this position and moreover the dimerization reaction forming **161b** must suffer from severe steric hindrance in light of the four peri-hydrogens. In order to prevent this pathway, di(9-anthryl-)carbene (**10c**) having 2,6-dimethyl-4-*tert*-butylphenyl groups at each of the two C$_{10}$ positions was generated (Scheme 54). The ESR signals of ^{3}**10c** changed very little even when the matrix was warmed to 300 K and recooled to 100 K. The signal of ^{3}**10c** survived for hours even at 300 K.

Photolysis of $\mathbf{10c}$-N$_2$ in degassed benzene resulted in the appearance of new absorption bands (330, 360, and 452 nm), which are assigned to the triplet carbene ^{3}**10c**, since essentially the same bands were observed with ^{3}**10c** (Table 78). The bands ascribable to ^{3}**10c** were very stable under these conditions; the characteristic absorption bands were clearly observable *even after standing for one week at room temperature*. The decay was too slow to determine the exact kinetics at this temperature. The bands did not decay at a significant rate until the temperature was raised to 70 °C. The decay curve under these conditions was analyzed by a combination of first- and second-order kinetics. At 70 °C, the main decay (77%) was fitted to a first-order kinetics ($k = 1.08 \times 10^{-2}$ min^{-1}, $\tau = 93$ min), while a minor one (23%) was found to be a second-order kinetics ($2k/\varepsilon l = 4.24 \times 10^{-2}$ min^{-1}, $t_{1/2} = 68$ min). The Arrhenius plot of the main (first-order) decay rate is linear, which gives the following kinetic parameters: $A = 1.72 \times 10^{11}$ s^{-1}, $\Delta E = 23.7$ kcal/mol. From the plot, the decay rate at 25 °C is estimated to be 4.8×10^{-5} min^{-1}, *with the lifetime of* ^{3}***10c*** *at 25 °C being 14.5 days* (Table 79).

The marked stability of ^{3}**10c** is also shown in its reaction toward typical triplet carbene quenchers (Table 79). The decay rate of ^{3}**10c** increased dramatically when it was

Scheme 54

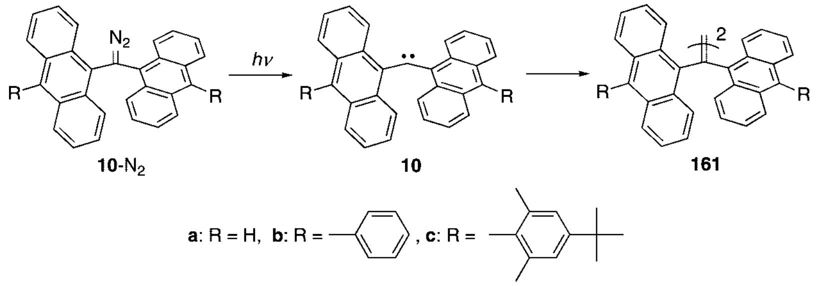


Table 77. ESR Data of Di(10-aryl-9-anthryl)carbenes[a]

Carbene 10	T (K)	$\|D/hc\|$ (cm^{-1})	$\|E/hc\|$ (cm^{-1})	E/D	T_d (K)	ref
b	77	0.105	4.4×10^{-4}	4.2×10^{-3}	270	202
c	110	0.102	7.9×10^{-4}	7.7×10^{-3}	300	206

[a] Measured in MTHF.

Table 78. UV−Vis Spectroscopic Data of Di(10-aryl-9-anthryl)carbenes[a]

Carbene 10	T (K)	λ_{max} (nm)	T_d (K)	ref
b	77	343, 362, 475	300	202
	110	343, 362, 454		
c	77	330, 360, 452	-	203

[a] Measured in MTHF.

generated in the presence of oxygen, and a new broad band with a maximum at 505 nm appeared at the expense of the absorption band due to ^{3}**10c**. The quenching rate constant of the reaction of ^{3}**10c** by oxygen, k_{O_2}, was determined to be 5.5×10^4 M^{-1} s^{-1}, which is about 1/10 of that observed for triplet di(2-bromo-4-phenyl-6-trifluoromethylphenyl)carbene (^{3}**114b**), the most stable triplet diphenylcarbene (k_{O_2} = 5.4×10^5 M^{-1} s^{-1}).[167b]

The absolute rate constant for the reaction of ^{3}**10c** with the diene, k_{CHD}, was determined to be 0.02 M^{-1} s^{-1}, which is some 3 orders of magnitude smaller than that observed for ^{3}**114b** (k_{CHD} = 6.7 M^{-1} s^{-1}).[167b]

A simple modification of triplet di(anthryl)carbene, thus, results in a rather unexpectedly large increase in the stability.

