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Structure Determination of Triplet Diphenylcarbenes by in Situ X-ray Crystallographic Analysis

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Abstract: Crystalline-state photoreactions of the following diphenyldiazomethanes were investigated by in situ X-ray crystallography, spectroscopy, and theoretical calculations: bis(2,4,6-trichlorophenyl)diazomethane (**1**-N$_2$), bis(2,4,6-tribromophenyl)diazomethane (**2**-N$_2$), bis(2,6-dibromo-4-methylphenyl)diazomethane (**3**-N$_2$), bis(2,6-dibromo-4-*tert*-butylphenyl)diazomethane (**4**-N$_2$), (2,4,6-tribromophenyl)-(2,6-dimethyl-4-*tert*-butylphenyl)diazomethane (**5**-N$_2$), bis(4-bromophenyl)diazomethane(**6**-N$_2$), and diazofluorene (**7**-N$_2$). Crystal structures of photoinduced triplet diphenylcarbenes (DPCs) of **1**, **2**, and **4** were determined. We found remarkable differences between their structural information obtained in the crystalline state and that previously obtained spectroscopically in a glass matrix. Although the triplet DPCs of **1**, **2**, and **4** have significantly different stabilities in solution, only subtle differences in their structural parameters, except for their C(:)−Ar bond lengths, are observed. It is noteworthy that the average bond length of C(:)−Ar for **4** (1.374 Å) is considerably shorter than those for ^{3}**1** and ^{3}**2** (1.430 and 1.428 Å, respectively), provided that the two C(:)−Ar bonds being compared were chemically equivalent. The most likely explanations for the small and large differences in bond lengths in **1**, **2**, and **4** may be derived from the packing effect. The packing patterns of **1** and **2** are identical, but that of **4** is totally different from those of **1** and **2**. Moreover, these results are interpreted as indicating that triplet DPCs undergo relaxation upon softening of the environments. Theoretical calculations indicate that the potential energy surface of triplet DPCs in terms of the carbene angle is extremely flat and changes in the angles have little effect on the energies. Triplet DPCs with a sterically congested carbene center are trapped in a structure dictated by the precursor structure in a rigid matrix, even if this is not the thermodynamically most stable geometry, but undergo geometrical relaxation upon softening the matrix to relieve steric compression. ESR studies indicate that the interplanar angles are more flexible than the bond angles.

Introduction

The past two decades have witnessed tremendous advances in techniques to observe highly elusive species with only fleeting existence at room temperature.[1] Generation of extremely reactive molecules under low-temperature matrix isolation conditions has provided considerable information on these otherwise elusive molecules.[2] Time-resolved laser experiments have permitted the spectroscopic detection of ephemeral species with lifetimes as short as picoseconds.[3] Moreover, rapid advances in computational chemistry have made it possible to predict the structures and properties of reactive intermediates fairly precisely.[4] Thus, researchers' understanding of the properties of these highly elusive species has been deepened tremendously. This is especially important since one of the central objectives of the study of chemistry is sufficient knowledge to permit the forecasting of the chemical and physical properties of a substance directly from its structure and since it is the properties of these reactive intermediates that often control the outcome of chemical reactions.

Other approaches to reactive intermediates have also been investigated. Organic chemists have attempted to isolate oth-

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erwise transient species by chemical modification. Many of those species have been stabilized, some of which have been isolated under ambient conditions[5] and even structurally fully characterized by X-ray crystallographic techniques. Such "direct" observations, reinforced by theoretical predictions, have revealed many previously unknown aspects of those species.

Carbenes became very attractive target molecules. Carbenes are neutral, divalent derivatives of carbon. The carbene atom has two electrons, not involved in bonding, that can be spin-paired (singlet state) or unpaired (triplet state). Thus, the species presents many challenging issues, not present in other reactive species, such as the effect of structure on singlet−triplet energy gap, chemical reactivities of each state, intersystem-crossing efficiency, and so on.[6] A great deal of spectroscopical[7] as well as theoretical works[8] have been devoted to these issues and have revealed the nature of the species in considerable detail.

Simultaneously, efforts to stabilize and isolate those highly elusive species have also been made.[9] Singlet carbenes undergo thermodynamic stabilization more easily than the triplet states and are stabilized with substituents such as R_2N and R_2P. Some of these species are thermodynamically more stable than their alkene dimerization products. The structures of those carbenes are fully characterized by X-ray crystallographic analysis.[10,11]

Stable forms of triplet carbenes are more difficult to obtain.[9] The dimerization reactions of triplet methylene, phenylcarbene, and vinylcarbene are exothermic by 728, 628, and 610 kJ/mol, respectively, indicating that conjugation with π systems will not lead to thermodynamically stable triplet carbenes.[9g] Hence, kinetic stabilization is a more promising approach to persistent triplet carbenes.

A great effort to stabilize triplet carbenes has been made, by which fairly stable ones have been realized.[12] However, they are still not stable enough to be isolated under ambient conditions. Thus, it is still not possible to obtain a crystal of stable triplet carbene for X-ray crystallographic analysis.

A very powerful technique to characterize the crystal structure of highly elusive species emerges. This technique enables us to observe in situ the 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,[13] triplet nitrenes,[14] the photoinduced metastable state of a transition-metal nitrosyl complex,[15] and triplet excited states of $[Pt_2(H_2P_2O_5)_4]^{4-}$ ion[16] and $[Rh_2(1,3\text{-diisocyanopropane})_4]^{2+}$ ion.[17]

In light of the fact that even the structures of very persistent triplet diphenylcarbenes (DPCs) have been characterized only by "indirect" spectroscopic methods,[18] it is very tempting to use this in situ method to characterize the structures of triplet carbenes. The fact that carbenes can be efficiently and cleanly generated by photolysis of precursor diazo compounds[19] makes the idea feasible. Actually, we have shown that triplet bis(2,4,6-trichlorophenyl)carbene (**1**), photolytically generated in a single crystal of the corresponding precursory diazo compound, could be structurally characterized by using this method. In this way, the molecular structure of triplet diphenylcarbene was revealed for the first time.[20]

As an extension of this approach, we have carried out the in situ observation of photoinduced DPCs in single crystals of a series of diphenyldiazomethanes (DDMs) at low temperatures. The diazo precursors were chosen so as to generate triplet DPCs with different stabilities (Chart 1). Those chosen are bis(2,4,6-tribromophenyl)diazomethane (**2**-N_2),[21] bis(2,6-dibromo-4-methylphenyl)diazomethane (**3**-N_2),[21] bis(2,6-dibromo-4-*tert*-butylphenyl)diazomethane (**4**-N_2),[21] and (2,4,6-tribromophenyl)-(2,6-dimethyl-4-*tert*-butylphenyl)diazomethane (**5**-N_2),[21] in addition to bis(2,4,6-trichlorophenyl)diazomethane (**1**-N_2),[22] all

