6904 *J. Am. Chem. Soc.* **2001,** *123,* 6904−6908

Structure Analysis of a Transient Triplet Carbene Trapped in a Crystal

Masaki Kawano,*[§] Katsuyuki Hirai,[‡] Hideo Tomioka,[‡] and Yuji Ohashi*[§,†]

Contribution from the CREST, Japan Science and Technology Corporation, Kawaguchi, Saitama 332-0012 Japan, Department of Chemistry and Materials Science, Tokyo Institute of Technology, Tokyo 152-8551, Japan, and Chemistry Department for Materials, Faculty of Engineering, Mie University, Tsu, Mie 514-8507, Japan

Received March 9, 2001. Revised Manuscript Received May 22, 2001

Abstract: A light-induced transient bis(2,4,6-trichlorophenyl)carbene trapped in a yield of ca. 20% in the crystal of the precursor diazomethane was characterized by X-ray crystallography at low temperatures. The most interesting geometrical parameters are the carbenic angle θ and the bond distances between the carbenic carbon and the phenyl carbons. The obtained θ is 142(2)°, while the distances are 1.437(15) and 1.423(16) Å, respectively. These values are significantly different from the corresponding values for the precursor diazomethane (127.1(1)° and 1.477(1) and 1.480(1) Å, respectively). On the basis of IR spectroscopy and theoretical calculations, the carbene is judged to be in the triplet ground state.

Introduction

A carbene is an unstable species and has a very reactive carbon center that has two nonbonded (or free) electrons. Carbenes have unique reactivity and physical properties attributable to the two electrons, which may occupy either the different orbitals separately (triplet state) or one orbital with opposite spins (singlet state). The pioneering work of Staudinger during the 1910s on the decomposition of diazo compounds contributed much to the recognition of carbenes as a new reactive species.[1−3] However, it is rather surprising to note that stable carbenes attracted little attention until two groups announced the discovery of these species; Bertrand obtained phosphinocarbene as a distillable red oil in 1988 and Arduengo isolated imidazol-2-ylidene as a crystal with a high melting point in 1991. These carbenes are stabilized by heteroatom substituents connected to the carbenic atom and thus each has a singlet ground state. Moreover, interpretation of these species as free carbenes has been a topic of debate, especially concerning the possible contribution of the ylidic character as a result of pπ−pπ delocalization.[4] The structure of the singlet carbene was analyzed by X-ray crystallography at room temperature.[5,6] On the other hand, triplet carbenes stable enough for X-ray analysis have not yet been realized. This is partly because a triplet state is less readily stabilized thermodynamically than its singlet counterpart. Many attempts have been made to stabilize triplet carbenes kinetically by protecting the carbene center with a bulky group, but the voracious appetite of carbenes for electrons has made it extremely difficult to realize a triplet carbene stable enough for isolation and crystallographic analysis, although fairly stable triplet carbenes have become available.[7,8]

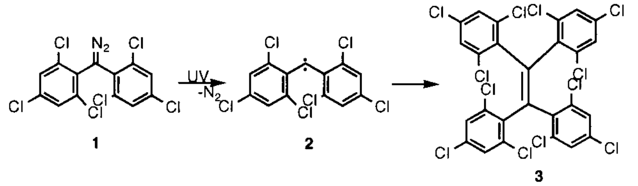

Figure 1. Photolysis of **1** in benzene solution.

For this study, we chose bis(2,4,6-trichlorophenyl)diazomethane (**1**), which is well-known as one of the representative precursors for persistent triplet carbenes.[9,10] In benzene solution, photolysis of **1** with ultraviolet light generates a dinitrogen molecule to leave a triplet carbene, bis(2,4,6-trichlorophenyl)carbene (**2**), very cleanly. This carbene subsequently undergoes dimerization to yield the chlorinated tetra(phenyl)ethylene (**3**) (Figure 1).[10]

The application of small-molecule crystallography to the in situ study of unstable species in crystalline-state reactions is very rare[11−14] because of considerable stress and reorganization in a narrow cavity leading to the loss of crystallinity, although there are a few in situ studies of proteins having a large flexible space for a movable active site.[15−17] Our approach toward the

---

[§] CREST, Japan Science and Technology Corporation.
[‡] Mie University.
[†] Tokyo Institute of Technology.

(1) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1961 and 1971.

(2) Moss, R. A.; Jones, M., Jr., Eds. *Carbenes*; Wiley: New York, 1973 and 1975; Vols. I and II.

(3) Brinker, U. H., Ed. *Advances in Carbene Chemistry*; JAI Press: Greenwich and Stamford, 1994, 1998, and 2000; Vols. 1 and 2.

(4) Heinemann, C,; Muller, T.; Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023.

(5) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.

(6) Arduengo, A. J., III *Acc. Chem. Res.* **1999**, *32*, 913.

(7) Tomioka, H. *Acc. Chem. Res.* **1997**, *30*, 315.

(8) Tomioka, H. In *Advances in Carbene Chemistry*; Brinker, U. H., Ed.; JAI Press Inc.: Greenwich and Stamford, 1998, Vol. 2; 2000, Vol. 8.

(9) Zimmerman, H. E.; Paskovich, D. H. *J. Am. Chem. Soc.* **1964**, *86*, 2149.

(10) Tomioka, H.; Hirai, K.; Fujii, C. *Acta Chim. Scand.* **1992**, *46*, 680.

(11) Kawano, M.; Sano, T.; Abe, J.; Ohashi, Y. *Chem. Lett.* **2000**, *12*, 1372.

(12) Harada, J.; Uekusa, H.; Ohashi, Y. *J. Am. Chem. Soc.* **1999**, *121*, 5809.

