*J. Phys. Chem. A* **1999,** *103,* 9280−9284

# Effect of Para Substituents on the Molecular and Electronic Structures of Sterically Congested Triplet Diphenylcarbenes

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*Received: May 14, 1999; In Final Form: September 21, 1999*

A series of triplet di(2,6-dimethylphenyl)carbenes ($^3$**2**) bearing nine symmetrical para di-substituents with well-distributed electronic properties have been generated by the irradiation of the corresponding diazo precursors and studied using electron paramagnetic resonance spectroscopy. The zero field splitting parameters, *D* and *E*, were measured in matrices of different viscosities and are analyzed in terms of a sigma-dot ($\sigma^\bullet$) scale of spin-delocalization substituent constants. Fairly good correlation ($r > 0.9$) with $\sigma^\bullet$ based on the spin delocalization in the absence of polar effects was found for the *D* values of $^3$**2** in its minimum energy geometry, but not for those in the metastable state. The magnitude of $\rho$ for $^3$**2** was larger than that for *o*-unsubstituted diphenylcarbenes and is discussed in terms of the difference in the geometry between the two carbene systems.

## Introduction

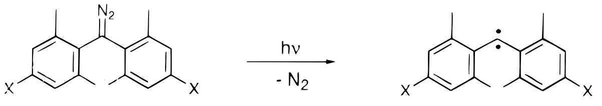
While the history of stable and persistent radicals is long and impressive,[1] that of persistent triplet carbenes is short, and triplet carbenes capable of surviving under normal conditions have not been realized yet.[2,3] Two basic strategies, i.e., thermodynamic and kinetic stabilization, are possible for the stabilization of reactive species. Studies examining the relationship between structure and reactivity have shown that thermodynamic stabilization (electronic conjugation effect) usually plays an important role in stabilizing the singlet state and that the singlet state undergoing the stabilization becomes less reactive due to the contribution of the conjugation to such an extent that the species can be isolated under ambient conditions.[4,5] On the other hand, kinetic stabilization (steric protection) is more effective in stabilizing the triplet counterpart since the introduction of sterically bulky groups around the carbenic center results in an increase in the carbene bond angle. In this case, the triplet state is thermodynamically stabilized with respect to the singlet.

To this end, attempts have been made whereby triplet diphenylcarbenes (DPCs) were stabilized by introducing a series of substituents at the ortho positions,[3,4] and triplet DPCs surviving more than an hour in solution at room temperature were realized.[6] Even though this is a long lifetime for a triplet carbene, it is still ephemeral.

To realize a stable triplet carbene, it is necessary to explore kinetic protectors which are bulky yet unreactive toward the carbenic center. This approach encounters a limitation when diazo compounds are used as a precursor since introduction of the diazo group becomes more difficult as more bulky groups are introduced at the ortho positions.

The other strategy we have not examined extensively is the electronic (thermodynamic) effect of para substituents on the stability of kinetically protected triplet diphenylcarbenes. To explore this effect, we generated a series of triplet di(2,6-dimethylphenyl)carbenes (**2**) bearing nine symmetrical para di-substituents with diverse electronic properties by photolysis of the diazo precursor (**1**) and studied their structure and reactivities by using electron paramagnetic resonance (EPR) spectroscopy. The zero-field splitting (ZFS) parameters were analyzed in terms of the spin delocalizing power of the para substituents.

**SCHEME 1**



**1** **2**

**a**: X = H, **b**: X = Me, **c**: X = $^t$Bu, **d**: X = F,
**e**: X = Cl, **f**: X = Br, **g**: X = OMe,
**h**: X = CN, **i**: X = NO$_2$,

## Experimental Section

**A. Synthesis.** All of the diazo compounds (**1**) used in this study were prepared by the reduction of the corresponding *N*-nitrosodiaryl ketimine with $LiAlH_4$ according to the procedure developed by Zimmerman and Paskovich.[7] Full details of the procedure and their spectroscopic data will be published elsewhere.[8] The diazomethanes were purified by repeated chromatography on a Shodex GPC H-2001 (20 mm × 50 cm) gel permeation column eluted with $CHCl_3$ immediately before the irradiation.