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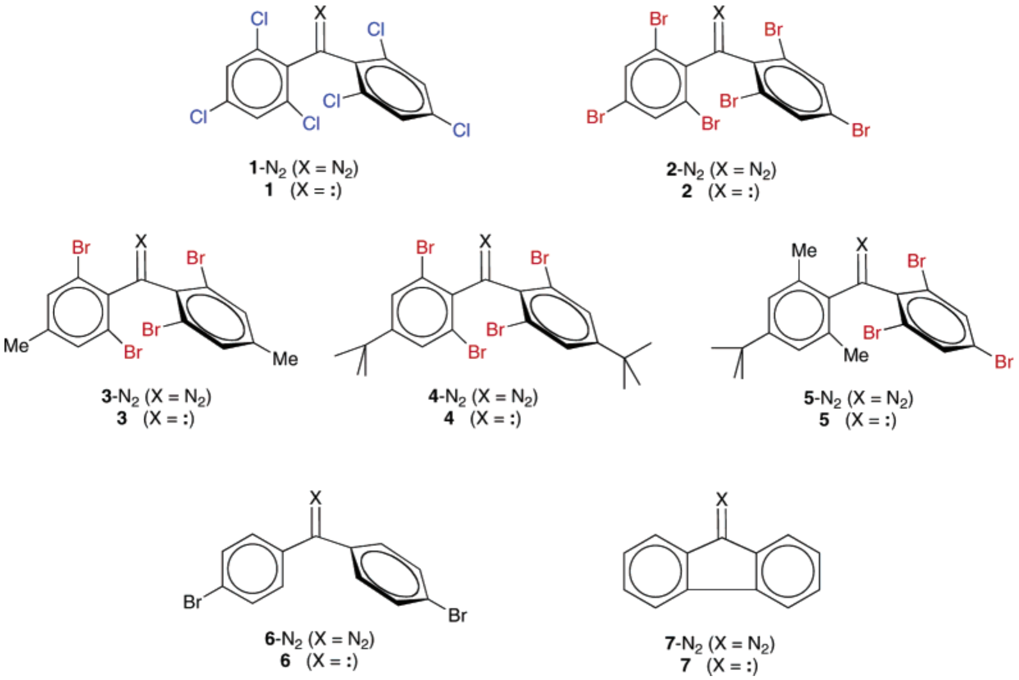
Chart 1



of which can generate persistent triplet DPCs, but their lifetimes span from several tens of milliseconds to several tens of seconds in solution at room temperature. Thus, one will be able to obtain direct information on how the stability of DPCs is affected by the substituents if one compares the structural parameters obtained from X-ray crystallographic analysis. We also used diaryldiazomethanes having no ortho substituents, i.e., bis(4-bromophenyl)diazomethane (**6**-N_2)[23a] and diazofluorene (**7**-N_2),[23b] which are not expected to generate persistent triplet carbenes, in order to check the versatility of the method and, it is hoped, to obtain the molecular structures of triplet DPCs not perturbed by kinetic protectors. We found remarkable differences between the structural information obtained in the crystalline state in this work and that obtained previously, spectroscopically, in a glass matrix.

Results and Discussion

X-ray Crystal Structures of Precursor Diazo Compounds. In order to analyze the crystal structures of triplet DPCs generated in a crystal of DDMs, the crystal structures of the DDMs themselves must be clarified in connection with the photochemical reactivity of the crystal sample and the molecular structures of the triplet carbenes to be generated within the crystal.

Crystals suitable for X-ray analysis were obtained for all seven DDMs shown in Chart 1. Crystallographic information on the DDMs studied in this work is provided in the Supporting Information (Chart 2).[24]

We carried out DFT calculations (RB3LYP/6-31G*) for all DDMs employed in order to examine how well theoretical calculations can reproduce the experimental structural parameters determined by X-ray crystallography. The selected bond lengths and angles are displayed in Table 1. Comparison of the calculated and experimental data indicates that the calculated values for the diazo carbon C−C−C angle (θ) and the C−C distances (d_1, d_2) between aromatic and diazo carbons and the distances (d_3, d_4) between C−N_1 and N_1−N_2 are in fair agreement with the observed ones (<±1.4° for θ and ±1% for d values). On the other hand, the difference between the calculated and observed values for the interplanar angle (ω) is slightly larger, being <±3% for DDMs having ortho substituents and increasing to 10% for DDM having no ortho substituent (**6**-N_2). This can be interpreted as indicating that this angle is sensitive to the crystal environment, presumably due to a shallow energy surface along the rotation of the phenyl rings along the $C(=N_2)$−Ar bond. These results indicate that DFT methods can reproduce the diazo carbon C−C−C angle (θ) and the C−C distances (d_1−d_4) in the crystalline state reasonably well.

Characteristic differences in the crystal packing among these DDMs should also be noted here in connection with the photochemical reactivity of the crystal sample and the molecular structures of the triplet carbenes to be generated within the crystal (vide infra). Generally speaking, the molecules are three-dimensionally connected with two kinds of contacts, i.e., π−π stacking interaction between phenyl rings and dipolar interaction between positively charged nitrogen atoms of the diazo group and negatively charged halogen atoms (only for halogenated DDMs).

The interplanar distances (due to π−π stacking interaction) are very similar for **1**-N_2, **2**-N_2, **3**-N_2, and **6**-N_2 (3.5−3.6 Å), where the stacking is observed. However, for DDMs having *tert*-butyl groups, i.e., **4**-N_2 and **5**-N_2, π−π stacking interaction between phenyl rings is not seen, probably due to the bulkiness of the butyl group. In diazofluorene **7**-N_2, the molecules are tightly packed without π−π stacking. On the other hand, the distances N···Br (due to dipolar interaction) range from 3.1 Å

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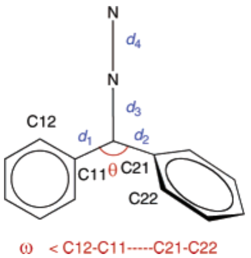
Table 1. Selected Bond Lengths and Angles for **1**-N_2 to **7**-N_2[a]