6. Persistent Triplet Carbenes in Constrained Media

Recently, much attention has been paid to the chemistry of carbenes generated within the confines of host compounds.[204] Various carbenes generated in constrained media demonstrate increased selectivity and lifetime, markedly different from those found in solution, since their usual decay pathways are blocked. For instance, fluoro(phenoxy)carbene, an electronically stabilized singlet carbene, does not undergo intramolecular reaction inside the hemicarcerand (HC) host and, hence, persists for days within its HC cage.[205] Hosts used in such studies include cyclodextrins,[206] hemicarcerands,[207] zeolites,[208] and crystals.[209] In spite of those potential interests in the behaviors of persistent triplet carbenes in constrained media, not many attempts to generate and investigate persistent triplet carbenes in constrained media have been made.

6.1. In Zeolites

Ample studies have been carried out on the generation and confinement of reactive intermediates in the cavities and channels of zeolites because the zeolites often allow guest species to have remarkably long lifetimes which normal solution cannot offer at room temperature. For instance, the strongest reducing agent, electrons, is known to be trapped inside the sodalite cages of zeolites A, X, and Y in the form of sodium ion clusters such as Na_4^{3+}.[210] The species is stable and survives even at room temperature in dehydrated zeolites. Stabilization at room temperature was also found for electronically excited states, radicals, and radical ions.[211−213] For instance, room temperature phosphorescence with remarkable lifetimes similar to that at 77 K was observed for aromatic species such as naphthalene and 9-ethylcarbazole confined in a channel-type zeolite L.[211] Presumably, the rigid zeolite medium restricts vibrational and rotational motions of the tightly fitted guest species, leading to a fast intramolecular relaxation process. Spontaneous radical cation formation in acidic zeolites and photochemical generation of radical cations in zeolites with an electron-accepting nature as well as that of radical anions in zeolites with an electron-donating nature have been investigated.[211,212] It was found that the rigid framework of the zeolite hosts serves as an excellent matrix, stabilizing otherwise reactive or unstable radical ions, presumably by immobilization in the inert container, which also protects these species from external attacks. Furthermore, radical persistence was demonstrated for radicals such as benzyl and diphenylmethyl generated in zeolite MFI (ZSM-5).[213]

We have attempted to generate and characterize a triplet carbene, bis(2,4,6-trichlorophenyl)carbene (^{3}**100a**) in zeolites in which a possible dimerization and the reaction with the precursor of carbene are significantly retarded, thus making triplet carbene longer-lived than in solution at room temperature.[214] The adsorption of a corresponding diazomethane (**100a**-N_2), the precursor of **100a**, was carefully examined by comparing the absorption spectrum after adsorption with that of **100a**-N_2 in *n*-pentane, which revealed that **100a**-N_2 was adsorbed with the diazo group intact only in VPI-5, while in other zeolites, **100a**-N_2 was found to be decomposed upon adsorption. This difference in reactivity of the hosts is ascribed to the absence of Brønsted-acid sites in VPI-5. The irradiation (350 nm) of **100a**-N_2 in VPI-5 at 77 K was monitored by emission spectroscopy, which revealed that only the emission due to di(2,4,6-trichlorophenyl)methyl radical (**100a**-H) with λ_{max} = 560 nm was observed under these conditions. This rather unusual observation is ascribable to the fact that, in light-scattering media such as powders, the light travels considerably long path lengths by repeated reflection and refraction at the interface between the void space and the solid particle before coming

Table 79. Kinetic Data of Di(10-aryl-9-anthryl)carbenes[a]

Carbene **10**	T (°C)	λ_{max} (nm)	$2k/\varepsilon l$ (s^{-1})	$t_{1/2}$ [or τ]	k_{O2} ($M^{-1}s^{-1}$)	k_{CHD} ($M^{-1}s^{-1}$)	ref
b	20	344, 362, 454	5.2×10^{-4} s^{-1}	19 min	9.5×10^{4}	0.047	202
c	rt	330, 360, 452	-	[14.5 d]	5.5×10^{4}	0.02	203

[a] Measured in benzene.

