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# Generation, Reactions, and Kinetics of Sterically Congested Triplet Diphenylcarbenes. Effects of Bromine Groups

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***Abstract:*** A series of polybrominated diphenylcarbenes (DPCs) are generated by irradiation of the corresponding precursor diazomethanes, and their reactivities are investigated by means of low-temperature spectroscopies as well as laser flash photolysis. Triplet bis(2,4,6-tribromophenyl)carbene was shown to decay by undergoing dimerization 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 DPC. Anomalous effects of para substituents on the stability of the triplet are noted. Thus, while the replacement of a 4-bromine group with a methyl group resulted in a sharp decrease in the lifetime, introduction of a *tert*-butyl group resulted in a dramatic increase in the lifetime; triplet bis(2,6-dibromo-4-*tert*-butylphenyl)carbene was shown to have a half-life of 16 s in solution at room temperature. Attempts to increase the stability of these polybrominated DPCs by buttressing effects of a *m*-bromine group and by the synergetic effect of bromine and methyl groups are also described.

For a long time, carbenes were believed not to be stable enough to be isolated in macroscopic amounts at room temperature. However, the recent syntheses of stable singlet carbenes,[1,2] i.e., phosphinocarbenes and imidazol-2-ylidenes, have upset this extreme view. These carbenes are obviously thermodynamically stabilized by the $\pi$-donating ability of the heteroatom substituent directly attached to the carbenic carbon. Naturally, interpretation of these species as “free” carbene has been a topic of debate,[3] since the possible contribution of the ylidic character as a result of $p\pi-p\pi$ delocalization should not be neglected.

The stabilization of a triplet carbene emerges as a challenging target since triplet carbene is less susceptible to conjugative stabilization and hence is more likely to keep the electronic integrity as a free carbene, i.e., one centered diradical. Steric protection (kinetic stabilization) is an ideal method for stabilizing the triplet since a protecting group, when introduced near the carbene center, not only blocks the carbenic center from external reagents but also results in thermodynamic stabilization with respect to the singlet by increasing the central angle.[4]

Attempts have been made along this line whereby triplet diphenylcarbenes (DPCs) were stabilized by introducing a series of substituents at the ortho positions.[5-9] However, a high affinity of carbenes for electrons makes it very difficult to explore the usual protecting groups for this extremely reactive center with only two modifiable substituents; carbenes can react even with very poor sources of electrons, such as C−H bonds.[10] For instance, the *tert*-butyl group, which has been successfully employed as one of the most effective protecting groups for many other reactive centers in organic chemistry, was found to be ineffective,[8b,c] much less effective even than methyl and chlorine groups in protecting triplet DPCs.

In this light, it is crucial to develop a protecting group which is sterically congesting and yet unreactive toward triplet carbenes. Bromine atoms appear to be promising as a protecting group toward the triplet carbene center because, while the van der Waals radius is similar to that of methyl (Br, 185 pm; Me, 175 pm),[11] the C−Br bond length (181 pm) is longer than the C−C (Me) (177 pm),[11] suggesting that the *o*-bromo groups must

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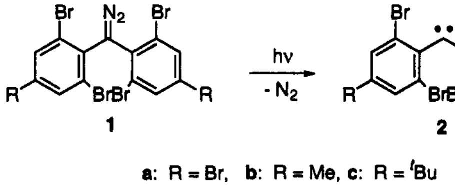
Scheme 1



overhang the reactive site more effectively. Moreover, halides are usually reactive toward singlet carbenes to form halonium ylides, but they are not reactive with the triplet state.[10] In addition, the value of $\xi_1$, which gives a measure of the strength of the spin−orbit interaction, is increased rather dramatically on going from chlorine (586 cm$^{-1}$) to bromine (2460 cm$^{-1}$),[12] suggesting that the intersystem crossing from the nascent singlet carbene to the triplet should be accelerated by introducing a bromine atom.

Thus, we generated polybrominated diphenylcarbenes by photolysis of the precursor diazomethane and found that these carbenes exhibited an enormously prolonged existence even in solution at room temperature, most probably due to steric shielding of the carbene center by bromine groups at the ortho positions.[13]

## Results and Discussion

**A. Bis(2,4,6-tribromophenyl)carbene.** Irradiation of bis(2,4,6-tribromophenyl)diazomethane (**1a**) in 2-methyltetrahydrofuran (2-MTHF) glass at 77 K gave a fine-structure ESR line shape characteristic of randomly oriented triplet molecules with a large *D* value attributable to one-center n$\pi$ spin−spin interaction at a divalent carbon of diarylcarbene (Scheme 1, Figure 1A-(a)).[14] The fine-structure constants were $|D| = 0.3958$ cm$^{-1}$, $|E| = 0.0295$ cm$^{-1}$, showing unequivocally that the triplet signals are due to triplet hexabromodiphenylcarbene (**2a**) generated by photodissociation of **1a**. The ESR signals not only were stable at this temperature but also survived even at 130 K. However, as the samples were warmed, the *x* and *y* lines of the spectrum moved closer together, resulting in essentially zero *E* value (Figure 1A-(b)). Cooling the sample did not reverse this change.

This is interpreted in terms of geometrical change of carbenes often observed for sterically congested carbenes.[14c,15,16] The ESR spectra of carbenes are characterized by two parameters, *D* and *E*. The *D* value is related to the separation between the unpaired electrons. The value of *E*, when weighted by *D*, is a measure of the carbene from axial symmetry, or, more plainly, it describes the extent to which the molecule is bent. Therefore, the substantial reduction in the *E* value upon annealing the matrix indicates that the carbene relaxes to a structure with an expanded C−C−C angle, presumably to gain relief from steric compression. Thus, when a carbene is formed at low temperature, it should have the bent geometry and the conformation dictated by those of the precursor. Even if the thermodynamically most stable geometry and/or conformation of the carbene is different from those at the birth, the rigidity of the matrix prevents it from assuming its minimum energy structure. However, when the matrix is softened upon annealing, the carbene can relax to a stabler geometry, depending on the softness of the media.