		θ, deg Ar–C–Ar	dihedral angle ω, deg Ar···Ar	d_1, Å Ar–C	d_2, Å C–Ar	d_3, Å C=N_2	d_4, Å N=N
1-N_2		127.1(1)	87.09 (2)	1.480(1)	1.477(1)	1.326(1)	1.141(1)
		126.3	*88.93*	*1.480*	*1.480*	*1.313*	*1.140*
2-N_2		127.6(1)	86.45(4)	1.470(2)	1.479(2)	1.329(2)	1.135(2)
		126.3	*85.55*	*1.480*	*1.480*	*1.311*	*1.140*
3-N_2		125.6(1)	82.46(5)	1.480(2)	1.479(2)	1.319(2)	1.137(2)
		126.2	*85.41*	*1.481*	*1.481*	*1.310*	*1.141*
4-N_2		127.0(1)	87.74(2)	1.480(1)	1.479(1)	1.324(1)	1.137(1)
		126.2	*84.69*	*1.481*	*1.481*	*1.310*	*1.141*
5-N_2	molecule 1	125.8(1)	85.36(5)	1.481(2)[b]	1.491(2)[c]	1.314(2)	1.143(2)
	molecule 2	125.4(1)	82.95(4)	1.476(2)[b]	1.490(2)[c]	1.318(2)	1.140(2)
		126.9	*88.77*	*1.479*[b]	*1.491*	*1.310*	*1.145*
6-N_2		127.9(1)	46.61(3)	1.464(2)	1.484(2)	1.314(2)	1.146(2)
		126.5	*52.32*	*1.477*	*1.477*	*1.311*	*1.146*
7-N_2	molecule 1	109.5(2)	1.36(13)	1.460(3)	1.460(3)	1.317(3)	1.134(3)
	molecule 2	109.4(2)	1.12(10)	1.455(3)	1.451(3)	1.322(3)	1.133(3)
		109.0	*0.00*	*1.461*	*1.461*	*1.303*	*1.145*

[a] The values shown in italics are those calculated at the RB3LYP/6-31G* level of theory. [b] Ar($PhBr_3$)−C bond distance. [c] Ar($PhMe_2$-*t*-Bu)−C bond distance.

Chart 2



(for **2**-N_2) to 3.4 Å (for **5**-N_2). In **3**-N_2, there is no special short contact between N and Br (>3.5 Å).

The reaction cavity volume about a diazo group surrounded by the spheres whose centers and radii are the neighboring atomic positions and the van der Waals radii plus 1.2 Å, respectively, is the smallest (1.2 Å^3) for **3**-N_2, followed by **6**-N_2 and **7**-N_2, while **4**-N_2 has the largest volume (2.9 Å^3). DDMs having no protecting group around the diazo carbon, i.e., **6**-N_2 and **7**-N_2, have a more planar structure and hence are tightly packed.

In Situ Observation of DPCs Induced by Irradiation of Single Crystals of DDMs at Low Temperature. Photolyses of single crystals of DDMs (**1**-N_2 to **7**-N_2) were performed with slow rotation about the ϕ axis at 80 K using a high-pressure mercury lamp. Low temperature, close to the boiling point of liquid nitrogen, is essential to suppress thermal motion of dinitrogen molecules trapped in a crystal. Photolysis with unfiltered light from the lamp resulted in a gradual decay of the crystal, partly because photoirradiation with all emission lines from a high-pressure mercury lamp induced dimerization of carbenes, which caused large geometrical changes in the crystal. Therefore, the wavelength of the irradiating light was carefully selected by using appropriate band path filters to suppress crystal decay (see the Experimental Section).

The crystallinity was retained in the case of irradiation of DDMs **1**-N_2, **2**-N_2, **4**-N_2, and **5**-N_2 with a band path filter, while **3**-N_2 and **6**-N_2 showed deterioration upon irradiation. Interestingly, no decomposition was observed for **7**-N_2, even upon prolonged irradiation. Therefore, in situ crystallographic analysis was possible only for DDMs **1**-N_2, **2**-N_2, **4**-N_2, and **5**-N_2. Reliable crystal data were obtained for the corresponding DPCs, **1**, **2** and **4**, while the crystallinity of the irradiated sample of **5**-N_2 was not good enough to characterize the structure of **5**.

X-ray Crystal Structures of DPCs. The ORTEP views of DPCs **2** and **4** are shown in Figures 1 and 2, respectively, and crystallographic data are presented in Table 2 (the crystal structure of **1** was reported in ref 20). Selected bond angles and bond lengths for the main framework of DPCs are listed in Table 3, where θ is the carbene carbon C−C−C angle (°) and ω the interplanar angle (°) between the two phenyl rings, while d_1 and d_2 are the C−C distances (Å) between the aromatic and carbene carbons, respectively. Table 3 includes the data for **1** for comparison.

In order to confirm that those carbenes generated in the crystals of precursor diazo compounds are indeed in the triplet

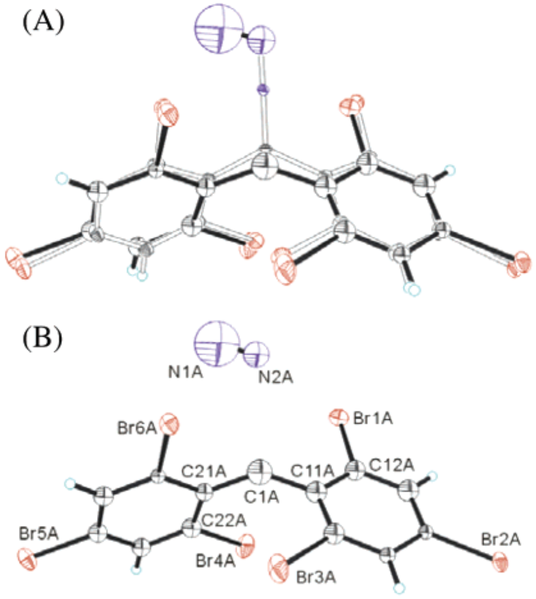


Figure 1. Thermal ellipsoid (50%) plots: (A) a disordered structure of bis(2,4,6-tribromophenyl)carbene **2** (open line) and photoinduced carbene (solid line), and (B) without the initial structure of **2**-N_2.