Table 80. Selected Bond Lengths and Angles for Diphenyldiazomethanes[218]

Diazo Compound	α (°)	θ (°)	Å			
			d_1 Ar - C	d_2 C - Ar'	d_3 C = N_2	d_4 N = N
8b-N_2	126.9(8)	45.6(8)	1.48(1)	1.45(1)	1.29(1)	1.14(1)
100a-N_2	127.2(2)	70.2(2)	1.469(2)	1.478(2)	1.307(3)	1.138(3)
102a-N_2	127.0(1)	70(1)	1.48(1)	1.48(1)	1.29(1)	1.29(1)
102c-N_2	126.9(4)	67.9(5)	1.473(5)	1.460(5)	1.318(5)	1.129(5)
105b-N_2	126.0(1)	65(1)	1.47(3)	1.47(3)	1.32(3)	1.12(3)
114c-N_2	127.8(4)	80.8(4)	1.471(6)	1.471(6)	1.312(6)	1.152(6)

out. For instance, the diffusely reflected light remains more than 10−20 ps when a single 350 fs white-light continuum pulse was introduced into a 2 mm thick sample of 1−100 μm PMMA [poly(methyl methacrylate)] latex particles, suggesting that the light travels at least a 30−60 times longer path length in a limited space than in a transparent medium.[215] This means that the light can visit the same place many times in the light-scattering medium. An effect similar to this may bring about multiple excitation of the carbenes once generated in the molecular sieve crystals. This will enhance the opportunity for hydrogen abstraction because the excited states of triplet carbenes are known to be more efficient at hydrogen abstraction than the ground-state species.[216]

In accord with this interpretation, the emission due to ^{3}**100a** (λ_{max} = 490 nm) was observed when irradiation was carried out on a translucent glassy sample prepared by submerging VPI-5 incorporating **100a**-N_2 in a refractive index-matching fluid such as propylene glycol or glycerol. ESR signals ascribable to ^{3}**100a** were also observed under these conditions (Table 48). Laser photolysis of **100a**-N_2 in VPI-5 at room temperature with fast detection of both emission and absorption showed that the bands due to **100a**-H were detected in the nanosecond time regime probably because of the extremely fast hydrogen-abstraction by ^{3}**100a**. However, a variable-temperature ESR study showed that the signals due to ^{3}**100a** survive up to 220 K in VPI-5 while the signals disappear at 120 K in MTHF, suggesting that triplet carbene is stabilized in VPI-5.

6.2. In Crystals

Carbenes have been generated in the crystalline solid phase of their precursors both at ambient temperature and below.[217] Reaction selectivities are markedly different from those found in solution at various temperatures and within rigid glassy matrices at very low temperatures because various conformers can exist in liquid solutions and amorphous solids.

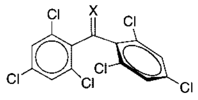
Although fairly persistent triplet carbenes are realized, they are not still stable enough to allow us to isolate and crystallize them for X-ray crystallographic analysis and hence they are generated in a single crystal of the precursor diazomethanes at low temperature in order to characterize the crystal structures of triplet carbenes.