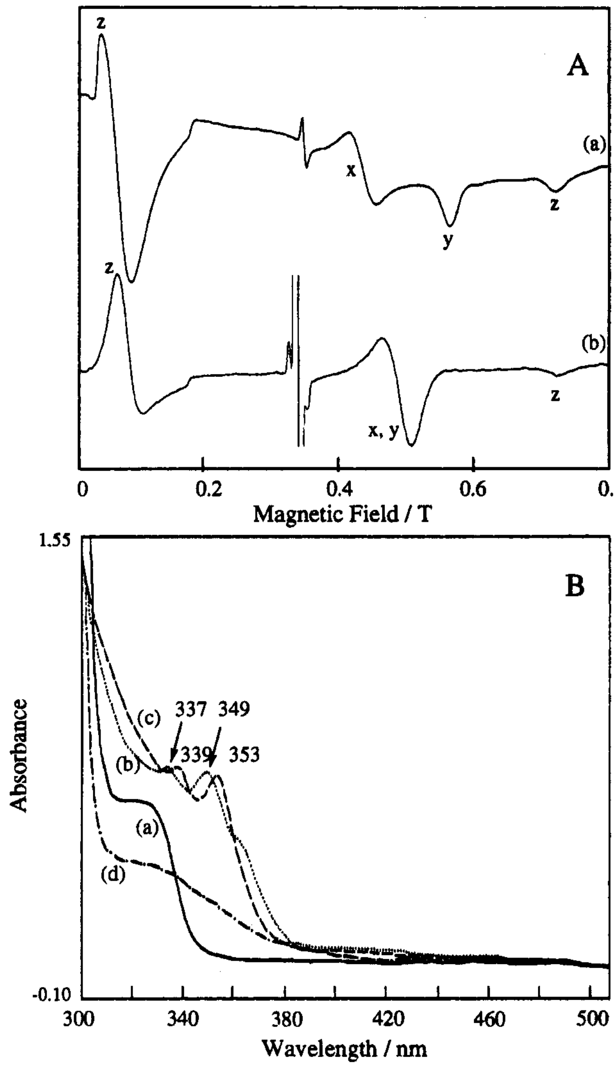


***Figure 1.*** (A) ESR spectra of bis(2,4,6-tribromophenyl)carbene (**2a**) in 2-methyltetrahydrofuran (2-MTHF) (a) at 77 K and (b) at 110 K. (B) UV/vis spectra obtained by irradiation of **1a** in 2-MTHF: (a) spectra of **1a** in 2-MTHF at 77 K; (b) same sample after 10 min irradiation ($\lambda > 350$ nm); (c) same sample after warming to 95 K; (d) same sample after warming the matrix to room temperature and refreezing to 77 K.

It should be interesting to note here that the fine-structure constants observed for **2a** in a softer matrix, i.e., 3-methylpentane (3-MP),[17] were essentially the same as those observed for the relaxed carbenes even at 77 K and that the spectrum did not change upon annealing in this case. This suggests that the initial geometry is perturbed by the softness of environment, not by temperatures.

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Optical spectroscopical monitoring in the frozen medium gave analogous results. Irradiation ($\lambda > 350$ nm) of **1** ($1 \times 10^{-4}$ M) in 2-MTHF glass at 77 K resulted in the appearance of new absorption bands at the expense of the original absorption due to **1**. As shown in Figure 1B-(b), the new spectrum consists of two identifiable features, two intense UV bands with maxima at 337 and 349 nm and weak and broad bands with apparent maxima around 480 nm. These features are usually present in the spectra of triplet diarylcarbenes in organic matrixes at 77 K.[14,18] The glassy solution did not exhibit any changes for several hours when kept at 77 K. However, when it was allowed to warm to room temperature and then cooled to 77 K, the characteristic bands disappeared (Figure 1B-(d)). On the basis of these observations coupled with ESR data (vide supra), the absorption spectrum can be attributed to triplet carbene ($^3$**2**).

Monitoring of the spectral changes as a function of temperature shows two interesting features. First, the absorption maxima shifted slightly but distinctly from 337 and 349 nm to 339 and 353 nm when the matrix was warmed from 90 to 95 K (Figure 1B-(c)). This change was not reversed when the samples were cooled. This change should be ascribable to the geometrical change of the triplet carbene associated with changes in viscocity of the matrixes upon annealing, as has been revealed in ESR experiments. It should be noted here that such a distinct shift in a UV/vis spectrum has not previously been observed for other relatively congested diarylcarbenes undergoing similar geometrical changes. Second, while absorption bands of most triplet diarylcarbenes disappear in the temperature range 100−105 K, where the viscocity of the matrix changes dramatically from $10^7$ to $10^3$ P,[19] no appreciable changes were observed for the absorption bands ascribable to $^3$**2** in 2-MTHF up to 120 K, where the samples were almost completely fluid. Significant decomposition began only at 130 K (viscocity is 1.6 P),[19] where the "first-order" half-life ($t_{1/2}$) was approximately 15 min. In more viscous solvents, **2** was able to survive at much higher temperatures: 190 K in dibutylphthalate ($t_{1/2} = 37$ min) and 210 K in triacetine ($t_{1/2} = 33$ min).

Laser flash photolysis (LFP) of **1a** ($1 \times 10^{-4}$ M) in a degassed benzene solution at room temperature with a 10 ns, 70−90 mJ, 308 nm pulse from a XeCl excimer laser produced a transient species showing a strong absorption at 355 nm and a weak absorption extending from 420 to 500 nm, which appeared coincident with the pulse (Figure 2). The transient signals disappeared rather gradually, persisting for at least 30 s under those conditions. On the basis of the low-temperature spectrum, we assign the transient product to $^3$**2a**. The inset (a) in Figure 2 shows the decay of $^3$**2a** in the absence of trapping reagents, which is found to be second order ($2k/\epsilon l = 8.9$ s$^{-1}$). The rough lifetime of $^3$**2a** is estimated in the form of half-life, $t_{1/2}$, to be 1 ± 0.1 s.

Support is lent to this assignment by trapping experiments using oxygen. When LFP was carried out on a non-degassed benzene solution of **1a**, the half-life of $^3$**2a** decreased dramatically, and a broad absorption band with a maximum at 410 nm appeared at the expense of the absorption due to $^3$**2a**. The spent solution was found to contain hexabromobenzophenone (**4**) as the main product. It is well-documented[20] that the diarylcarbenes with triplet ground states are readily trapped by oxygen to generate the corresponding diaryl ketone oxides, which are easily observed directly either by matrix isolation or by flash photolysis and show a broad absorption band centered at 396−450 nm. Thus, the observations can be interpreted as indicating that $^3$**2a** is trapped by oxygen to form the carbonyl oxide (**3**), which confirms that the transient absorption quenched by oxygen is due to $^3$**2a**.

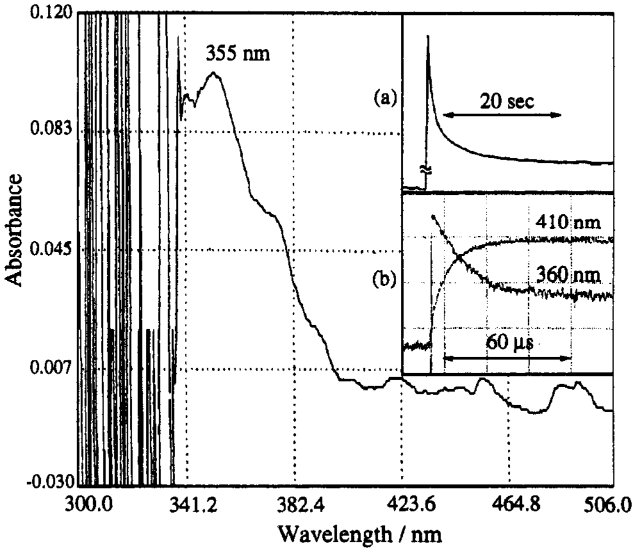

***Figure 2.*** Absorption spectrum of the transient products formed during the irradiation of **1a** in degassed benzene solution at 20 °C, recorded 50 $\mu$s after excitation. Inset (a) shows an oscillogram trace monitored at 355 nm. Inset (b) shows oscillogram traces monitored at 360 and 410 nm during the irradiation in a non-degassed benzene solution.

