

Effects of *para*-Substituents on the Reactivities of Sterically Congested Triplet Diphenylcarbenes

Yingmo Hu, Katsuyuki Hirai, and Hideo Tomioka*

Chemistry Department for Materials, Faculty of Engineering, Mie University, Tsu, Mie 514-8507

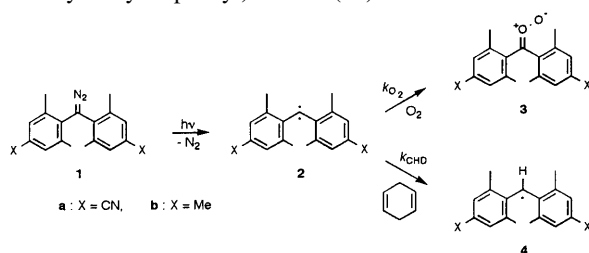
(Received October 8, 1999; CL-990867)

Kinetically stabilized triplet di(2,6-dimethylphenyl)carbene is thermodynamically stabilized further by a spin-delocalizing *para*-substituent, whereby making the persistent triplet carbene longer-lived.

The stabilization of a triplet carbene has emerged as a challenging target¹ since the isolation of carbenes in the singlet state has been realized recently.^{2,3} Steric protection is an ideal method for stabilizing the triplet state since a protecting group when introduced near a carbene center not only blocks the carbene center from external reagents but also results in thermodynamic stabilization by increasing the carbene bond angle. Attempts have been made in this direction whereby triplet diphenylcarbenes (DPCs) were stabilized by introducing a series of substituents at the ortho positions and triplet DPCs surviving more than an hour were realized.⁴

This approach encounters a limitation when diazo compounds are used as precursor since, as more bulky groups are used at the ortho positions, introduction of the diazo group becomes more difficult.

The other strategy we have not examined extensively is the electronic (thermodynamic) effect of *para*-substituents on the stability of kinetically protected triplet DPCs. It is well-documented in radical chemistry that the abilities of various substituents to delocalize the spin on a carbon radical plays an important role to stabilize the radical.⁵ In order to explore this effect on the reactivity of triplet diphenylcarbene, we decided to generate and study sterically congested DPC having significantly strong spin-delocalizing group at the *para*-positions. Cyano group is a very attractive substituent for such studies as a significant ability of 4-cyano group to delocalize the unpaired electron is known.⁵ We wish to report here our study in this direction whereby we generated and studied triplet di(2,6-dimethyl-4-cyanophenyl)carbene (**2a**).



Irradiation of di(2,6-dimethyl-4-cyanophenyl)diazomethane (**1**)⁶ in a 2-methyltetrahydrofuran (MTHF) glass at 77 K gave a paramagnetic species readily characterized from its EPR spectrum as triplet carbene **2a**.⁷ The zero-field splitting (ZFS) parameters were $|D| = 0.340 \text{ cm}^{-1}$ and $|E| = 0.0093 \text{ cm}^{-1}$. The EPR signals were not only stable at this temperature but also survived even around 180 K. However, as the samples

were warmed, the *x* and *y* lines of the spectrum moved closer together, resulting in essentially zero $|E|$ value ($2.7 \times 10^{-6} \text{ cm}^{-1}$). Smaller but distinct shifts in the *z* lines were also noted and $|D|$ was decreased to 0.283 cm^{-1} at 110 K. Cooling the samples did not reverse this change.

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.⁸ This interpretation is supported by the observation that it is accompanied by a significant reduction in *D* value since this means that the unpaired electrons are more delocalized and 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 in order to gain relief from steric compression.⁹

It is very interesting to compare the ZFS parameters of **2a** with that of dimesitylcarbene **2b**.^{7,10} ($D/E = 0.368/0.0117$ and $0.331/2.6 \times 10^{-6}$ in MTHF at 77 K and 110 K, respectively) under the identical conditions. A marked reduction in the *D* value is noted as methyl groups at 4 positions are replaced with cyano group, especially in their relaxed geometries. This suggests that 4-cyano groups ($\sigma_a^* = 0.040^{11}$) delocalize the unpaired electrons effectively than 4-methyl groups ($\sigma_a^* = 0.015^{11}$), as now well-documented in radical chemistry, and this delocalization effect is more prominent in the relaxed, more linear and perpendicular geometries of the diphenylcarbenes. It is also interesting to note here that the EPR signals of **2b** disappeared irreversibly around 120 K.