**B. ESR Measurements.** Diazo compounds were dissolved in the appropriate organic solvent ($10^{-3}$ M), and the solution was degassed in a quartz EPR tube by three freeze-degas-thaw cycles. The sample was cooled in an quartz Dewar filled with liquid nitrogen and irradiated with a Wacom 500 W Xe lamp using a Pyrex filter in an optical transmission EPR cavity at 77 K. EPR spectra were measured on a JEOL JES TE 200 spectrometer (x-band microwave unit, 100 kHz field modulation). The signal positions were read by the use of a gauss meter.

For samples used in the temperature dependence studies, the EPR tube was placed in the spectrometer equipped with a JEOL ES-DVT3 liquid nitrogen transfer system and was irradiated at 110 K. The temperature of the sample was monitored and controlled by a PID controller. The sample temperature was raised in 10 K increments to the desired temperature, allowed to stand for 1 min, and recooled to 110 K to measure the signal.

All solvents employed were of spectroscopic grade and purified by distillation just prior to use.

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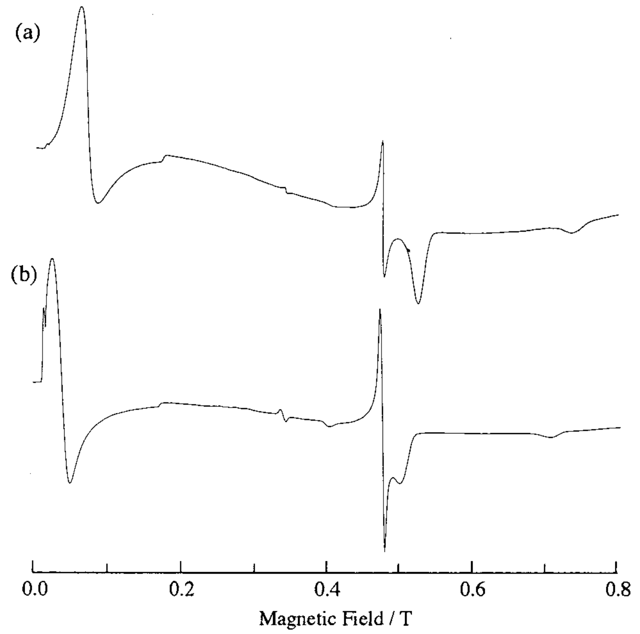


**Figure 1.** ESR spectra of di(2,6-dimethyl-4-*tert*-butylphenyl)carbene (**2c**) in 2-methyltetrahydrofuran (2-MTHF) (a) and 3-methylpentane (3-MP) (b) at 77 K.

**TABLE 1: *D* and *E* Values for Di(2,6-dimethylphenyl)carbenes (2) in 2-Methyltetrahydrofuran (2-MTHF) at 77 K**

| carbenes (**2**) | 4,4′-substituents | *D* ($cm^{-1}$) | *E* ($cm^{-1}$) | $T_d$ (K)[a] |
|---|---|---|---|---|
| **2a** | H | 0.337 | 0.0101 | 140 |
| **2b** | Me | 0.368 | 0.0117 | 120 |
| **2c** | $^t$Bu | 0.373 | 0.0134 | 170 |
| **2d** | F | 0.377 | 0.0129 | 120 |
| **2e** | Cl | 0.354 | 0.0144 | 120 |
| **2f** | Br | 0.353 | 0.0117 | 120 |
| **2g** | OMe | 0.368 | 0.0134 | 120 |
| **2h** | CN | 0.340 | 0.0093 | 180 |
| **2i** | $NO_2$ | 0.335 | 0.0081 | 170 |

[a] Temperature at which the triplet signal disappeared.