The apparent built-up rate constant, $k_{obs}$, of the carbonyl oxide (**3**) is essentially identical with that of the decay of $^3$**2a** (inset (b) in Figure 2), and $k_{obs}$ is expressed as given in eq 1, where

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

$k_0$ represents the rate of decay of $^3$**2a** in the absence of oxygen and $k_{O_2}$ is the quenching rate constant of $^3$**2a** by oxygen. A plot of the observed pseudo-first-order rate constant of the formation of the oxide against [O$_2$] is linear (Figure 3). From the slope of this plot, $k_{O_2}$ was determined to be $1.1 \times 10^7$ M$^{-1}$ s$^{-1}$, which is approximately 2 orders of magnitude smaller than that observed with the "parent" $^3$DPC ($k_{O_2} = 5.0 \times 10^9$ M$^{-1}$ s$^{-1}$).[20b]

When a degassed benzene solution of **1a** containing 1,4-cyclohexadiene (CHD) was excited, a new species was formed, showing an absorption with $\lambda_{max} = 359$ nm, formed as the 355 nm signal of $^3$**2a** decayed. The decay of $^3$**2a** was again found to be kinetically correlated with the growth of the new species. Thus, this new signal was attributable to the hexabromodiphenylmethyl radical (**5**) formed as a result of H abstraction of $^3$**2a** from the diene, since it is now well-documented[21,22] that triplet arylcarbenes, generated in good hydrogen donor solvents, undergo H abstraction leading to the corresponding radicals which show transient absorptions at longer wavelengths than those of the precursor carbenes. The excellent hydrogen donor properties of CHD have been well-recognized.[23] A plot of the observed pseudo-first-order rate constant of the formation of

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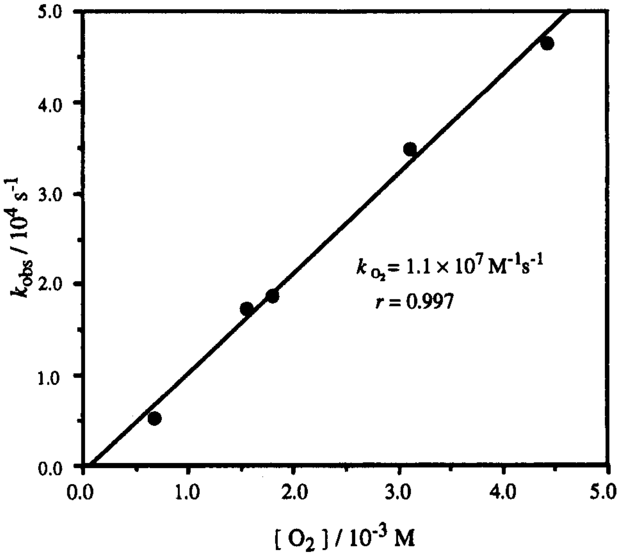

***Figure 3.*** Plot of the growth rate of the benzophenone oxide (**3a**) as a function of oxygen concentration.

the radical against [CHD] is linear, and the slope of this plot yields the absolute rate constant for the reaction of $^3$**2a** with the diene, $k_{CHD} = 7.4 \times 10^2$ $M^{-1}$ $s^{-1}$, which is some 5 orders of magnitude smaller than that observed with $^3$DPC ($k_{CHD} = 1 \times 10^7$ $M^{-1}$ $s^{-1}$).[21b]

Thus, the half-life ($t_{1/2}$) and the quenching rate constants ($k_{O_2}$ and $k_{CHD}$) of triplet hexabromodiphenylcarbene ($^3$**2a**) as opposed to those of triplet dimesitylcarbene clearly suggest that bromine groups are better kinetic protectors than methyl groups, as expected.

**B. Anomalous Effects of Para Substituents.** Reactions of carbenes are shown to be sensitive to electronic perturbation, probably due to the fact that a small shift in energy may invert the energy difference between the singlet and triplet states ($\Delta G_{ST}$). Generally speaking, electron donor groups stabilize the electrophilic singlet carbene more than they do the radical-like triplet and lead to smaller $\Delta G_{ST}$.[24] The two phenyl rings in the triplet diphenylcarbene do not lie in the same plane in the solid state[25] and probably not in solution due to unfavorable steric interactions. This is most likely true for singlet diphenylcarbene as well. Therefore, the electronic effects on the diphenylcarbene reactivities are not straightforward. Actually, the electronic effect on the triplet diphenylcarbene reactivities is not well-characterized.[26,27]

Thus, we prepared bis(4-methyl-2,6-dibromophenyl)- (**1b**) and bis(4-*tert*-butyl-2,6-dibromophenyl)diazomethanes (**1c**) and investigated the reactivities of carbenes (**2b**,**c**) therefrom, which revealed that the *p*-alkyl groups exhibited unexpectedly large effects on the lifetime of triplet polybrominated diphenylcarbenes ($^3$**2**).

Anomalous effects of para substituents on the reactivities of $^3$**2** were shown by monitoring the UV/vis spectra of $^3$**2** at low temperature as a function of temperature. Irradiation ($\lambda > 350$ nm) of **1c** in 2-MTHF glass at 77 K resulted in the appearance of new bands with maxima at 331 and 344 nm at the expense of the original absorption due to **1c**. The new bands exhibited no change when kept at 77 K but disappeared upon thawing the matrix to room temperature. On the basis of these observations coupled with EPR data (vide supra), the absorption spectrum can be attributed to $^3$**2c**. The stability of carbene was then examined by slowly warming the matrix containing $^3$**2c** (5 °C/15 min) from 77 K. No appreciable changes were observed for the absorption bands due to $^3$**2c** 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 $^3$**2a**, 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 $^3$**2**. Thus, in MTHF matrix, $^3$**2b** decayed very fast even below 100 K.

LFP studies also indicated that the stability of $^3$**2** was dramatically affected by substituents at the para positions. LFP of **1c** in a degassed benzene produced a transient species showing a strong absorption at 340 nm and a weak absorption extending from 380 to 400 nm, which we assigned to $^3$**2c** on the basis of the UV/vis spectrum and ESR measurement at low temperature. The transient signals due to $^3$**2c** decayed very slowly, much slower than that of $^3$**2a**; it took more than 200 s before all the signals disappeared completely under these conditions. The decay was found to be second order ($2k/\epsilon l = 0.36$ $s^{-1}$). The rough lifetime of $^3$**2c** is estimated in the form of a half-life, $t_{1/2}$, to be 16 s. These values clearly indicate that $^3$**2c** is some 20 times longer-lived than $^3$**2a**. In marked contrast, the transient absorption due to $^3$**2b** obtained by LFP of **1b** under identical conditions decayed rather rapidly within 1 s. The decay was found to be best fit to a first-order decay ($k = 4.7$ $s^{-1}$) in this case, and the lifetime is estimated to be 0.21 s ($t_{1/2} = 0.22$ s).