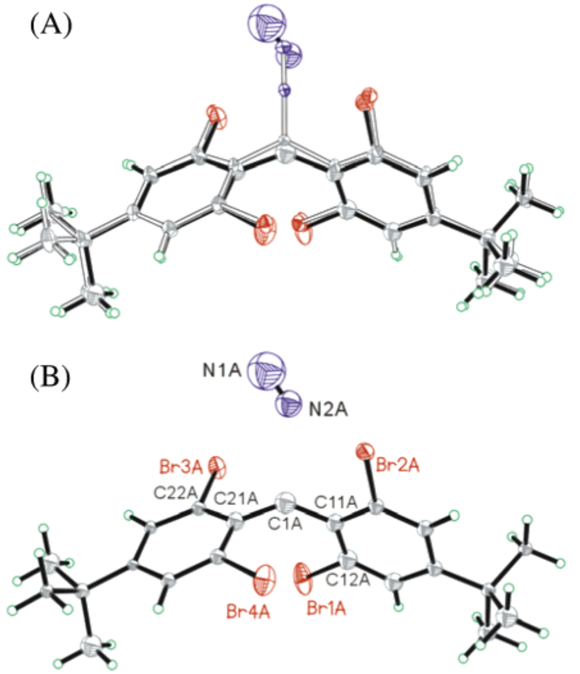


Figure 2. Thermal ellipsoid (50%) plots: (A) a disordered structure of bis(2,6-dibromo-4-*tert*-butylphenyl)carbene **4** (open line) and photoinduced carbene (solid line), and (B) without the initial structure of **4**-N_2.

Table 2. Crystallographic Data for Carbenes ^{3}**2** and ^{3}**4**

	^{3}**2** after 16 min irrad of **2**-N_2 Co39B filter	^{3}**4** after 10 min irrad of **4**-N_2 Co39B filter
chemical formula	$C_{13}H_4N_2Br_6$	$C_{21}H_{22}N_2Br_4$
M_r	667.64	622.05
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
temp, K	80(2)	80(2)
a, Å	9.9776(3)	13.9645(3)
b, Å	13.0960(4)	10.1039(3)
c, Å	12.6356(4)	17.5479(4)
β, deg	91.409(1)	112.625(1)
V, Å^3	1650.55(9)	2285.4(1)
Z	4	4
d_{calcd}, mg/m^3	2.687	1.808
abs coeff, mm^{-1}	14.587	7.053
crystal dimens, mm	0.40 × 0.22 × 0.22	0.38 × 0.30 × 0.30
no. of reflns measd	58 051	223 835
$2\theta_{max}$, deg	80	102
no. of symm-unique reflns	10 005	25 177
merging R(I)	0.0609	0.1080
merging R(sigm)	0.0506	0.0663
no. of retained reflns with $I > 2\sigma(I)$	6758	13 350
no. of variables	247	298
no. of restraints	13	46
$R1(F)$ ($I > 2\sigma(I)$)	0.0408	0.0473
$wR2(F^2)^a$ (all data)	0.0848	0.1082
GOF	1.054	0.991
residual electron density		
max, e Å^{-3}	1.452	1.452
min, e Å^{-3}	−1.580	−2.189

[a] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [2F_c^2 + \max(F_o^2,0)]/3$.

Table 3. Selected Geometrical Parameters for Triplet Carbenes ^{3}**1**, ^{3}**2**, and ^{3}**4**, Obtained by X-ray Analysis and Theoretical Calculations^a

	θ, deg Ar–C–Ar	dihedral angle ω, deg Ar···Ar	d_1, Å Ar–C	d_2, Å C–Ar
^{3}**1**	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}**2**	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}**4**	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 listed in the first row for each carbenes are those obtained by X-ray analysis, while those in the second and third rows are estimated by DFT UB3LYP/6-31G* and CASSCF(6,8)/6-31G* theoretical calculations, respectively.

Table 4. ESR Zero-Field Splitting Parameters (D and E)^a and Kinetic Data^b Observed for Triplet Diphenylcarbenes

	D (cm^{-1})	E (cm^{-1})	E/D	$t_{1/2}{}^c$ (s)	$k_{CHD}{}^d$ (M^{-1} s^{-1})	$k_{O_2}{}^e$ (M^{-1} s^{-1})
^{3}**1**	0.371	0.013	0.036	0.018	3.5×10^3	7.4×10^7
	(0.360)	(0.011)	(0.029)			
	0.389	*0.010*	*0.026*			
^{2}**2**	0.396	0.030	0.075	1	7.4×10^2	1.1×10^7
	(0.368)	(0.0003)	(0.0007)			
	0.369	*0.015*	*0.042*			
^{3}**4**	0.397	0.031	0.078	16	5.3×10^2	2.3×10^7
	(0.442)	(~0)	(~0)			
	0.423	*0.030*	*0.070*			

[a] See text for the relationship between the ZFS parameters and the structures of the triplet carbenes. In 2-methyltetrahydrofuran at 77 K. The values in parentheses and in italics refer to those observed in 3-methylpentane at 77 K and in the crystalline state at 20 K, respectively. [b] In degassed benzene at room temperature. [c] Half-life. [d] The rate constant for H abstraction of carbene from 1,4-cyclohexadiene. [e] The rate constant for quenching carbenes by oxygen.

ground state, we carried out ESR measurements. Irradiation of single crystals of DDMs **1**-N_2, **2**-N_2, and **4**-N_2 gave rise to a weak, broad signal around 334 mT. This has been occasionally observed in crystalline samples of triplet carbenes, probably because of strong exchange coupling of the triplet states and/or antiferromagnetic interactions. However, we also observed weak signals ascribable to a triplet species with large D values (Figures S7−S9). Zero-field splitting (ZFS) parameters estimated from those signals reported in Table 4 are similar to those observed in 2-methyltetrahydrofuran at 77 K for the corresponding triplet carbenes.[21,22] Thus, it is highly likely that carbenes generated in the single crystals of DDMs are in the triplet ground states. Theoretical calculations support this assignment (vide infra).

Inspection of the data in Table 3 reveals two interesting features. First, there is only a subtle difference not only in the angles (θ and ω) but also in the distances (d_1 and d_2) between hexachlorinated (^{3}**1**) and hexabrominated DPCs (^{3}**2**), although there are significant difference in bulkiness between their ortho substituents (vide infra). Second, ^{3}**4** exhibits slightly but clearly different parameters for both angles and distances in comparison to the other two DPCs, especially ^{3}**2**, which has the same ortho substituents. Thus, on going from ^{3}**2** and ^{3}**1** to ^{3}**4**, θ and ω values decrease from 141(2)°/87.2(4)° and 142(2)°/86.4(4)° to 138(1)°/89.9(3)°, and distances d_1 and d_2 also decrease from 1.431(18)/1.425(18) Å and 1.423(16)/1.437(15) Å to 1.375(17)/1.373(17) Å, respectively. It is noteworthy that the average bond length C(:)−Ar of ^{3}**4** (1.374 Å) is considerably shorter than those of ^{3}**1** and ^{3}**2** (1.430 and 1.428 Å, respectively), provided that the two lengths of C(:)−Ar for each carbene were chemically equivalent.