## Results and Discussion

**The Zero-Field Splitting Parameters.** Irradiation ($\lambda > 300$ nm) of precursor diazomethanes (**1**) in 2-methyltetrahydrofuran (2-MTHF) at 77 K gave rise to a paramagnetic species readily characterized from its EPR spectrum as a derivative of triplet methylene ($^3$**2**). Figure 1a shows the spectra observed for triplet di(4-*tert*-butyl-2,6-dimethylphenyl)carbene ($^3$**2c**). As shown in Figure 1, the spectra were sufficiently intense that four lines could be observed ($H_{z1}$, $H_{x2}$, $H_{y2}$, $H_{z2}$) under these conditions. The EPR spectra of all the other diphenylcarbenes investigated in this study exhibited similar spectroscopic features.

Carbene triplet signals were assigned in terms of the Hamiltonian[9]

$$H = g\beta H\cdot S + D\left(S_z^{\,2} - \frac{1}{3}S^2\right) + E(S_x^{\,2} - S_y^{\,2})$$

The zero-field splitting (ZFS) parameters, *D* and *E*, which were obtained from the observed spectra by employing an iterative computer program, are reported in Table 1. The *D* value, which is related to the separation between the unpaired electrons, varies considerably with the nature of the triplet. While the overall magnitude of *D* is characteristic of a particular class of triplets, smaller variations in this parameter, which reflect structural differences between various triplet carbenes, are seen within a given class.

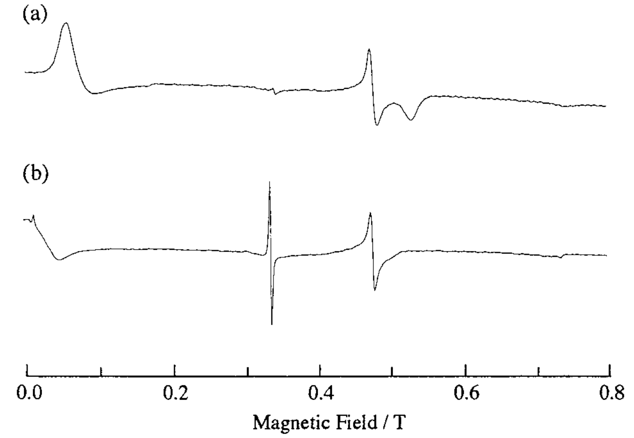
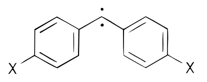


**Figure 2.** ESR spectra of di(2,6-dimethyl-4-*tert*-butyl-phenyl)carbene (**2c**) in 1,2,3-propanetriol triacetate (PT). (a) Sample at 110 K. (b) Same sample after annealing to 200 K and recooling to 110 K.

The *E* value, 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.[9,10]

The ZFS parameters observed for all of the carbenes (**2**) are significantly smaller than those of “parent” DPC and for most 4,4′-disubstituted DPCs (**3**) (vide infra).



**3**

**a**: X = H, **b**: X = $NMe_2$, **c**: X = OMe,
**d**: X = CN, **e**: X = $NO_2$,

**Effects of Temperatures and Matrices.** Similar irradiation of **1** in a more viscous matrix, i.e., 1,2,3-propanetriol triacetate (PT), at 110 K also gave rise to a typical set of triplet signals due to $^3$**2** with ZFS parameters similar to those obtained in 2-MTHF at 77 K, as shown in Figure 2a for $^3$**2c**.

When the PT glass containing carbene **2** was warmed gradually to 200 K in 10 K increments, another new set of triplet peaks appeared at the expense of the original peaks which disappeared rapidly around 180 K (see Figure 2b). These changes were not reversible; when the sample was cooled to 110 K, no change took place except that the signal intensity increased according to the Curie law. A signal due to a doublet species also started to appear around 180 K (see Figure 2b). The triplet signals eventually disappeared around 210 K and were taken over by the signal due to doublet species.