The results clearly suggest that the lifetime of triplet polybrominated DPC ($^3$**2**) was dramatically affected by the remote para substituents, which are not expected to exert a significant effect on the steric congestion around the carbenic center. To know the origin of these puzzling effects, the following studies were carried out.

ESR spectra of $^3$**2a**−**c** were obtained in 2-MTHF glasses at 77 K by subjecting a frozen solution of **1** to a short period of photolysis, and the spectra were analyzed in terms of *D* and *E* values, which are reported in Table 1. Inspection of the data in the table clearly indicates that there are no significant change in *E*/*D* values as one changes the para substituents. These observations indicate that the para substituents exhibit little effect on the geometries of $^3$**2**, as expected. PM3 calculations[28] also

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***Table 1.*** $D$ and $E$ Values for Triplet Bis(2,6-dibromophenyl)carbenes (**2**) in 2-Methyltetrahydrofuran (2-MTHF) at 77 K[a]

| carbene | $D$/cm$^{-1}$ | $E$/cm$^{-1}$ | $E/D$ |
|---|---|---|---|
| **2a** | 0.396 | 0.0295 | 0.0745 |
|  | (0.368) | (0.00026) | (0.0007) |
| **2b** | 0.396 | 0.0275 | 0.0695 |
|  | (−) | (−) | (−) |
| **2c** | 0.397 | 0.0311 | 0.0784 |
|  | (0.442) | (∼0) | (∼0) |
| **2d** | 0.484 | 0.0151 | 0.0311 |
|  | (0.600) | (0.0119) | (0.020) |

[a] The values in parentheses refer to those observed in 3-methylpentane (3-MP) at 77 K. No ESR signals ascribable to **2b** were observed in 3-MP at 77 K.

***Table 2.*** UV/Vis Spectra and Kinetic Data for Triplet Bis(2,6-dibromophenyl)Carbenes (**2**)

| carbene | $\lambda_{max}$ (nm) | $2k/\epsilon l$ (s$^{-1}$) | $t_{1/2}$ (s) | $k_{O_2}$ (M$^{-1}$ s$^{-1}$) | $k_{CHD}$ (M$^{-1}$ s$^{-1}$) |
|---|---|---|---|---|---|
| **2a** | 339, 353 | 8.9 | 1.0 | $1.1 \times 10^7$ | $7.4 \times 10^2$ |
| **2b** | 335, 350 | (4.7) | 0.2 | $2.3 \times 10^7$ | $3.2 \times 10^2$ |
| **2c** | 335, 349 | 0.35 | 16 | $2.1 \times 10^7$ | $5.3 \times 10^2$ |
| **2d** | 343, 357 | 0.35 | 16 | $4.6 \times 10^6$ | $2.5 \times 10^2$ |

[a] UV/vis spectra were obtained in 2-MTHF matrix at 77 K. [b] All measurements were done in benzene at ca. 20 °C.

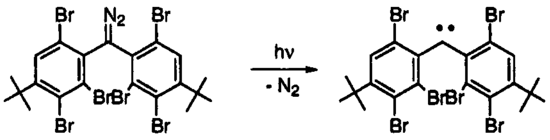
indicate that both the central angle (α) and the dihedral angle ($\theta$) of the two aryl rings are essentially the same between the three carbenes ($^3$**2a**−**c**).

The reactivities of **2** toward typical triplet quenchers, i.e., oxygen and 1,4-cyclohexadiene (CHD), were then investigated by using LFP, and the rate constant ($k_{O_2}$) for quenching $^3$**2** by oxygen and the rate constant ($k_{CHD}$) for H abstraction of $^3$**2** from CHD are reported in Table 2. Inspection of the data summarized in the table suggests that the reactivities of $^3$**2** toward those triplet quenchers are again not significantly affected by the para substituents.

These observations clearly support a naive idea based on intuition that the para substituents exert almost no steric effects around the remote carbenic center of $^3$**2**, at least in terms of steric congestion. Electronic effects,[29] which usually affect the singlet state energy more effectively than the triplet,[24] on the other hand, seem also not so important as to change the reactivity of $^3$**2** so significantly.

What is the origin of the marked para effect on the stability of $^3$**2** in benzene, then? Benzene is known to be one of the least reactive solvents toward triplet carbenes. Thus, most of the persistent triplet diphenylcarbenes undergo dimerization in benzene to form tetra(aryl)ethylenes as almost exclusive isolable product.[4] Carbene $^3$**2a** also underwent dimerization, as evidenced by the second-order decay kinetics in benzene. However, product analysis of the spent solution showed that carbenic dimer was formed in surprisingly smaller amount (vide infra) as opposed to the yield of carbene dimer from other sterically congested diphenylcarbenes, e.g., dimesitylcarbene.[8,13] This suggests that simple dimerization of $^3$**2** 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.

***Scheme 2***



**1d** **2d**

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.[30] Thus, it is likely that the brominated diphenylcarebenes (**2**) 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.[31] On the other hand, tri($p$-tolyl)methyl undergoes rapid disproportionation to yield tri($p$-tolyl)methane and a quinoid compound which rapidly polymerizes.[32] However, the coupling at the para positions is retarded by a *tert*-butyl group at this position.[33]

Thus, rather large stabilizing effects of *tert*-butyl groups at the para positions on the lifetime of $^3$**2** compared to those of bromo and methyl groups are compatible with the effect of substituents observed in the coupling reaction of trityl radicals. The complexity of the products observed in the reaction of $^3$**2** may be partly due to the complexity associated with the coupling reactions. The α-para coupling of triplet DPCs, for instance, unlike that of trityls, does not lead to a final stable product and gives rise to an intermediate open-shell molecule whose subsequent reactions will be complicated by possible ambient reactivity.

**C. Effects of Meta Substituents.** It is well-known that, in 1,2-disubstituted benzene derivatives, introduction of substituents in the 3-position exerts a very large effect on the rate of appropriate reactions, which are considered in light of the importance of bond bending: the 3-substituents "buttress" the 2-substituents.[34] 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.[35]

This has been shown in the reaction of polymethylated diphenylcarbenes;[8] the lifetime of triplet states increased on going from dimesityl- to didurylcarbenes.

Bis(2,3,6-tribromo-4-*tert*-butylphenyl)diazomethane (**1d**) again generated carbene **2d** (Scheme 2) as a result of facile dissociation of $N_2$ upon photoexcitation not only in solution at ambient temperature but also in matrix at low temperature, which enabled us to observe and investigate triplet carbene $^3$**2d** in detail. The results are somewhat contrary to that expected, however. Thus,

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(29) Hammett-type polar substituent constants $\sigma_p(\sigma_p{}^+)$[11] for Br, Me, and $t$-Bu groups are 0.23 (0.15), −0.17 (−0.31), and −0.11 (−0.26), respectively, and spin-delocalization substituent constants $\sigma_c{}^\bullet$ devoid of polar effects for the three groups are 0.13, 0.11, and 0.13, respectively. (a) Creary, X. *J. Org. Chem.* **1980**, *45*, 280. Creary, X.; Mehrsheik-Mohammadi, M. E.; McDonald, S. *J. Org. Chem.* **1987**, *52*, 3254.