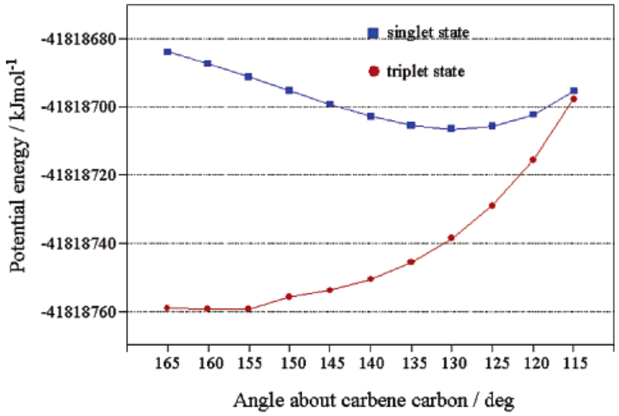


Figure 3. Potential energy surface of bis(2,4,6-tribromophenyl)carbene **2** as a function of the carbene bond angle (θ) in the range of 115−165°, calculated at the UB3LYP/6-31G* level of theory.

The structures were then optimized for the triplet ground states of ^{3}**1**, ^{3}**2**, and ^{3}**4** at the UB3LYP/6-31G* levels of theory, and selected bond lengths and angles are also given in Table 3. UB3LYP methods give essentially identical C−Ar bond lengths *d* (1.38 Å) for all three triplet carbenes. This length is smaller, when compared with the observed values, for ^{3}**1** and ^{3}**2** (ca. 1.43(2) Å) but very close for ^{3}**4** (1.37(2) Å). On the other hand, the carbene angles (θ) are not identical for the three, decreasing from 160° for ^{3}**1** to 155° for ^{3}**4**. Those values are significantly larger (by 17−18°) than the observed ones (142(2)−138(1)°), although the trend of decreasing order is similar to the observed one. The interplanar angles (ω) are also not identical for the three and are much larger (by 5−21°) than the observed ones (86(1)−90(1)°). The increasing of ω determined by UB3LYP methods on going from *o*-chlorinated to *o*-brominated DPCs, i.e., from ^{3}**1** to ^{3}**2** and ^{3}**4**, is reversed from the observed trend.

We also calculated a potential energy surface of **2** as a function of θ for both singlet and triplet states in the range of 115−165° in order to explore further the assignment of the spin state of **2** in the crystal. The results (Figure 3) clearly indicate that ^{3}**2** is always more stable than ^{1}**2**. Especially important is the fact that the singlet−triplet energy gap at an angle of 140° is 47.7 kJ/mol, which is large enough to ensure that the spin state could be the triplet state. It is also interesting to note here that both ^{1}**2** and ^{3}**2** have very shallow potential energy surfaces.

Since DFT is not able to treat multiconfigurational problems properly,[8] an improved method to take some type of configurational interaction (CI) into account is required in order to optimize the structures of these open-shell species more adequately. Thus, the structures are also optimized at CASSCF/6-31G* levels of theory for the ground state of ^{3}**1**, ^{3}**2**, and ^{3}**4**, and selected bond lengths and angles are given in Table 3. Interestingly, the CASSCF(6,8) method gives identical C−Ar lengths of 1.43 Å and angles of 141° for all three carbenes, and these values are in better agreement with the observed ones than those predicted by DFT, although one should perform the CASSCF calculations with a larger basis set for more accurate comparison. The interplanar angles (ω) are not identical for the three and are smaller than the observed ones (86−90°), but the discrepancy (by 6−20°) is smaller than that predicted by DFT.

Before discussing the structural differences in terms of the stability, we would like to summarize what has been observed for three carbenes by “indirect” methods.

Kinetics Data and ESR Parameters Observed for Triplet DPCs. The structural and kinetic data concerning triplet DPCs, ^{3}**1**, ^{3}**2**, and ^{3}**4**, generated from diazo precursors are summarized in Table 4.[21,22] They are kinetic data measured by laser flash photolysis (LFP) in a degassed benzene solution at room temperature and zero-field splitting (ZFS) parameters measured by electron spin resonance (ESR) spectroscopy in an organic matrix at low temperatures.

The lifetime (or half-life) of triplet DPCs obtained provides direct information about their stability in solution. The data in Table 4 show two prominent trends in the effect of structure on the stability of triplet DPCs.

First, ^{3}**1** is the least stable among the three DPCs. The half-life ($t_{1/2}$) of ^{3}**1** in benzene at room temperature is 0.018 s, 2 and 3 orders of magnitude smaller than those of ^{3}**2** ($t_{1/2} = 1$ s) and ^{3}**4** ($t_{1/2} = 16$ s), respectively. But half-life is just a measure of lifetime and cannot be regarded as a quantitative scale for reactivity. In this respect, the rate constant of the triplet carbene, measured 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).[25] Therefore, the rate constants of the trapping reactions by O_2 and CHD, i.e., k_{O_2} and k_{CHD}, respectively, are used as a more quantitative scale to estimate the reactivities of the triplet carbenes. These values again show that ^{3}**1** is more reactive than ^{3}**2** and ^{3}**4**. This is interpreted in terms of the difference in van der Waals radius between chlorine and bromine groups. In other words, the carbene center in ^{3}**2** and ^{3}**4** is shielded more tightly than that in ^{3}**1**.

Second, among *o*-brominated DPCs, i.e., ^{3}**2** and ^{3}**4**, the half-life is significantly increased once the bromine groups at the para position are replaced with *tert*-butyl groups. However, the rate constants for quenching of ^{3}**2** and ^{3}**4** by O_2 and CHD are not affected by this change. Similarly, there is little difference in the ESR structural parameters between ^{3}**2** and ^{3}**4** (vide infra). Therefore, this difference can be ascribed not to structural changes in the carbene itself but to the effect of the para substituents on the decay pathway of the two DPCs in benzene. The main decay pathway of those DPCs in benzene is dimerization at the carbene center, but, in *o*-brominated DPCs, dimerization at the para positions becomes significant due to severe steric hindrance at the carbene center.[26] Therefore, a significant increase in the lifetime upon substitution of a *tert*-butyl group in benzene (in the absence of a trapping reagent) is interpreted in terms of steric hindrance of the dimerization at the para position.[27]

ZFS parameters *D* and *E* give information on the molecular and electronic structures of triplet carbenes.[28,29] The *D* value is related to the separation between the unpaired electrons. The *E*

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(25) Tomioka, H. In *Reactive Intermediate Chemistry*; Moss, A. M., Platz, M. S., Jones, M., Jr., Eds.; Wiley: New York, 2004; pp 375−461.