In the new set of triplet peaks, the *x* and *y* lines moved closer together, resulting in a substantial reduction in *E*. Smaller but distinct shifts in the *z* lines were also noted, indicating that *D* had also diminished.

Since the *E* value, when weighted by *D*, depends on the magnitude of the central angle, it indicates that the carbene adopts a structure with an expanded C−C−C angle upon annealing. This interpretation is supported by the observation that the substantial reduction of *E* is accompanied by a significant reduction in *D*, indicating that the electrons are becoming more delocalized. Thus, the interpretation is consistent with the concept of angular expansion.

Changes of this kind have been often observed for sterically congested triplet diarylcarbenes and are usually interpreted in terms of geometrical changes.[11] Thus, when a carbene is generated in rigid matrices at very low temperature, it should have the geometry dictated by that of the precursor. Even if the

**TABLE 2: *D* and *E* Values for Di(2,6-dimethylphenyl)carbenes (2) in 1,2,3-Propanetriol Triacetate (PT) at 110 K**

| carbenes (**2**) | 4,4′-substituents | $D$ (cm$^{-1}$)[a] | $E$ (cm$^{-1}$)[a] | $T_d$ (K)[b] |
|---|---|---|---|---|
| **2a** | H | 0.354<br>(0.335) | 0.0093<br>($2.8 \times 10^{-6}$) | 240 |
| **2b** | Me | 0.381<br>(0.331) | 0.0121<br>($2.6 \times 10^{-6}$) | 210 |
| **2c** | $^t$Bu | 0.371<br>(0.328) | 0.0128<br>($2.6 \times 10^{-6}$) | 210 |
| **2d** | F | 0.377<br>(0.344) | 0.0116<br>($2.8 \times 10^{-6}$) | 220 |
| **2e** | Cl | 0.354<br>(0.326) | 0.0120<br>($2.5 \times 10^{-6}$) | 220 |
| **2f** | Br | 0.348<br>(0.327) | 0.0118<br>($2.5 \times 10^{-6}$) | 220 |
| **2g** | OMe | 0.370<br>(−)[c] | 0.0129<br>(−)[c] | 200 |
| **2h** | CN | 0.344<br>(0.283) | 0.0093<br>($2.7 \times 10^{-6}$) | 230 |
| **2i** | $NO_2$ | 0.330<br>(0.259) | 0.0078<br>($2.7 \times 10^{-6}$) | 220 |

[a] The values in parentheses refer to those observed upon anneling the matrix. [b] Temperature at which the triplet signals disappeared. [c] The triplet signals disappeared before the relaxation.

**TABLE 3: *D* and *E* Values for Di(2,6-dimethylphenyl)carbenes (2) in 3-Methylpentane (3-MP) at 77 K**

| carbenes (**2**) | 4,4′-substituents | $D$ (cm$^{-1}$) | $E$ (cm$^{-1}$) |
|---|---|---|---|
| **2a** | H | 0.349 | 0.0049 |
| **2b** | Me | 0.347 | 0.0059 |
| **2c** | $^t$Bu | 0.347 | 0.0061 |
| **2d** | F | 0.361 | 0.0081 |
| **2e** | Cl | 0.337 | 0.0052 |
| **2f** | Br | 0.333 | 0.0054 |
| **2g** | OMe | 0.343 | 0.0087 |
| **2h** | CN | —[a] | —[a] |
| **2i** | $NO_2$ | —[a] | —[a] |

[a] Triplet signals were so weak that the ZFS parameters could not be assigned.

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. When matrices are softened by annealing, the carbene undergoes relaxation to the preferred geometry probably to gain relief from steric compression. It has been shown that the ZFS parameters of sterically unperturbed diphenylcarbenes show little sensitivity toward the temperature of the matrix.[10b,11c]

Similar changes in the *D* and *E* values upon annealing were also observed for other carbenes employed in this study, although the temperatures ($T_d$) at which the triplet signals of the relaxed species disappeared were somewhat sensitive to the para substituents as summarized in Table 2. In the case of 4,4′-dimethoxy derivative (**2f**), the triplet signals disappeared around 200 K before the carbene relaxed to its minimum-energy geometry. As a result, the ZFS parameters for the relaxed geometry were not estimated.