The EPR study clearly suggest that sterically congested (kinetically stabilized) triplet diphenylcarbenes are further stabilized thermodynamically by spin delocalization.

In order to reveal how those thermodynamic stabilizations are reflected on the persistency of triplet carbene under normal conditions, i.e., in solution phase at room temperature, kinetic studies were carried out. First, irradiation of **1a** in matrices at low temperatures was monitored by UV/vis spectroscopy⁷ in order to know the spectroscopic feature of the triplet carbene (**2a**). Irradiation of **1a** in MTHF glass at 77 K produced new absorption bands at the expense of the original absorption ($\lambda_{\text{max}} = 335$ and 345 nm) due to **1a** (Figure 1). The new spectrum consists of two identifiable features, intense UV bands with maxima at 300 and 331 nm and weak and broad one at 488 nm. These features are usually present in the spectra of triplet diarylcarbenes in organic glass at 77 K.⁸ The glassy solution did not exhibit any changes for several hours when kept at 77 K, but the characteristic bands disappeared irreversibly when the matrix was allowed to warm to room temperature. On the basis of these observations, coupled with the EPR result, the absorption spectrum can be safely assigned to triplet carbene **2a**.

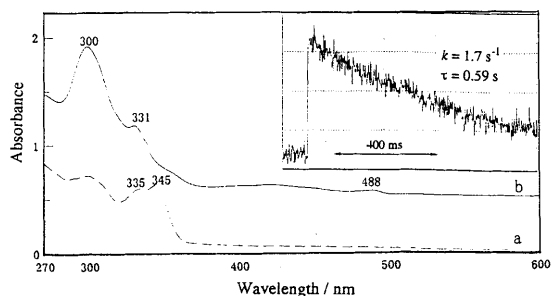


Figure 1. UV/vis spectra obtained by irradiation of **1a**. (a) Spectrum of **1a** in MTHF at 77 K. (b) Same sample after 5 min irradiation ($\lambda > 300$ nm) at 77 K. Inset shows a plot of the absorbance at 480 nm as a function of time in a degassed benzene at 20 °C.

Table 1. Kinetic and EPR data for triplet diphenylcarbenes

Carbenes	τ/s	$k_{O_2}/M^{-1}s^{-1}$	$k_{CHD}/M^{-1}s^{-1}$	D/cm^{-1}	E/cm^{-1}
2a	0.59	3.1×10^7	1.3×10^2	0.283	2.7×10^{-6}
2b	0.16	2.0×10^8	4.6×10^2	0.331	2.6×10^{-6}

Laser flash photolysis (LFP)⁷ of **1a** in a degassed benzene solution at 20 °C with a 10 ns, 70–90 mJ, 308 nm pulse from a XeCl excimer laser produced a transient species showing a weak absorption around 480 nm. On the basis of the low-temperature spectrum, we assign the absorption to triplet **2a**. Unfortunately, the strong absorption around 300–330 nm, which are observed in the low-temperature spectrum, was in a region of very difficult detection since the region falls underneath that of the precursor diazomethane and hence the samples are not sufficiently transparent for adequate monitoring. However, the absorption at 480 nm was sufficiently strong to run kinetic measurements. The decay of **2a** is found to be first order ($k = 1.7 s^{-1}$) and the lifetime is determined to be 0.59 s (Figure 1).

The reactivities of **2a** toward typical triplet quenchers, i.e., oxygen and cyclohexa-1,4-diene (CHD), were then investigated by using LFP. Thus, when LFP was carried out on a non-degassed benzene solution of **1a**, the lifetime of the absorption due to **2a** decreased dramatically, and a broad absorption band with a maximum at 400 nm appeared as the band due to **2a** decayed. The observation can be interpreted as indicating that the triplet **2a** is trapped by oxygen to generate carbonyl oxide (**3a**)¹², thus confirming that the transient absorption quenched by oxygen is due to **2a**. A plot of the observed pseudo-first-order rate of carbonyl oxide formation vs oxygen concentration yields the quenching rate constant $k_{O_2} = 3.1 \times 10^7 M^{-1} s^{-1}$. Similarly, LFP of **1a** on a degassed benzene solution in the presence of CHD generated a new signal at 380 nm attributable to the diarylmethyl radicals (**4**) as the signals of **2a** decayed, showing that triplet **2a** abstracts H from the diene.¹¹ The rate constant (k_{CHD}) of H abstraction of **2** from CHD is determined from a plot of the apparent build-up rate constant of the radical vs [CHD]. The data are summarized in Table 1 along with those obtained in the reaction of **2b**.