Table 81. Bond Distances between Ortho Carbon Atoms and Ortho Substituents (X) and van der Waals Radius of X for Diphenyldiazomethanes[218]

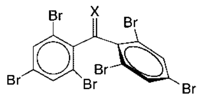
Diazo Compound	ortho Substituent (X)	C - X Å	van der Waals radius of X Å
8b-N_2	H	0.95	1.0
100a-N_2	Cl	1.74	1.75
102a-N_2	Br	1.86-1.90	1.85
102c-N_2	Br	1.88-1.90	1.85
105b-N_2	Br	1.89-1.90	1.85
	CH_3	1.50-1.51 (C - C)	2.0
114c-N_2	Br	1.89-1.90	1.85
	CF_3	1.60-1.61 (C - C)	2.7

6.2.1. X-ray Crystallographic Studies of Precursor Diazomethane

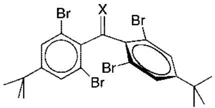
Since the structure of diphenylcarbenes (DPCs) is thought to be affected by that of the precursor to some extent, X-ray crystallographic structures were initially determined for five diphenyldiazomethanes (DDMs, **100a**-N_2, **102a**-N_2, **102c**-N_2, **106b**-N_2, and **114c**-N_2), all having various substituents at the ortho positions, along with **8b**-N_2 having no ortho substituents.[218] Selected bond lengths and angles of the main frameworks of DDMs are listed in Tables 80 and 81, where α is the diazo carbon C−C−C angle and θ is the interplanar angle between the aromatic rings, while d_1 and d_2 are the C−C distances between the aromatic rings and diazo carbons and d_3 and d_4 are the distances between C−N and N−N, respectively.



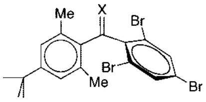
100a-N$_2$ (X = N$_2$)
100a (X = :)



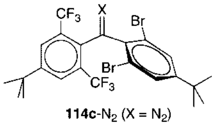
102a-N$_2$ (X = N$_2$)
102a (X = :)



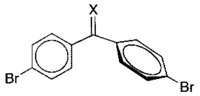
102c-N$_2$ (X = N$_2$)
102c (X = :)



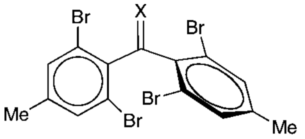
105b-N$_2$ (X = N$_2$)
105b (X = :)



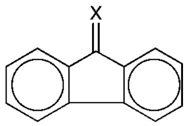
114c-N$_2$ (X = N$_2$)
114c (X = :)



8b-N$_2$ (X = N$_2$)
8b (X = :)



102b-N$_2$ (X = N$_2$)
102b (X = :)



135a-N$_2$ (X = N$_2$)
135a (X = :)

The most prominent structural difference between DDMs having no ortho substituents and those bearing ortho substituents is seen in the interplanar angle (θ) between the two phenyl rings. Thus, in **8b**-N$_2$, this angle is 45.6°, while the angles in other DDMs having ortho substituents are in the range of 65−80.8°. As the angles of diazo carbon (α) change very little on going from **8b**-N$_2$ to the others having ortho substituents, the observation suggests that the steric repulsion between the ortho substituents is mitigated by rotating the phenyl ring along the $C(=N_2)-C(Ar)$ bond rather than by expanding the diazo carbon C−C−C angle. In this way, procarbenic diazo carbon is shielded more effectively from external reagents by the protector. This situation is likely to be maintained in the carbon after losing nitrogen upon photoexcitation.

6.2.2. Persistent Triplet Carbenes Generated in Precursor Diazomethane Crystals. X-ray Crystallographic Studies

A very powerful technique to characterize the crystal structure of highly elusive species emerges. This technique enables us to observe the *in situ* molecular structure of unstable species generated photochemically in a single crystal of an appropriate precursor molecule to the extent that the crystallinity of the sample is retained. Starting with single-crystal-to-single-crystal reaction of various organic and organometallic compounds, the *in situ* method has been successfully used to characterize the molecular structures of very unstable species such as radical pairs from hexaarylbiimidazole derivatives,[219] triplet nitrenes,[220] the photoinduced metastable state of a transition-metal nitrosyl complex,[221] and the triplet excited states of $[Pt_2(H_2P_2O_5)_4]^{4-}$ ion[222a] and $[Rh_2(1,3\text{-diisocyanopropane})_4]^{2+}$ ion.[223]