When the carbenes were generated in a soft matrix, i.e., 3-methylpentane (3-MP),[12] the ZFS parameters observed at 77 K were significantly smaller than those observed in 2-MTHF at 77 K and were similar to those of the relaxed geometry in TA at around 200 K (see Figure 1b and Table 3). This indicates that the 3-MP glass is not sufficiently rigid to restrict the motion of the carbene, even at 77 K, and that the carbene can easily assume its minimum-energy geometry under these conditions. In this matrix, however, the typical set of triplet signals was always accompanied by a signal due to a doublet species. This indicates that the triplet carbene undergoes hydrogen abstraction from 3-MP even at 77 K to form a radical species. In the case of 4,4′-dicyano- (**2h**) and 4,4′-dinitro derivatives (**2i**), major signals were due to doublet species and triplet signals were so weak that assignment of the field position was impossible.

**Analysis of the ZFS Parameters.** It is interesting to compare the ZFS parameters of di(2,6-dimethylphenyl)carbenes ($^3$**2**) with “parent” DPC[10] under identical conditions. As expected, a marked reduction both in the *E* and *D* values is noted as four methyl groups are introduced at all the ortho positions of DPC, i.e., continuously $^3$DPC ($D = 0.5055$ cm$^{-1}$, $E = 0.0194$ cm$^{-1}$) to $^3$**2a**, for instance, in 2-MTHF at 77 K. Thus, both of these parameters decrease with increasing steric crowding in the carbenes and reflect the steric influence of *o*-methyl groups which force an expansion of the central angle to some extent even in rigid matrix. The ZFS parameters of $^3$**2** undergo further reduction upon annealing the matrix to gain relief from steric congestion. In marked contrast, the parameters of $^3$DPC exhibit little sensitivity to the temperature and/or the softness of the matrix. This indicates that the minimum energy geometry of $^3$DPC has a considerably smaller C−C−C angle than that in $^3$**2** and that the matrix provides sufficient space for it to take that geometry even at low temperature.

It is then worth examining how these structural differences affect the influence of para substituents on the electronic structures of triplet diphenylcarbene systems.

The effect of *p*-substituents on the *D* values of *o*-unsubstituted DPCs (**3**) has been systematically investigated by Arnold and co-workers.[13] Although the substituent effects on the *D* value of **3** are not large, those authors revealed two trends. First, *p*-substitution generally causes a decrease in *D* over that in the parent DPC. Second, the decrease in *D* is largest when DPC is substituted with one para electron withdrawing group (e.g., $NO_2$) and one para′ electron donating group (e.g., $NMe_2$). The second effect is interpreted in terms of merostabilization,[14] in which the contribution of the charge-separated resonance structures is assisted by those unsymmetrical substituents and allows the unpaired electron in the $\pi$-orbital of the diphenylcarbenes to be delocalized. Since this type of substitution pattern is not used in the present study, we will focus on the first effect here.

In the case of *o*-unsubstituted DPCs (**3**), both mono- and symmetrical di-substitution both cause a decrease in *D*. No trend, however, is consistent with the Hammett substituent parameters ($\sigma$, $\sigma^+$, etc.). This is in accord with the results obtained for the substituent effects on the ESR hyperfine splittings of substituted benzyl radicals.[15]