(26) Oligomerization from the aromatic ring in the reaction of sterically congested diphenylcarbenes usually resulted in complex mixtures, but the formation of trimer and tetramer as a result of oligomerization from aromatic ring is noted for bis(9-anthryl)carbene: (a) Takahashi, Y.; Tomura, M.; Yoshida, K.; Murata, S.; Tomioka, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3478. (b) Yoshida, K.; Iiba, E.; Nozaki, Y.; Hirai, K.; Takahashi, Y.; Tomioka, H.; Lin, C-T.; Gaspar, P. P. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1509.

(27) The lifetime of bis(9-anthryl)carbenes is greatly increased by introducing a bulky group at the 9 position, where oligomerization takes place: (a) Tomioka, H.; Iwamoto, E.; Itakura, H.; Hirai, K. *Nature* **2001**, *412*, 626. (b) Iwamoto, E.; Hirai, K.; Tomioka, H. *J. Am. Chem. Soc.* **2003**, *125*, 14664.

value, on the other hand, when weighted by D, is a measure of the deviation from axial symmetry. For diarylcarbenes, this value will thus depend on the magnitude of the central C−C−C angle. 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 π-orbital contribution and a smaller value for E. Although the values D and E depend on the electronic distribution, there is a good correlation between the E/D ratio and the bond angle at the divalent carbon atom.

ZFS parameters in 2-methyltetrahydrofuran at 77 K show that the D values of ^{3}**1** are slightly smaller than those of ^{3}**2** and ^{3}**4**, while the E/D values of ^{3}**1** are much smaller than those of ^{3}**2** and ^{3}**4**. This suggests that ^{3}**1** has a less bent structure where unpaired electrons are more delocalized. In other words, ^{3}**1** is thermodynamically more stable than ^{3}**2** and ^{3}**4**. This prediction, however, is not in accord with the kinetic data obtained in solution at room temperature.

ZFS parameters of sterically congested DPCs generated in a rigid matrix at low temperature are known to change when the matrix is warmed, as observed for the three DPCs in Table 4. These changes are interpreted in terms of geometrical relaxation of triplet DPC as the matrix is softened.[30,31] Thus, when a carbene is generated in rigid matrices at low temperatures, its initial geometry should be dictated by that of the precursor. Even if the thermodynamically most stable geometry of the carbene is different from that at birth, the rigidity of the matrices prevents the carbene from achieving its minimum-energy geometry. But when the matrix is softened by warming, the carbene is allowed to relax to its preferred geometry, probably to gain relief from steric compression.

The data in Table 4 indicate that this change is larger for ^{3}**2** and ^{3}**4** than for ^{3}**1**. Thus, ^{3}**2** and ^{3}**4** undergo relaxation to nearly linear geometry, as judged from their nearly zero E/D values, while ^{3}**1** has still a bent structure in its relaxed geometry. In other words, ^{3}**2** and ^{3}**4** are considered to be thermodynamically more stable than ^{3}**1** in their relaxed geometries. Since it is probable that those DPCs react in their relaxed geometry in solution at room temperature, ZFS parameters obtained in a softened matrix correlate with kinetic data in solution better than those obtained in a rigid matrix.

Structural Parameters and Reactivity. How can one correlate those data from ESR and LFP with the structural features noted by in situ crystallographic observation of three triplet DPCs?

First, the rather subtle difference in structural parameters between ^{3}**1** and ^{3}**2** in Table 3 is not in accord with the observed significant difference in stability in solution at room temperature ($t_{1/2} = 0.018$ s for ^{3}**1** and 1 s for ^{3}**2**) and the ESR parameters in a matrix at low temperatures ($E/D = 0.0133/0.371$ for ^{3}**1** and 0.0297/0.396 for ^{3}**2**) between two DPCs.

Bromine has a larger van der Waals radius (1.85 Å) than chlorine (1.70 Å), but the bond distance of C−Br (1.95 Å) is longer than that of C−Cl (1.80 Å).[32] This may mean that *o*-Br groups can hang over the carbene center better than *o*-Cl groups without interacting with each other. However, the extent of geometrical relaxation of triplet DPC upon softening of the matrix is larger for ^{3}**2** than for ^{3}**1**, as judged by comparing the extent of change in E/D upon warming between the two DPCs. This means that steric repulsion between *o*-bromine groups in ^{3}**2** is more severe than that between *o*-chlorine groups in ^{3}**1**. A significant decrease in the reactivity in solution is clearly noted on going from ^{3}**1** to ^{3}**2** and is interpreted as reflecting this difference. Thus, it is rather surprising to note that the structural parameters between the two carbenes are unexpectedly small.

Second, significantly smaller values for both angles and distances are observed for ^{3}**4** as opposed to those observed for the other two DPCs, especially for ^{3}**2**. A decrease in the bond length in ^{3}**4** as opposed to ^{3}**2** (and ^{3}**1**) may indicate that ^{3}**4** is thermodynamically more stabilized than ^{3}**2** (and ^{3}**1**).

Since the only difference in structure between ^{3}**4** and ^{3}**2** is the substituents at the para position, one needs to examine the difference in effect of *p*-bromine vs *p*-*tert*-butyl groups on the stability of triplet DPCs.

The dominant interaction of the unpaired electrons in a π-radical is with the electrons paired in the π-bonds. Such interactions are characterized by the delocalization of the spin throughout the π-system. To estimate the relative abilities of substituents to delocalize the spin, sigma-dot substituent constants ($\sigma\cdot$) have been proposed.[33]

Attempts to correlate the D values with $\sigma_a\cdot$ have been carried out for bis(4-X-2,6-dimethylphenyl)carbene (**8**),[34] where a series of X substituents with different $\sigma\cdot$ values are employed. The D values observed for carbenes **8** in their minimum-energy geometries, attained upon annealing, are found to correlate relatively well ($\rho = 0.589$, $r = 0.9$) with $\sigma_a\cdot$.[35]

However, the ability of the para substituents to delocalize unpaired electrons is essentially identical for ^{3}**2** and ^{3}**4** ($\sigma_C\cdot = 0.13$ for both 4-Br and 4-*t*-Bu).[36] Thus, one cannot explain the difference in the geometry observed between the two in terms of delocalization of unpaired electrons.