As an extension of this approach, we have carried out *in situ* observation during the irradiation of a single crystal of a series of diphenyldiazomethanes (DDMs) at low temperature in which the diazo precursors are chosen so as to generate triplet DPCs with different stability. They are **100a**-N$_2$, **102a**-N$_2$, **102b**-N$_2$, **102c**-N$_2$, and **105b**-N$_2$, all of which have various substituents at the ortho positions and can generate persistent triplet diphenylcarbenes, but their lifetimes span from several tens milliseconds to several tens seconds in solution at room temperature. We also used **8b**-N$_2$, having no ortho substituents, and diazofluorene (**135a**-N$_2$), which are not expected to generate persistent triplet carbenes, in order to check the versatility of the method and hopefully to obtain the molecular structure of triplet diphenylcarbenes not perturbed by kinetic protectors.[224]

Photolysis of single crystals of DDMs was performed with slow rotation about the ϕ axis at 80 K using a high-pressure mercury lamp. Low temperature is essential to suppress the thermal motion of dinitrogen molecules trapped in a crystal. Photolysis with unfiltered light from the lamp resulted in gradual decay of the crystal. This is partly because of photoinduced dimerization of carbene generated in the crystal, which usually induced large geometrical changes in a crystal. Therefore, the wavelength of the irradiating light was carefully selected by using appropriate filters.

The crystallinity was retained in the case of the irradiation of **100a**-N$_2$, **102a**-N$_2$, **102c**-N$_2$, and **105b**-N$_2$ under these conditions, while **102b**-N$_2$ and **8b**-N$_2$ showed deterioration upon irradiation. Interestingly, no decomposition was observed for **135a**-N$_2$ even upon prolonged irradiation. Therefore, *in situ* crystallographic analysis was possible only during the photolysis of **100a**-N$_2$, **102a**-N$_2$, **102c**-N$_2$, and **105b**-N$_2$. Reliable crystal data were obtained for the corresponding diphenylcarbenes (DPCs), **100a**, **102a**, and **102c**, while the crystallinity of the irradiated sample of **105b**-N$_2$ was not good enough to characterize the structure of **105b**.

The ORTEP view of **100a** is shown in Figure 7, and the selected bond angles and bond lengths concerning the main framework of **100a**, **102a**,and **102c** are listed in Table 82, where α is the carbene carbon C−C−C angle (deg) and θ is the interplanar angle (deg) between two phenyl rings, while d_1 and d_2 are the C−C distances (Å) between aromatic and carbene carbons, respectively.

Irradiation of a single crystal of **100a**-N$_2$, **102a**-N$_2$, and **102c**-N$_2$ gave rise to signals ascribable to a triplet species with large *D* values. Zero-field splitting (ZFS) parameters estimated from those signals are similar to those observed in MTHF at 77 K for the corresponding triplet carbenes. Thus, it is highly likely that the carbenes generated in a single crystal of DDMs are in the triplet ground state. Theoretical calculations support this assignment (vide infra).

Inspection of the data in Table 82 reveals two interesting features. First, there is only a subtle difference not only in angles (α and θ) but also in distances (d_1 and d_2) between hexachlorinated (^{3}**100a**) and hexabrominated DPCs (^{3}**102a** and **c**), although there are significant difference in bulkiness between their ortho substituents (vide infra). Second, ^{3}**102c** exhibits slightly but clearly different parameters in both angles and distances in comparison to the other two DPCs, especially ^{3}**102a**, which has the same ortho substituents. Thus, on going from ^{3}**100a** and ^{3}**102a** to ^{3}**102c**, α/θ values decrease from 142/86.4 and 141/87.2 to 138/89.9, respectively, and distances d_1/d_2 also decrease from 1.423/1.437 and 1.431/1.425 to 1.375/1.373, respectively. It is noteworthy that the average bond length C(:)−Ar of ^{3}**102c** (1.374 Å) is considerably shorter than those of ^{3}**100a** and ^{3}**102a** (1.430 and 1.428 Å, respectively).

The structures are optimized for the triplet ground states of ^{3}**100a**, ^{3}**102a**, and ^{3}**102c** at the UB3LYP/6-31G(d) and CASSCF/6-31G(d) levels of theory, and the selected bond lengths and angles are given in Table 85.

These results indicate that the structures optimized by CASSCF methods are in better agreement with that observed by in situ X-ray crystallographic analysis than those optimized by DFT.