(30) Reviews of triarylmethyls: (a) Sholle, V. D.; Rozantsev, E. G. *Russ. Chem. Rev.* **1973**, *42*, 1011. (b) McBride, J. M. *Tetrahedron* **1974**, *30*, 2009.

(31) Bowden, S. T.; Watkins, T. F. *J. Chem. Soc.* **1940**, 1249.

(32) Marvel, C. S.; Rieger, W. H.; Mueller, M. B. *J. Am. Chem. Soc.* **1939**, *61*, 2769, Marvel, C. S.; Mueller, M. B.; Himel, C. M.; Kaplan, J. F. *J. Am. Chem. Soc.* **1939**, *61*, 2771.

(33) Neumann, W. P.; Uzick, W.; Zarkadis, A. K. *J. Am. Chem. Soc.* **1986**, *108*, 3762. Rajca, A.; Utamupanya, S. *J. Org. Chem.* **1992**, *113*, 2552.

(34) Westheimer, F. H. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley: New York, 1956; pp 523−555.

(35) For buttressing effect in carbene chemistry, see: Tomioka, H.; Kimoto, K.; Murata, H.; Izawa, Y. *J. Chem. Soc., Perkin Trans. 1* **1991**, 471.

irradiation of **1d** in 2-MTHF matrix at 77 K produced a UV/vis absorption band similar to that observed for $^3$**2c**. Monitoring of the spectral change as a function of temperature indicated that the absorption ascribable to $^3$**2d** was also persistent up to 170 K, where the half-life of $^3$**2d** was essentially identical with that of $^3$**2c**.

Kinetic measurements in the solution phase made by using LFP provided more quantitative data. LFP of **1d** in a degassed benzene produced transient absorption ascribable to $^3$**2d**, which also decayed very slowly in second order. The rate constant was, however, essentially the same as that of $^3$**2c** under the same condition. Quenching rate constants of $^3$**2d** by oxygen and CHD were determined and are reported in Table 2, which also indicate that the reactivity of $^3$**2d** is not significantly changed compared to that of $^3$**2c**.

The observations suggest that the buttressing effect, which exerted a signficant effect on the reactivity of triplet polymethylated diphenylcarbenes,[8] shows little influence on the reactivity of triplet polybrominated diphenylcarbenes. To get some insight into the origin of this rather unexpected result, structural information was collected by means of ESR measurements and theoretical calculations. Zero-field splitting parameters observed for $^3$**2d** in 2-MTHF at 77 K were similar to those obtained for $^3$**2c** under the same conditions. Since 2-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).[15,16] In a soft matrix, i.e., 3-MP,[12] where carbenes can relax to a more stable geometry even at 77 K, the $D$ and $E$ values are distinctly different between $^3$**2c** and $^3$**2d**. Thus, the $E$ value of $^3$**2c** was estimated to be essentially zero, while in $^3$**2d**, $E$ was still significant (Table 1). This is exactly the reverse of what was observed with polymethylated DPCs,[8] where $E$ values decrease as more methyl groups are introduced. It may be that the *m*-bromo substituents intrinsically bias the electronic structure of carbene **2d** in a manner that destroys the near-axial symmetry of carbene **2c**. Thus, one may not deduce the bond angle difference from consideration of the $E$ values as in the case of polymethylated DPCs.

Semiempirical calculations provided intriguing results. The optimized geometries calculated by PM3/UHF suggested that $^3$**2c** has almost linear ($\alpha = 179.82°$) and perpendicular ($\theta = 89.9°$) structure. Similar optimization of $^3$**2d** resulted in three main conformers, i.e., I ($\alpha = 167.9°$, $\theta = 75.7°$), II ($\alpha = 170.0°$, $\theta = 80.8°$), and III ($\alpha = 179.4°$, $\theta = 89.7°$), that are very close in energy (±0.04 kcal/mol). Although two conformers ($^3$**2d**, I and $^3$**2d**, II) have a definitely smaller bond angle ($\alpha$) than in $^3$**2c**, the third one ($^3$**2d**, III) has essentially the same $\alpha$ and $\theta$ values as for $^3$**2c**. However, the distances from the carbene carbon to the *o*-bromo groups are notably different between the two carbene systems. This distance in $^3$**2c** is 3.057 Å. On the other hand, the distances to the two bromine groups are marginally different in all three conformers of $^3$**2d**; the distances to the 2-bromine group, which should be buttressed by 3-bromine, in I, II, and III are 3.236, 3.228, and 3.200 Å, respectively, while those to 2-bromine are 2.996, 3.005, and 3.054 Å. This means that 2-bromine groups, which are expected to get closer to the carbenic center than 6-bromine, are actually moving in the opposite direction. Therefore, the carbenic center in $^3$**2d** is considered to be not protected as tightly as expected. A closer inspection of the geometry revealed that the benzene ring in $^3$**2d** is distorted, probably due to steric repulsion between the two adjacent bromine groups at the 2 and 3 positions, and that the two bromine groups are tilted, one up, one down, with respect to the benzene plane by ca. 2°. Therefore, the buttressed 2-bromine group is forced to move away from the carbenic center and hence cannot block it from external reagents more effectively than the unbuttressed 6-bromine group.

It may be intriguing to examine the difference in buttressing effects between polymethylated and polybrominated diphenylcarbenes. The Taft steric substituent constants ($E_s$) of bromine and methyl groups are the same.[36] The difference, then, can be ascribable to the difference in other more specific natures between methyl and bromine groups. Bromine groups are spherically symmetrical and therefore interact with each other with little directional factor. Therefore, a benzene ring is forced to be distorted when two bromine groups are introduced at adjacent position. On the other hand, in the case of methyl groups, 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 position can be accepted on the benzene ring without causing severe distortion by simply rotating each other to minimize the interaction potential. This will result in the restraint of free rotation of the *o*-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.

**D. Possible Synergetic Effects of Bromine and Methyl Groups.** The results show that bromine and methyl groups can both serve as effective kinetic protectors toward triplet carbene, but they seem to shield the center in different fashion, as expected from the differences in shape and size. In the case of dimesitylcarbene, for instance, the directional factor is an important one, and hence van der Waals potential functions for the interaction between methyl groups at the ortho positions are not simple. They can rotate each other harmonically to diminish the interaction potential between the hydrogens. Such a directional factor is less important in polybrominated diphenylcarbenes, as we saw already in the previous section. On the other hand, the electronic properties of the two groups are different.[29] From these considerations, it is very intriguing to generate $^3$DPC protected by the two substituents and investigate reactivities in order to examine possible synergetic effects of the two kinetic protectors on the stability of $^3$DPC. Above all things, almost nothing is known concerning the reactivity of sterically congested DPCs bearing unsymmetrical kinetic protectors.