The difference in bulkiness between bromine and *tert*-butyl groups is significant. However, it is unlikely that the *tert*-butyl group is large enough to effect steric congestion at the remote carbene center.

ZFS parameters and rate constants for quenching by triplet carbene trapping reagents suggest that the difference in half-life between ^{3}**2** and ^{3}**4** in benzene (in the absence of trapping

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(28) A large number of triplet carbenes have been characterized by ESR spectroscopy since the pioneering work of Wasserman et al.: Wasserman, E.; Hutton, R. S. *Acc. Chem. Res.* **1997**, *10*, 27. Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

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(31) For a review, see: Tomioka, H. In *Advances in Strained and Interesting Organic Molecules*; Halton, B., Ed.; JAI Press: Greenwich, CT, 2000; Vol. 8, pp 83−112.

(32) Rowland, R. S.; Taylor, R. *J. Phys. Chem.* **1996**, *100*, 7384.

(33) For a review, see: Jiang, X.-K. *Acc. Chem. Res.* **1997**, *30*, 283.

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(35) (a) Tomioka, H.; Hu, Y.; Ishikawa, Y.; Hirai, K. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 2207. (b) Hu, Y.; Hirai, K.; Tomioka, H. *J. Phys. Chem. A* **1999**, *103*, 9280.

(36) Creary's $\sigma_C\cdot$ scale is also useful, since it is based on the thermal rearrangement that is devoid of polar character in the transition state: (a) Creary, X. *J. Org. Chem.* **1980**, *45*, 280. (b) Creary, X. Mehrsheik-Mohammadi, M. E.; McDonald, S. *J. Org. Chem.* **1987**, *52*, 3254.

reagents) is explained in terms of steric inhibition of the decay pathway from the aromatic ring rather than an inherent increase in kinetic protection of the carbene center (vide supra).

It is interesting to compare ZFS parameters observed in an organic glass (both before and after warming) and in the crystalline state (Table 4). The most prominent difference appears in the E values, especially for brominated DPCs, ^{3}**2** and ^{3}**4**. The E values observed for both carbenes in the crystalline state are significant (0.015 for ^{3}**2** and 0.030 for ^{3}**4**), while they reduced from significant (0.030 for ^{3}**2** and 0.031 for ^{3}**4**) in a rigid matrix to nearly zero (0.0003 for ^{3}**2** and $\sim$0 for ^{3}**4**) in a softened matrix. The significant E values in the crystalline state suggest bent structures for the three triplet DPCs, in accord with the structures directly observed by the present method. On the other hand, triplet DPCs undergo relaxation to less bent and probably more stable geometry in soft, unconstrained environments like in a solution phase before they react. In other words, the structures of triplet DPCs observed in the crystalline state are not exactly the same as the ones reacting in solution.

Origin of the Difference in Crystalline-State Photoreactivity of DDMs. The observation that diazofluorene **7**-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. Diazofluorene, for instance, efficiently generates the corresponding carbene when irradiated in an argon matrix at temperature as low as 10 K.[37] It is very important to examine the origin of the sluggishness of **7**-N_2 to photodissociation in the crystalline state.

The Ar−C distances for **7**-N_2 are shorter than those of the other DDMs, but the $C{=}N_2$ and $N{=}N$ bond lengths in the diazo functional groups are comparable with other ones. Thus, it is unlikely that the inherent reactivity of the diazo group is forced to change in the crystalline state. The reaction cavity volume[38] about a diazo group in the crystal of **7**-N_2 is not smallest among the DDMs studied and is slightly larger than that of the smallest one, **3**-N_2. Since **3**-N_2 undergoes smooth photodissociation of nitrogen under these conditions, the cavity seems to not be a crucial factor controlling the photoreactivity of DDMs. On the other hand, the molecules are most tightly packed in the **7**-N_2 crystal among the DDMs employed, as judged by the smallest non-hydrogen atomic volume. This volume is pretty large for **3**-N_2, which has the smallest reaction cavity but undergoes photodissociation. Thus, it seems that nitrogen cannot easily leave the procarbenic carbon in the crystal of **7**-N_2. Moreover, since fluorenylidene **7** is incorporated in a five-membered ring, its singlet−triplet energy gap is much smaller than that of the diphenylcarbene derivative of **7**,[39] so that nascent singlet **7** generated upon photodissociation of nitrogen undergoes relaxation to the corresponding triplet state less reluctantly than singlet diphenylcarbene derivatives do, especially in the crystalline state. It is then not unreasonable to assume that, even if **7** is generated upon irradiation of **7**-N_2 in a crystal, the nascent singlet state of **7** is immediately trapped by nitrogen, which is tightly trapped near the carbene center, to reproduce **7**-N_2.[40]

Among DDMs that undergo photodissociation of nitrogen in the crystalline state, **3**-N_2 and **6**-N_2 decomposed without keeping their crystallinity, while other DDMs retained their crystallinity at least to an extent that allowed us to observe the corresponding carbene. It will not be easy to find a reliable factor to control this difference, since this will be affected by differences in the crystal form between the precursor diazo compound and the product carbene and also in the relative easiness of subsequent reaction of the carbene generated in the crystal.

Concluding Remarks

The structural parameters of three persistent triplet diphenylcarbenes with significantly different stabilities are obtained by in situ X-ray crystallographic observations. Surprisingly subtle differences in structural parameters (except for carbene−phenyl group bond length) are observed for those three triplet DPCs, the half-lives of which span from 0.02 to 18 s in solution at room temperature. Noteworthy is that the average bond length of carbene−phenyl group for ^{3}**4** is considerably shorter than those for ^{3}**1** and ^{3}**2**. Such geometrical parameters can be obtained only by crystallographic analysis. At this moment, the most likely explanation for the small and large differences in bond lengths in **1**, **2**, and **4** may be derived from the different packing patterns of these DPCs. The packing patterns of **1** and **2** are identical, but that of **4** is totally different. Therefore, their intermolecular interactions should be quite different. In order to determine the crucial factor in the differences, we should investigate these DPCs under various conditions. Moreover, these rather unexpected results are interpreted as indicating that triplet DPCs undergo relaxation upon softening of the environment, since the carbenic centers are sterically congested before they decay in solution.