The data clearly suggest that the reactivity of kinetically stabilized triplet diphenylcarbenes toward typical triplet quenchers is significantly decreased by the spin-delocalizing substituent at the *para* positions. Accordingly, the persistency of the triplet carbenes in solution at room temperature is increased. These observations suggest that the kinetically stabilized triplet DPC will be further stabilized more effectively by stronger spin-delocalizing substituents at *para* positions.

The further studies in this direction are in progress in this laboratory.

The authors are grateful to the Ministry of Education, Science, Sports 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 EPR measurements is also acknowledged.

References and Notes

- See for reviews a) H. Tomioka, *Acc. Chem. Res.*, **30**, 1315 (1997). b) H. Tomioka, *Adv. Carbene Chem.*, **2**, 175 (1998).
- Phosphinocarbene and imidazol-2-ylidene were prepared as “bottle-able” singlet carbenes in 1988 and 1991, respectively. See a) A. Igau, H. Grützmacher, A. Baceiredo, and G. Bertrand, *J. Am. Chem. Soc.*, **110**, 6463 (1988). b) A. J. Arduengo, III, R. L. Harlow, and M. Kline, *J. Am. Chem. Soc.*, **113**, 361 (1991).
- D. Bourisson, O. Guerret, F. D. Gabbai, and G. Bertrand, *Chem. Rev.*, **100**, in press (2000).
- K. Hirai and H. Tomioka, *J. Am. Chem. Soc.*, **121**, 10123 (1999).
- For a review: X-K. Jiang, *Acc. Chem. Res.*, **30**, 283 (1997). See also R. W. Humphreys and D. R. Arnold, *Can. J. Chem.*, **57**, 2652 (1979).
- The diazomethane (**1a**) was prepared by the acyl cleavage of the corresponding *N*-alkyl-*N*-nitroso-urethane by potassium *tert*-butoxide. It was purified by gel permeation chromatography to afford an orange solid; mp 209–210 °C; ¹H NMR (CDCl₃) δ 2.11 (s, 12 H), 7.38 (s, 4 H) ppm; IR (NaCl) 2048 and 2224 cm⁻¹.
- For detail of the spectroscopic work, see, H. Tomioka, H. Okada, T. Watanabe, K. Banno, K. Komatsu, and K. Hirai, *J. Am. Chem. Soc.*, **119**, 1582 (1997).
- See for reviews of the EPR and UV/vis spectra of triplet carbene, a) W. Sander, G. Bucher, and S. Wierlacher, *Chem. Rev.*, **93**, 1583 (1993). b) A. M. Trozzolo, and E. Wasserman, “Carbenes,” ed by M. Jones, Jr. and R. A. Moss, Wiley, New York (1975), Vol. 2, pp. 185–206.
- a) H. Takeda, T. Sugawara, S. Murata, and H. Iwamura, *Tetrahedron Lett.*, **27**, 235 (1986). b) A. S. Nazran, E. J. Gabe, Y. LePage, D. J. Northcott, J. M. Park, and D. Griller, *J. Am. Chem. Soc.*, **105**, 2912 (1983). c) H. Tomioka, T. Watanabe, K. Hirai, K. Furukawa, T. Takui, and T. Itoh, *J. Am. Chem. Soc.*, **117**, 6376 (1995).
- Y-M. Hu, K. Hirai, and H. Tomioka, *J. Chem. Phys.*, **103**, 9280 (1999).
- a) J. M. Dust and D. R. Arnold, *J. Am. Chem. Soc.*, **105**, 1221 and 6531 (1983). b) D. D. M. Wayner and D. R. Arnold, *Can. J. Chem.*, **62**, 1164 (1984), and **63**, 2378 (1985).
- M. S. Platz and V. M. Maloney “Kinetics and Spectroscopy of Carbenes and Biradicals,” ed by M. S. Platz, Plenum Press, New York (1990), pp. 239–352.