The dominant interaction of the unpaired electron in a $\pi$-radical is with the electrons paired in the $\pi$-bonds. Such interactions are characterized by the delocalization of the spin throughout the $\pi$-system. To estimate the relative abilities of substituents to delocalize the spin, sigma-dot substituent constants, ($\sigma\bullet$), have been proposed.[16] Among the various approaches to the definition of a $\sigma\bullet$ scale, Arnold’s $\sigma_\alpha\bullet$ scale[17] is the most suitable for the analysis of the substituent effect on the *D* values of DPCs since this scale is a nonkinetic measure of radical stabilizing effects based on hyperfine coupling constants in the benzylic radical. Creary’s $\sigma_c\bullet$ scale[18] is also useful since, although this scale is based on the thermal rearrangement rate of substituted methylenecyclopropanes to the isopropylidenecyclopropanes, the rearrangement is shown to be a radical process that is devoid of significant polar character in the transition state. Actually the $\sigma_c\bullet$ scale is shown[18] to correlate reasonably well with $\sigma_\alpha\bullet$.

Figure 3 shows an attempt to correlate the *D* values[13] of $^3$-DPCs (**3a**∼**e**) with $\sigma_\alpha\bullet$. Since the data available for both *D* and

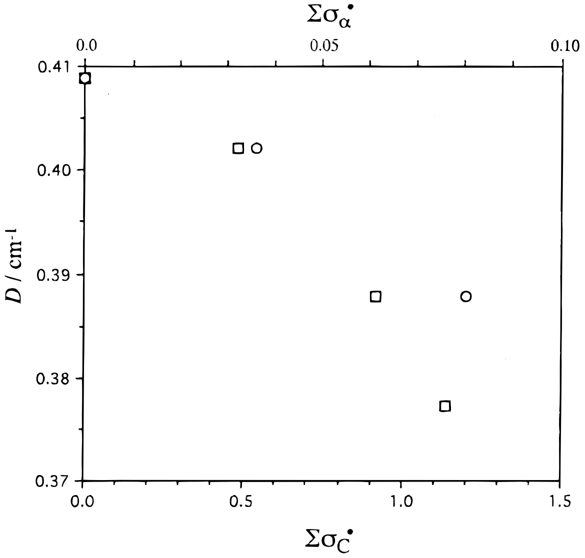


**Figure 3.** The plot of the $D$ values for 4,4′-disubstituted diphenylcarbenes (**3a**∼**e**) against $\sigma_\alpha{}^\bullet$ (○) and $\sigma_c{}^\bullet$ (□).

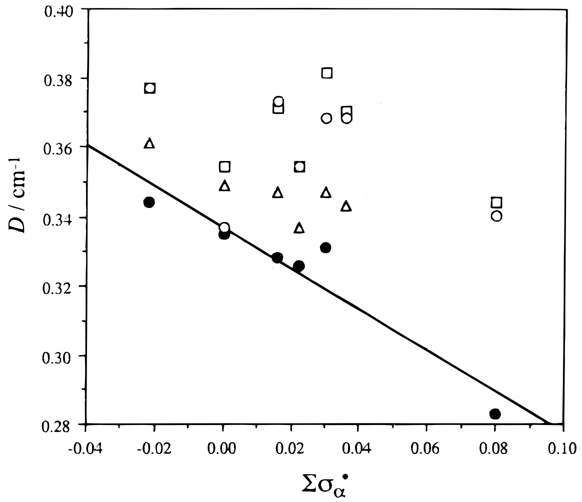


**Figure 4.** The plot of the $D$ values for di(2,6-dimethylphenyl)carbenes (**2**) against $\sigma_\alpha{}^\bullet$: ○ denotes the data in 2-methyltetrahydrofuran (2-MTHF) at 77 K; □ denotes the data for 1,2,3-propanetriol triacetate (PT) at 110 K; △ denotes the data for 3-methylpentane (3-MP) at 77 K; ● denotes the data for PT at 200 K.