Irradiation of (2,6-dibromo-4-*tert*-butylphenyl)(2,6-dimethyl-4-*tert*-butylphenyl)diazomethane (**1e**) in 2-MTHF glasses at 77 K gave typical ESR signals ascribable to triplet carbene $^3$**2e** (Scheme 3). The signals were analyzed in terms of $D$ and $E$ values and are reported in Table 3, which also includes the values of $^3$**2c** and bis(2,4-dimethyl-4-*tert*-butylphenyl)carbene (**2f**)[16] for comparison purpose. It is interesting to note that the values of $^3$**2e** are not intermediate between those for $^3$**2c** and **2f** but are very much like those of $^3$**2c**, indicating that the geometry

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(36) Taft, R. W., Jr. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley: New York, 1956; pp 556−695.

*Scheme 3*

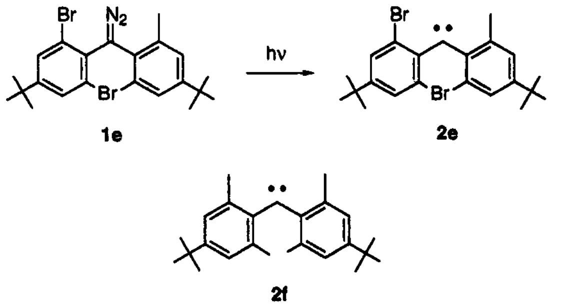


*Table 3.* ESR[a] and Kinetics[b] Data for Triplet Diphenylcarbenes (**2**)

| carbene | $D$/cm$^{-1}$ | $E$/cm$^{-1}$ | $E/D$ | $2k/\epsilon l$ (s$^{-1}$) | $k_i$ (s$^{-1}$)[c] | $t_{1/2}$ (s) |
|---|---|---|---|---|---|---|
| **2c**[d] | 0.397 | 0.031 | 0.0784 | 0.35 | | 16 |
| **2e** | 0.423 | 0.0324 | 0.0765 | 2.4 | 0.58 | 1.8 |
| **2f**[e] | 0.373 | 0.0134 | 0.0381 | 5.8 | 0.62 | 0.5 |

[a] ESR data were obtained in 2-MTHF at 77 K. [b] All measurements were done in degassed benzene at ca. 20 °C. [c] Intramolecular H migration rate constant. [d] The data in Tables 1 and 2 are included for comparison purpose. [e] Reference 16.

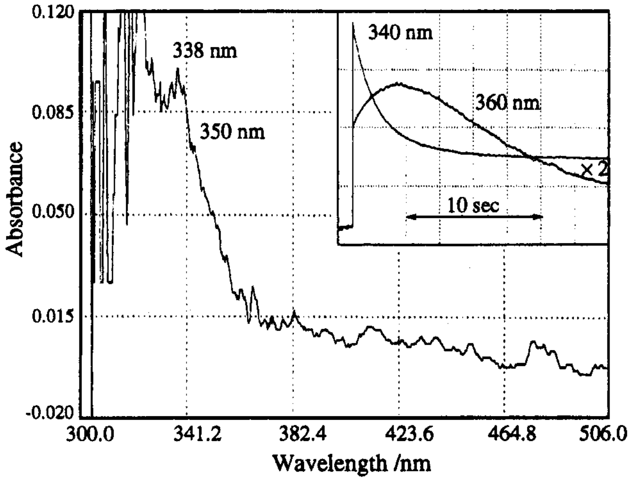
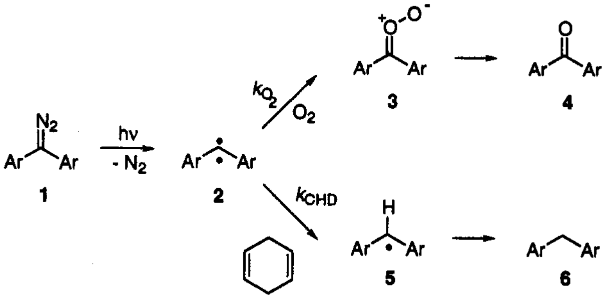


*Figure 4.* Absorption spectrum of the transient products formed during the irradiation of **1e** in degassed benzene solution at 20 °C, recorded 50 $\mu$s after excitation. The inset shows oscillogram traces monitored at 340 and 360 nm.

of $^3$**2e** 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 $^3$**2e** started to disappear significantly only at 170 K in 2-MTHF. Thus, the thermal stability of $^3$**2e** is comparable to that of $^3$**2c** but is much higher than that of $^3$**2f**,[16] which decomposed significantly already at 130 K.

Despite the notable similarity of the properties of $^3$**2e** to those of $^3$**2c** in low-temperature matrices, the behavior of $^3$**2e** in solution at room temperature was found to be more or less comparable to that of $^3$**2f** (Table 3). LFP of **1e** in a degassed benzene generated transient absorption due to $^3$**2e** which decayed within 10 s, considerably faster than $^3$**2c** (Figure 4). 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 for $^3$**2c** and comparable to that for $^3$**2f** ($t_{1/2}$ = 0.5 s).[37] The decay kinetics of $^3$**2e** indicated that a new species with an absorption maximum at 370 nm was formed as the carbene absorption at 340 nm decayed. Similar secondary products are observed in LFP of dimesitylcarbene[8] and are assigned to *o*-quinodimethane, presumably formed as a result of intramolecular 1,4-H shift from the *o*-methyl to the carbene center. The growth rate of *o*-quinodimethane, which is equal to the intramolecular H abstraction rate ($k_i$) of $^3$**2e**, was estimated to be 0.58 s$^{-1}$. This value is also comparable to that observed with $^3$**2f** ($k_i$ = 0.62 s$^{-1}$).[37] Thus, $^3$**2e** is shown to decay, at least in part, by abstracting hydrogen from the *o*-methyl group, while the main decay pathway for $^3$**2c** is dimerization. This intramolecular reaction channel available for $^3$**2e** explains the difference in lifetimes between the two carbenes. Product analysis results (vide infra) also supported this idea.

*Scheme 4*



The results suggest that DPC protected by unsymmetrical groups of 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; the configurations and stabilities of $^3$**2e** in a low-temperature matrix are dominantly affected by the bromine substituents, while the kinetics in solution phase are controlled by the methyl substituents. This can be explained in terms of the dependence of quenching processes possible for $^3$**2e** on the conditions. Presumably, at low temperatures, the main quenching pathway for $^3$**2e** is dimerization to form the carbene dimer. The carbene center in $^3$**2e** is well-protected by the two *o*-bromine groups and the two *o*-methyl groups. The methyl groups in $^3$**2e** are fixed more tightly than those in $^3$**2f**, as the substituents on the opposite side are spherically symmetrical bromine groups, and hence $^3$**2e** becomes thermally more stable than $^3$**2f**. On the other hand, when the temperature is raised, intramolecular H abstraction, which usually requires higher activation energy,[9] becomes also allowed and starts to compete with the dimerization. Thus, the reactivity of $^3$**2e** is affected by the reactive methyl groups at higher temperature.