A potential energy surface of **102a** was calculated as a function of α for both singlet and triplet states in the range of 115−165° in order to explore further the assignment of

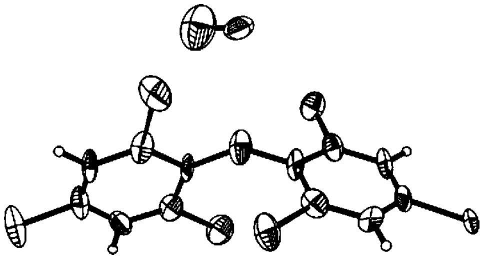


Figure 7. Thermal ellipsoid (50%) plots. A disordered structure of di(2,4,6-trichlorophenyl)carbene **100a**.

Table 82. Selected Geometrical Parameters of the Triplet Carbenes ^{3}100a, ^{3}102a, and ^{3}102c Obtained by X-ray Analysis and Theoretical Calculations[a,224]

Carbene	α (°) Ar-C-Ar	Interplanar angle θ (°) Ar•••Ar	d_1 (Å) Ar-C	d_2 (Å) C-Ar
^{3}**100a**	142(2)	86.4(4)	1.423(16)	1.437(15)
	160.0	*80.79*	*1.375*	*1.375*
	140.5	*81.33*	*1.431*	*1.431*
^{3}**102a**	141(2)	87.2(4)	1.431(18)	1.425(18)
	157.1	*68.75*	*1.379*	*1.379*
	141.4	*83.93*	*1.430*	*1.430*
^{3}**102c**	138(1)	89.9(3)	1.375(17)	1.373(17)
	154.7	*69.46*	*1.383*	*1.382*
	142.0	*84.00*	*1.422*	*1.422*

[a] The values in the first row listed for each carbenes are those obtained by X-ray analysis, while those in the second and third rows are estimated by the theoretical calculations DFT UB3LYP/6-31G(d) and CASSCF(6,8)/6-31G(d), respectively.

the spin state of **102a** in the crystal. The results clearly indicate that ^{3}**102a** is always more stable than ^{1}**102a**. Especially important is the fact that the singlet−triplet energy gap at the angle of 140° is 11.4 kcal/mol, which is large enough to ensure that the spin state could be the triplet state.

The potential energy surface of the triplet DPC in terms of the carbene angle is extremely flat and changes if the angles have little effect on the energies.[36,46b,225] In fact, a potential surface energy calculation of ^{3}**100a**[224] and ^{3}**102a** suggests that the energy difference between 140° and 160° is only 1 kcal/mol. This suggests that experimental α values will be readily affected by the rigidity of environment. This is reasonable in light of the fact that triplet DPCs with sterically congested carbene centers are trapped in a structure dictated by the precursor structure in a rigid matrix, even if this is not thermodynamically the most stable geometry, but undergo geometrical relaxation upon softening the matrix to gain relief from steric compression.

The most likely explanation for the small and large differences in bond length in **100a**, **102a**, and **102c** may be derived from the different packing patterns of these DPCs. The packing patterns of **100a** and **102a** are identical, but that for **102c** is totally different, and hence, their intermolecular interactions should be quite different.

The observation that diazofluorene **135a**-N_2 did not decompose upon irradiation in the crystalline state is rather surprising in light of the fact that most diazo compounds undergo smooth and efficient photodissociation of molecular nitrogen not only in solution at room temperature but also in a rigid matrix at very low temperature.[226]

The molecules are most tightly packed in a **135a**-N_2 crystal among the DDMs employed, as judged by the smallest nonhydrogen atomic volume. This volume is pretty large for **102b**-N_2, which has the smallest reaction cavity but undergoes photodissociation. Thus, it seems that nitrogen cannot easily leave from the procarbenic carbon in the crystal of **135a**-N_2.

7. Concluding Remarks

Our seemingly “never-ending” attempts to isolate triplet carbenes are still in progress. We still do not know how much longer we will have to go from here. All we have learned until now is just how reactive the species are.