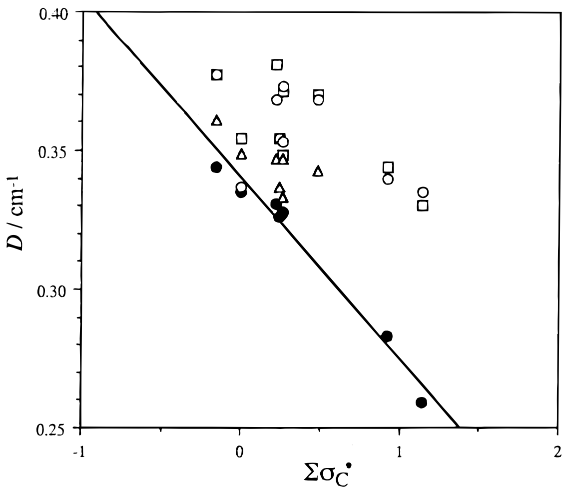


**Figure 5.** The plot of the $D$ values for di(2,6-dimethylphenyl)carbenes (**2**) against $\sigma_c{}^\bullet$: ○ denotes the data in 2-methyltetrahydrofuran (2-MTHF) at 77 K; □ denotes the data in 1,2,3-propanetriol triacetate (PT) at 110 K; △ denotes the data in 3-methylpentane (3-MP) at 77 K; ● denotes the data in PT at 200 K.

$\sigma_\alpha{}^\bullet$ are rather limited, the correlation cannot be assessed accurately. However, the $D$ values correlate reasonably well ($\rho = 0.264$, $r = 0.977$) with the $\sigma_\alpha{}^\bullet$ scale (Figure 3). Similar attempts with $\sigma_c{}^\bullet$ also give an analogous correlation ($\rho = 0.0273$, $r = 0.944$) (Figure 3). This is not unreasonable in the light of the nature of the $D$ values and $\sigma^\bullet$ employed.

Our attempts to correlate the $D$ values of sterically congested triplet carbene $^3$**2** with $\sigma_\alpha{}^\bullet$ and $\sigma_c{}^\bullet$ show that correlations are very sensitive to the geometric structures of the carbenes. Thus, the $D$ values observed for carbenes at birth in rigid matrices at low temperature, i.e., those obtained in 2-MTHF at 77 K and in PT at 110 K, where carbenes retain their metastable geometries, give a highly scattered plot when correlated against both $\sigma_\alpha{}^\bullet$ and $\sigma_c{}^\bullet$ (Figures 4 and 5). A general trend for $D$ values to decrease with increasing the power of radical stabilization of a substituent is seen. However, the correlations are disappointingly poor ($r < 0.5$).

Surprisingly, improved correlations are found when the $D$ values observed for the carbenes in their minimum-energy geometries, attained upon annealing and/or in soft matrices, are employed. Thus, the $D$ values in TA at 200 K correlate relatively well ($\rho = 0.589$, $r = 0.900$) with $\sigma_\alpha{}^\bullet$ (Figure 4) and fairly well ($\rho = 0.0654$, $r = 0.969$) with $\sigma_c{}^\bullet$ (Figure 5). A poor correlation with $\sigma_\alpha{}^\bullet$ obviously stems from the lack of the largest constant, i.e., $\sigma_\alpha{}^\bullet$, for the $p$-NO$_2$ group. The correlation of $D$ values in 3-MP at 77 K is rather poor with either $\sigma_\alpha{}^\bullet$ ($r = 0.68$) (Figure 4) or $\sigma_c{}^\bullet$ ($r = 0.51$) (Figure 5), but this is also due to the lack of necessary data.

**Electronic Effects on the Structure of Sterically Congested Triplet Diphenylcarbenes.** The present study has revealed the following facts concerning the effect of substituents on the electronic and molecular structures of sterically congested diarylcarbenes.

First, the linear free energy relationship between the ZFS parameters of sterically congested triplet diphenylcarbenes and the stabilization energy due to spin delocalization holds for the most thermodynamically stable geometry, not for the initial unrelaxed geometry. This is reasonable since the geometry at birth should be influenced by that of the precursor to some extent, and the spin delocalization in the system is not ideally developed. Once the temperature is raised and the matrix becomes soft, the carbene can relax to the most stable geometry which is electronically stabilized by para substituents depending on the radical stabilizing power. If one assumes that the magnitude of the steric strain in **2** is essentially the same regardless of the para substituents, the magnitude of the shift of the $D$ values upon annealing should reflect the delicate balance between the spin delocalization ability and the polar effect of a substituent. In the case of $o$-unsubstituted DPCs, the geometrical change from an initially formed geometry to one of minimum energy is so small that the change can be accomplished even in rigid matrices at low temperatures.