Theoretical calculations provide a clue toward understanding the situations in the structure observed by the present in situ method and those presumed by the traditional means. The potential energy surface of the triplet DPC in terms of the carbene angle is extremely flat, and changes in the angles have little effect on the energies. Only 8.1 kJ/mol is required to linearize the triplet DPC from its 142° equilibrium geometry.[41] This will be much lower for DPCs having sterically congested substituents at their ortho positions. In fact, a potential energy surface calculation for ^{3}**1** and ^{3}**2** indicates that the energy difference between 140° and 160° is only 4.2 kJ/mol.[20] This suggests that experimental θ values will be readily affected by the rigidity of the environment. This is reasonable in the light of the fact that triplet DPCs with a sterically congested carbene center are trapped in a structure dictated by the precursor structure in a rigid matrix, even if this is not the thermodynamically most stable geometry, but undergo geometrical relaxation upon softening of the matrix to gain relief from steric compression.

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It is important to point out here that recent ESR studies revealed that, upon warming the matrix containing ^{3}**1**, the *D* value decreases first, which is followed by a decrease in the *E* value.[42] This suggests that the phenyl ring rotates along the C(:)−Ar bond at the initial stage, while the matrix is still not highly fluid, and then the bond angle on the carbene center starts to open at the latter stage, when the matrix become more fluid. This means that the interplanar angles are more flexible than the bond angle.

In situ X-ray crystallographic analysis can be successfully employed to determine the molecular structure of triplet DPCs, which is otherwise impossible to analyze. However, the structural parameters obtained by this method are not in accord with those of the triplet DPCs that are involved in the reaction, mainly because triplet DPCs have very flat potential energy surfaces, and hence solvation effects cannot be ignored. This mobile complex nature of triplet carbenes reflects on their unique reactivity.

Experimental Section

General Considerations. Compounds **1**-N_2, **6**-N_2, and **7**-N_2 were prepared by the method described in refs 2, 22a, and 22b, respectively. A series of brominated diphenyldiazomethanes (**2**-N_2−**5**-N_2) were prepared by the method described in ref 20. Samples were irradiated with a 350-W high-pressure mercury lamp (SAN-EI UVF-35S) in combination with a band-path filter (Toshiba Co39B or UV-D36B).[43] UV−vis spectra were recorded on a JASCO CT-560 spectrophotometer in 2-methyltetrahydrofuran (2-MTHF) using an Oxford Instruments variable-temperature liquid nitrogen cryostat (DN 2704) equipped with a quartz outer window and a sapphire inner window and were also recorded on a Shimadzu UV-3100PC spectrophotometer in a KBr pellet. Fourier-transform infrared spectra were recorded on a JASCO FT/IR-5300 instrument. A sample dispersed in a KBr pellet (several DPC crystals were ground in a mortar) was attached to the coldfinger of a helium cryogenic refrigerator system (Daikin PS24SS) equipped with KBr or quartz windows. The presence of several micrometer-size microcrystals in a KBr pellet was confirmed with an optical microscope. ESR measurements were made on a JEOL TE-200 instrument equipped with an Oxford Instruments ESR910 temperature controller.

Single-Crystal X-ray Diffraction Analysis. (a) Sample Preparation. Single crystals of **1**-N_2, **6**-N_2, and **7**-N_2 were obtained by slow evaporation of benzene, that of **2**-N_2 from dichloromethane, and those of **3**-N_2−**5**-N_2 from acetone. Crystals were mounted on the tips of glass fibers with epoxy or Paratone oil and cooled to low temperatures (80 K), controlled by a Rigaku cryostat system equipped with a N_2 generator. The photoreaction and crystal quality were monitored on the basis of total intensities of selected frames and shapes of Bragg diffractions. Different crystals were used for the structure determination of the initial molecules and photoproducts.

(b) Data Collection and Reduction. Data were collected on a Siemens SMART CCD X-ray diffractometry system controlled by a Pentium-based PC running the SMART software package. Graphite-monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation was used with a Rigaku rotating anode generator (50 kV, 250 mA). A modification of the data collection strategy described in ref 20 was utilized. Frame data were integrated by using SAINT version 5, and intensity data were corrected with the SADABS program. Because polybrominated diphenyldiazomethanes react with Mo Kα radiation to emit X-ray fluorescence and yield carbene, the minimum exposure time should be used for data collection.

(c) Structure Refinement. All structures were solved by use of the direct method program XS, which is part of the SHELXTL program package.[44] Structure refinements were carried out with SHELXL-97.[43] All least-squares refinements minimized the function $\sum w(|F_o|^2 - k|F_c|^2)^2$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [2F_c^2 + \max(F_o^2,0)]/3$. Crystallographic data before and after irradiation are summarized in Tables S1 and 2.

The initial structure was treated as a rigid group and allowed to translate and rotate during the least-squares refinement, in which its thermal parameters were refined anisotropically. The structure was solved as a disordered structure. Chemical restraints were applied to the phenyl rings of the divalent species because of their severe overlapping with the diazo species.

Computational Procedures. Ab initio molecular orbital calculations[45] were carried out using the GAUSSIAN 98 program.[46] Optimized geometries were obtained at the (U)B3LYP/6-31G*[46,47] and CASSCF/6-31G* levels of theory. Vibrational frequencies obtained at the (U)B3LYP level of theory were scaled by 0.97. For the DFT calculations, UB3LYP wave functions were used to describe the open-shell triplet carbenes. For triplet carbenes, the active space used in the CASSCF calculations comprised six electrons in eight MOs (three π and four π* MOs plus a σ one), denoted as CASSCF(6,8). The carbene structures were optimized in C_2 and C_s symmetry, both of which gave identical structures. CASSCF calculations were performed using several combinations of the active space for the π MOs of the phenyl groups, except for two electrons assigned to the carbene center. CASSCF(6,8) calculations using each set of the aromatic π MOs resulted in similar bond lengths between the carbene center and phenyl rings, but the C−C bond distances in the phenyl rings depended considerably on the combination of the π MOs of the phenyl groups. This is not surprising, because we had to treat small active spaces for the phenyl rings because of the limitation of computer resources. In this paper, therefore, we discuss only the geometries about the carbene center.

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Supporting Information Available: Crystallographic information for DDMs (**2**-N_2−**7**-N_2), ESR spectra for **1**, **2**, and **4** measured in the crystalline state at 20 K (Figures S7−S9), Cartesian coordinates, absolute energies for all compounds calculated at the B3LYP/6-31G* level of theory, and complete ref 46 (PDF); X-ray crystallographic files (CIF; also deposited as CCDC 619889−619896). This material is available free of charge via the Internet at http://pubs.acs.org.

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