**E. Product Analysis Studies.** The reaction patterns observed for polybrominated diphenylcarbenes (**2**) were analogous to those observed with other sterically congested diphenylcarbenes. These carbenes did not react with the diazo precursors to form ketazines in a relatively inert solvent, e.g., benzene. Instead they underwent dimerization. However, the structure and yield of the dimer were notably different from those observed for other persistent $^3$DPCs, i.e., hexachlorodiphenylcarbenes[9] and dimesitylcarbenes,[8a,b,9] which produced tetra(aryl)ethylenes in fairly good yield (~80%). Thus, generation of **2a**−**c** in a degassed benzene solution by irradiating **1a**−**c** resulted in the formation of a tarry matter, from which a relatively small amount of dimeric product was isolated. $^1$H NMR analysis of the dimer exhibited the presence of four aromatic protons

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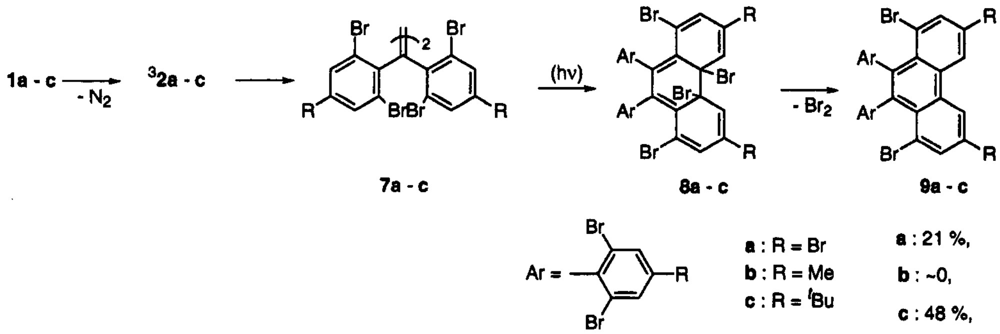
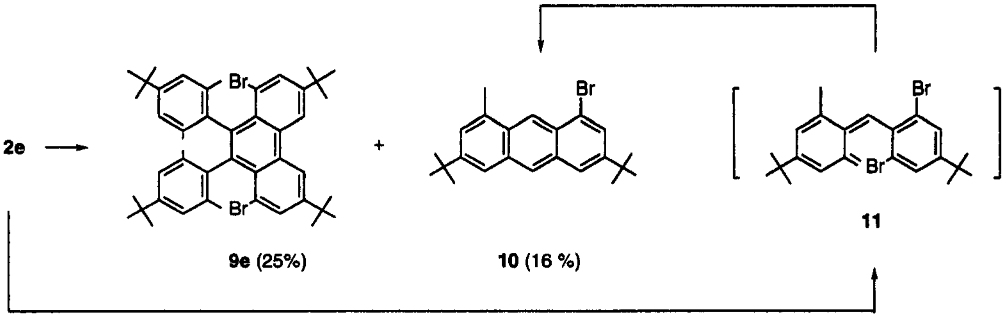
(37) Tomioka, H.; Yingmo, Y.-H.; Ishikawa, Y.; Hirai, K. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 2207.

Scheme 5



Scheme 6



notably shifted downfield in addition to the four protons in the "normal" region. MS analysis showed no peak corresponding to the $M^+$ ion calculated for simple tetra(aryl)ethylene (**7**), but the peak corresponding to the fragment formed as a result of loss of two bromine units from **7**. The structure of the product which explains the data best is phenanthrene derivatives (**9**) (Scheme 5). A presumable possibility is that triplet carbenes ($^3$**2**) undergo dimerization to form tetra(aryl)ethylenes (**7**), which subsequently cyclize to lead to phenanthrene (**9**), since the photocyclization of stilbene derivatives to give the corresponding phenanthrenes has been well-documented.[38] However, all attempts to detect or isolate **7** were unsuccessful. It may be that **7** is very sensitive under these conditions and is consumed to form **9** before it accumulates.

Irradiation of **1e** under identical conditions gave rise to a new product along with the phenanthrene-type dimer (**9e**). The new product was easily assigned as the anthracene derivative (**10**) on the basis of spectroscopic data. The formation of **10** is interpreted in terms of intramolecular hydrogen migration in triplet carbene $^3$**2e**, from the *o*-methyl group to the carbenic center, to generate *o*-quinodimethane (**11**), followed by subsequent cyclization and dehydrobromination (Scheme 6). The formation of **10** is in accord with the spectroscopic observation (vide supra). The structure of phenanthrene **9e** suggests that debromination is crucial for the formation of phenanthrene under these conditions.

## Summary

The present study has revealed unique properties of the bromine group as a kinetic protector toward the triplet carbene center. As expected, bromine groups shield the carbene center better than methyl groups. Thus, triplet carbene having a half-life over a second is realized. Taking into account the fact that the van der Waals radius of bromine is similar to that of methyl, this is in part due to the longer bond length of the C−Br bond than the C−C (Me), whereby the *o*-bromo groups overhang the reactive site more effectively than the *o*-methyl groups. More importantly, it is likely that this difference is mostly due to the difference in reactivities toward triplet carbene between the two groups.

One may wonder whether a through-space interaction between the triplet carbene center and the *o*-bromine groups may play a role in stabilizing the triplet carbene. ESR data clearly indicate, however, that there is no such interaction, at least in a rigid matrix at a low temperature. PM3 calculations also support this idea. A possible role of the heavy atom effect in stabilizing the triplet state is not clear, as the present techniques do not allow us to observe the singlet counterpart and hence the intersystem crossing process. The kinetic studies using a faster kinetic window will be required to clarify these effects.

Rather anomalous effects of para substituents are noted on the reactivities of polybrominated triplet DPCs to such an extent that have not been noticed in the reactions of any other analogous sterically congested triplet DPCs. This means that the carbenic center in polybrominated DPCs is so effectively shielded by the *o*-bromine groups that the aromatic positions become significant reactive sites to decay. Triplet carbene surviving more than a minute is realized for the first time by quenching this leaking process.

On the other hand, the buttressing effect is found to be ineffective in this case, probably because repulsion between two adjacent bromine groups on a benzene ring is so strong that the benzene ring is distorted to such an extent that the protecting bromine groups are forced to move away from the carbenic center.

Those observations give a clue to a longer-lived triplet carbene and a hope to isolate a stable triplet carbene in the near future.

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[38] (a) Mallory, F. B.; Mallory C. W. *Org. React.* **1984**, *30*, 1. (b) Gilbert, A. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Ed.; CRC Press: Boca Roton, FL, 1994; pp 291−300.

## Experimental Section

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

**Preparation of Polybrominated Diphenyldiazomethanes (1).** All diazomethanes employed in this study were prepared by treating diaryl(chloro)methane with ethyl carbamate in the presence of $AgBF_4$, followed by nitrosation of the resulting ethyl (diarylmethyl)carbamate and treatment of the resulting ethyl *N*-nitroso-*N*-(diarylmethyl)carbamate with t-BuOK, developed by Zimmerman and Paskovich.[9] The desired chlorides were obtained by nitration of benzophenones, followed by reduction of the resulting 3,3′-dinitrobenzophenone to 3,3′-diaminobenzhydrol, bromination with $Br_2$, and dediazoniation of the polybromo-3,3′-diaminobenzhydrols. The following diazomethanes were prepared.

**Bis(2,4,6-tribromophenyl)diazomethane** (**1a**): orange solid; mp 129−131 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.76 (s, 4 H); IR (KBr) 2064 $cm^{-1}$.