Second, the difference in the dependency of the $D$ values on $\sigma^\bullet$ between $^3$DPCs ($^3$**3**) and $^3$**2** is worthy of comment. The comparison of the $\rho$ value between the two carbene systems clearly indicates that the $D$ values of $^3$**2** are approximately two times more sensitive to $\sigma^\bullet$ than those of $^3$DPC. This is reasonable since carbenes **2** have a more linear and perpendicular geometry than $^3$**3**, as evidenced by the large decrease in both $D$ and $E$ values relative to that of $^3$**3**, and hence the unpaired electron can be delocalized more effectively in the $\pi$-system of aromatic rings including substituents.

DPCs exhibit significant $E$ values of 0.016−0.019 $cm^{-1}$ regardless of the para substituents.[10,13] This indicates that the two half-filled orbitals at the divalent carbon consist of a p-orbital perpendicular to the phenyl rings and an orbital occupying the plane of the molecule with considerable s character. The unpaired electron in the p-orbital is delocalized into the phenyl rings while the unpaired electron in the $\sigma$-orbital is localized at the divalent carbon.

On the other hand, the $E$ values observed for the relaxed $^3$**2** are essentially zero ($E < 0.00001$ $cm^{-1}$) regardless of the para substituents. A zero $E$ value in the ZFS parameters is generally interpreted as indicating that DPCs have a linear structure with the phenyl planes perpendicular to each other. Each unpaired electron is expected to be in the p-orbital and can be delocalized into the phenyl rings, leaving no localized unpaired electron at the divalent carbon atom.

Finally, the effect of the electronic (thermodynamic) stabilization on the stability of $^3$**2** was examined by measuring the temperature ($T_d$) at which the triplet signals completely disappeared not only in 2-MTHF (Table 1) but also in PT (Table 2). The data in PT appear to level off to some extent, presumably because $T_d$ in PT are close to the limit of the inherent stability of the carbenes $^3$**2**. Therefore the data in 2-MTHF are used to evaluate the thermodynamic effect on the stability of $^3$**2**. Inspection of the data in Table 1 indicates that 4-cyano and nitro groups exhibit significant stabilizing effects on $^3$**2**. Taking into account the increased ability of those substituents to delocalize the unpaired electron, this indicates that triplet carbenes kinetically stabilized by the ortho substituents can be further stabilized thermodynamically by spin-delocalizing para substituents.

Interestingly, the *para-tert*-Bu group is found to exert an equally significant effect on $T_d$. Since the $\sigma\bullet$ of this group is not large, the effect is explained in terms of a steric factor. Sterically congested DPCs usually decay by dimerization to form tetra(aryl)ethylenes in an inert solvent when other intramolecular reaction channels are not available.[2] However, it has been demonstrated that triplet DPCs also decay by undergoing coupling at the para positions, especially when the carbene center is effectively blocked by the ortho substituents.[19]

In this connection, the rather high $T_d$ observed for the para, para′-unsubstituted derivative (**2a**) is surprising since hydrogens at the para position have neither a spin-delocalizing effect nor steric protecting ability.

To obtain more insight into the combination of kinetic and thermodynamic factors on the stability of triplet carbenes, both kinetic studies using laser flash photolysis and product analysis studies in solution at room temperatures are required. Such studies are in progress in this laboratory.

**Acknowledgment.** The authors are grateful to the Ministry of Education, Science and Culture of Japan for support of this work through a Grant-in-Aid for Scientific Research. The help of Ms. Yui Ishikawa with the ESR measurements is also acknowledged.

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