One can learn how unstable carbon “radical” species become when the coordinate number changes from three to two. The tricoordinate species, radicals, is serendipitously prepared in solution by Gomberg simply by introducing three phenyl rings.[1] Diphenylcarbene, a dicoordinate counterpart, first generated by Staudinger[7] only about 10 years later, is ephemeral, more reactive even than methyl, the “parent” radical. Perchlorotriphenylmethyl has its half-life on the order of 100 years in solution at room temperature.[227] Even perchlorodiphenylmethyl is stable.[227] However, a divalent counterpart, perchlorodiphenylcarbene, has a half-life of only 18 ms.[160]

It is easy to point out how difficult it is to stabilize triplet carbene. It is not stabilized by a polar effect, either internally or externally, since it is an electronically neutral species. Only a spin-delocalizing substituent may be useful to stabilize it. It has only two substituents, meaning that it has only two handles one can manipulate to stabilize it.

Nevertheless, we managed to increase the lifetime to the extent that we can “see” it at least for a while under normal conditions. We also found an important clue to further increase the stability. A really stable carbene cannot be generated from the diazo precursor prepared according to Figure 6, since the procedure requires that the kinetic protectors should not be large enough to prevent a subsequent chemical procedure for constructing the diazo functional group. In other words, the carbene generated from such a diazo precursor should also have the space to be quenched by accepting a reagent externally. We found that the kinetic protectors introduced around the diazo carbon in order to protect the carbene also are able to protect the diazo carbon equally effectively. This means that we will be able to introduce a secondary protector after the diazo group is introduced. The idea is shown to work very well. For instance, we have been able to prepare, by the addition of benzyne to di(9-dianthryl)diazomethane, di(trypticyl)diazomethane,[39] which is otherwise impossible to prepare.

Persistent triplet carbenes would not merely be of fundamental interest but could also find numerous applications. One of the most attractive areas is molecular magnetism, in which spins of unpaired electrons in π-orbitals of light atoms such as carbon, nitrogen, and oxygen are mainly responsible for the magnetic properties. Actually, many attempts have been made to prepare organic ferromagnetic materials.

The spin sources used in such studies are mostly thermodynamically stable radicals such as phenoxyls,[228] triphenylmethyls,[229] and aminoxyls.[230] This is obviously due to their ease of preparation and use. Triplet carbenes are regarded as a more attractive spin source, since they have two nonbonding electrons on one carbon atom with $S = 1$ and hence higher spin states can be generated by using the same number of units as radicals. In addition, the magnitude of the exchange coupling between the neighboring centers is large.[231] Moreover, since carbenes are easily generated by the photolysis of precursor diazo compounds, high-spin polycarbenes can be generated by the photolysis of diamagnetic diazo compounds even at low temperatures in a rigid matrix.

However, it has been pointed out that those systems have two disadvantages that prevent this approach for practical magnetic materials. First, a triplet carbene unit is highly unstable and lacks the stability for practical application under ambient conditions. This disadvantage appears to be overcome by our efforts to prepare fairly stable triplet carbenes surviving for days. Second, diazo groups, precursors for triplet carbenes, are also generally labile and, hence, cannot be used as a building block to prepare a more complicated poly(diazo) compound. We found, however, that a diazo precursor for a persistent triplet carbene was also persistent for a diazo compound and, hence, can be further modified into a more complicated diazo compound that can generate persistent high-spin polycarbenes. In order to realize persistent high spin polycarbenes, we employed the following three approaches to prepare poly(diazo) compounds: (1) synthesis of dendritic molecules having peripheral diazo groups starting from diazo compounds,[169,232] (2) preparation of a poly(phenylacetylene) bearing a diazo unit using the Rh-complex catalyzed polymerization of diazo compounds bearing a *p*-ethynyl substituent,[233] and (3) preparation of a polymer chain as a result of complexation of the ligand pyridine introduced on diazo compounds with coordinatively unsaturated metal ions.[234] We also characterized the magnetic properties of photoproducts obtained by photolysis of those poly(diazo) compounds.[235] Although the spin-states observed for those photoproducts were not so high at present, the results suggest that our approach using persistent triplet carbenes will eventually lead us to a persistent high-spin polycarbenes by taking advantage of the stability of our diazo compounds.

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