**Bis(2,6-dibromo-4-methylphenyl)diazomethane** (**1b**): orange solid; mp 115−117 °C (dec); $^1$H NMR ($CDCl_3$) $\delta$ 2.31 (s, 6 H), 7.41 (s, 4 H); IR (KBr) 2064 $cm^{-1}$.

**Bis(2,6-dibromo-4-*tert*-butylphenyl)diazomethane** (**1c**): orange solid; mp 150−151 °C (dec); $^1$H NMR ($CDCl_3$) $\delta$ 1.30 (s, 18 H), 7.57 (s, 4 H); IR (KBr) 2064 $cm^{-1}$.

**Bis(2,3,6-tribromo-4-*tert*-butylphenyl)diazomethane** (**1d**): orange solid; mp 169−170 °C (dec); $^1$H NMR ($CDCl_3$) $\delta$ 1.53 (s, 18 H), 7.67 (s, 2 H); IR (KBr) 2064 $cm^{-1}$.

**(2,6-Dibromo-4-*tert*-butylphenyl)(2,6-dimethyl-4-*tert*-butylphenyl)diazomethane** (**1e**): orange solid; mp 121−122 °C; $^1$H NMR ($CDCl_3$) $\delta$ 1.29 (s, 9 H), 1.30 (s, 9 H), 2.17 (s, 6 H), 7.07 (s, 2 H), 7.57 (s, 2 H); IR (KBr) 2048 $cm^{-1}$.

**Irradiation for Product Analysis.** In a typical run, a solution of the diazo compound (**1**, ca. 10 mg) in solvent was placed in a Pyrex tube and irradiated with a high-pressure, 300-W mercury lamp until all the diazo compound was destroyed. The irradiation mixture was then concentrated on a rotary evaporator below 20 °C. Individual components were isolated by column chromatography or by preparative TLC and identified by NMR and MS.

In this way, the following products were isolated and characterized.

**1,3,6,8-Tetrabromo-9,10-bis(2,4,6-tribromophenyl)phenanthrene (9a)**: 30%; white solid; mp 334.3−334.7 °C; $^1$H NMR ($CDCl_3$) $\delta$ 7.60 (d, $J = 1.65$ Hz, 2 H), 7.65 (d, $J = 2.02$ Hz, 2 H), 8.15 (d, $J = 1.65$ Hz, 2 H), 8.84 (d, $J = 2.02$ Hz, 2 H).[39]

**1,8-Dibromo-3,6-di-*tert*-butyl-9,10-bis(2,6-dibromo-4-*tert*-butylphenyl)phenanthrene (9c)**: 63%; pale yellow solid; mp 129.1−131.3 °C; $^1$H NMR ($CDCl_3$) $\delta$ 1.28 (s, 18 H), 1.50 (s, 18 H), 7.28 (s, 4 H), 8.01 (d, $J = 1.84$ Hz, 2 H), 8.79 (d, $J = 1.84$ Hz, 2 H); HRMS calcd for $C_{42}H_{44}Br_6$ *m*/*e* 1021.8543, found 1021.8536.

**1,8-Dibromo-3,6-di-*tert*-butyl-9,10-bis(2,6-dimethyl-4-*tert*-butylphenyl)phenanthrene (9e)**: 25%; pale yellow solid; mp 196.4−199.3 °C; $^1$H NMR ($CDCl_3$) $\delta$ 1.23 (s, 18 H), 1.49 (s, 18 H), 1.68 (s, 12 H), 6.66 (s, 4 H), 7.96 (d, $J = 2.02$ Hz, 2 H), 8.79 (d, $J = 2.02$ Hz, 2 H); MS *m*/*e* (relative intensity) 770 (M + 4, 57.5), 768 (M + 2, 100), 766 ($M^+$, 50.8); HRMS calcd for $C_{46}H_{56}Br_2$ *m*/*e* 766.2748, found 766.2712.

**1-Bromo-3,6-di-*tert*-butyl-8-methylanthracene (10)**: 16%; pale yellow solid; mp 174.5−175.6 °C; $^1$H NMR ($CDCl_3$) $\delta$ 1.44 (s, 18 H), 2.85 (s, 3 H), 7.42 (s, 1 H), 7.73 (s, 1 H), 7.81 (s, 1 H), 7.85 (s, 1 H), 8.31 (s, 1 H), 8.75 (s, 1 H); MS *m*/*e* (relative intensity) 384 (M + 2, 100), 382 ($M^+$, 89.0), 367 (44.1), 57 (64.0); HRMS calcd for $C_{23}H_{27}Br$ *m*/*e* 382.1296, found 382.1242.

**ESR Measurements.** The diazo compound was dissolved in 2-methyltetrahydrofuran (2-MTHF, $5 \times 10^{-4}$ M), and the solution was degassed in a quartz cell by four freeze−degas−thaw cycles. The sample was cooled in an optical transmission ESR cavity at 77 K and irradiated with a Wacom 500-W Xe lamp using a Pyrex filter. ESR spectra were measured on a JEOL JES TE200 spectrometer (X-band microwave unit, 100 kHz field modulation). The signal positions were read by the use of a gaussmeter.

**Low-Temperature UV/Vis Spectra.** Low-temperature spectra at 77 K were obtained by using an Oxford variable-temperature liquid nitrogen cryostat (DN 2704) equipped with a quartz outer window and a sapphire inner window. The sample was dissolved in dry 2-MTHF, placed in a long-necked quartz cuvette of 1-mm path length, and degassed by four freeze−degas−thaw cycles at pressure near $10^{-5}$ Torr. The cuvette was flame-sealed under reduced pressure, placed in the cryostat, and cooled to 77 K. The sample was irradiated for several minutes in the spectrometer with a Halos 500-W high-pressure mercury lamp using a Pyrex filter, and the spectral changes were recorded at appropriate time intervals. The spectral changes upon thawing were also monitored by carefully controlling the matrix temperature with an Oxford Instrument Intelligent Temperature Controller (ITC 4).

**Laser Flash Photolysis.** All flash photolysis measurements were made on a Unisoku TSP-601 flash spectrometer. The excitation source for the laser flash photolysis was a XeCl excimer laser. A Hamamatsu 150-W xenon short arc lamp (L2195) was used as the probe source, and the monitoring beam guided using an optical fiber scope was arranged in an orientation perpendicular to the excitation source. The probe beam was monitored with a Hamamatsu R2949 photomultiplier tube through a Hamamatsu S3701-512Q linear image sensor (512 photodiodes used). Timing of the laser excitation pulse, the probe beam, and the detection system was achieved through an Iwatsu model DS-8631 digital synchroscope, which was interfaced to an NEC 9801 RX2 computer. This allowed for rapid processing and storage of the data and provided printed graphics capabilities. Each trace was also displayed on an NEC CRT N5913U monitor.

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

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**Supporting Information Available:** Experimental descriptions for **1a**−**e**; geometries of $^3$**2d** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[39] This compound was insoluble in most solvents and showed no volatility. Partly due to this difficult nature, all attempts to measure high-resolution mass spectra failed.