(13) Kawano, M.; Sano, T.; Abe, J.; Ohashi, Y. *J. Am. Chem. Soc.* **1999**, *121*, 8106.

(14) Coppens, P.; Fomitchev, D. V.; Carducci, M. D.; Culp, K. *J. Chem. Soc., Dalton Trans.* **1998**, 865−872.

10.1021/ja0106366 CCC: $20.00

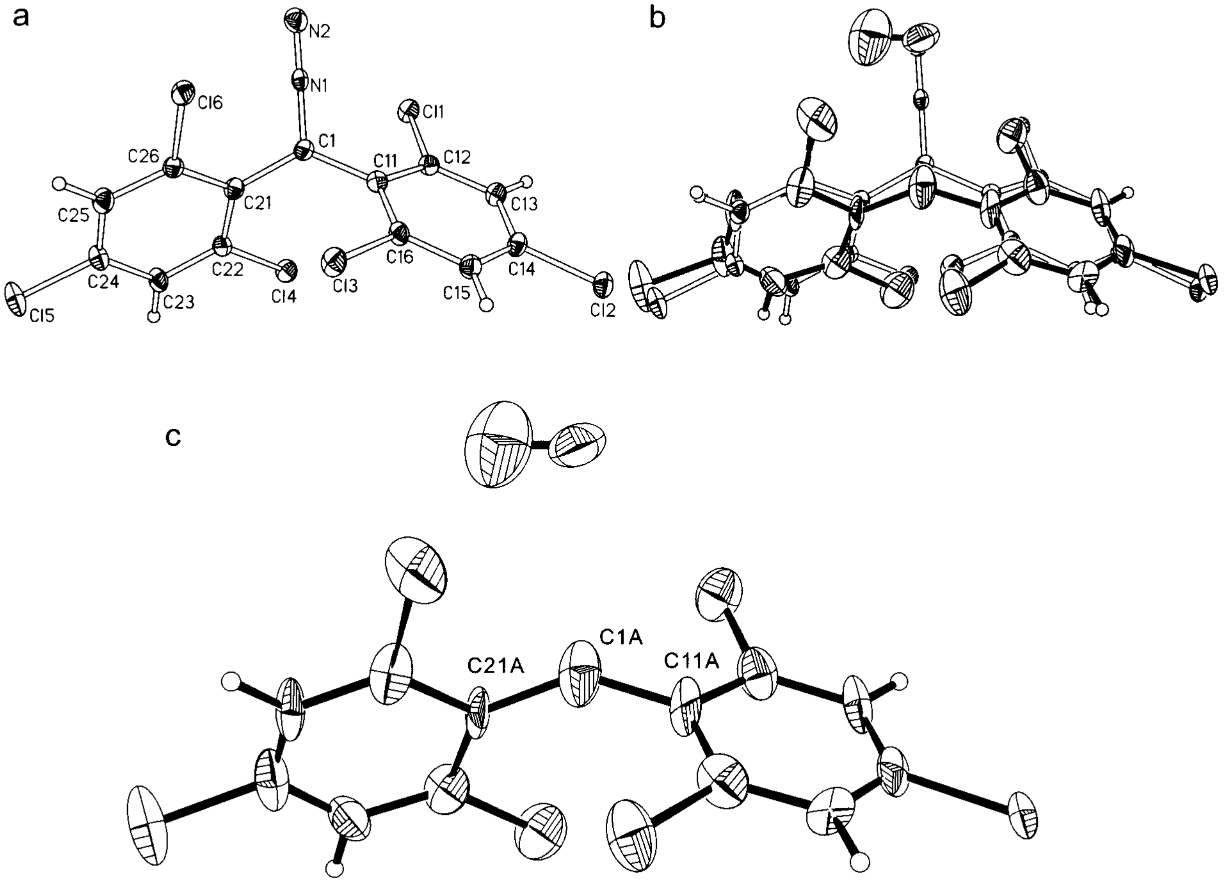

Figure 2. (a) Perspective view of **1**. The ellipsoids are drawn at the 50% probability level. Selected bond distances (calcd, Å) and angles (calcd, deg): C1−C11, 1.477(1) (1.480); C1−C21, 1.480(1) (1.480); C1−N1, 1.323(1) (1.313); N1−N2, 1.136(1) (1.140); C11−C1−C21, 127.1(1) (126.3); dihedral angle C26−C21−C11−C16, 70.2 (64.8). The calculated value was obtained by the B3LYP/6-31G* calculation. (b) Perspective view of a disordered structure of **1** (open line) and **2** (solid line). The ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and angle (deg): C1−C11, 1.437(15); C1−C21, 1.423(16); N1−N2, 1.05(3); C11−C1−C21, 142(2); dihedral angle C26−C21−C11−C16, 76. The dinitrogen molecule and the carbenic carbon are separated by 3.0 and 3.3 Å. Calculated bond distances (Å) and angles (deg) obtained by the (U)B3LYP/6-31G* calculation for ^{3}**2** (^{1}**2**): C11(21)−C1, 1.375 (1.403); C11−C1−C21, 160.0 (131.4); dihedral angle C26−C21−C11−C16, 97.6 (90.2). (c) Perspective view of **2** (with **1** omitted) in part b. The ellipsoids are drawn at the 50% probability level.

crystallographic characterization of unstable reactive species in a small-molecule crystal involves the use of in situ crystallography combined with light irradiation and a cryotrapping method. The structure of triplet diphenylcarbenes generated in single crystals of 1,1-diphenylethylene[18] or benzophenone[19] has been studied by ESR techniques. Reactivity of diarylcarbenes generated in the single crystal of the precursor diazomethanes, on the other hand, has been studied[20]by product analysis methods. However, no attempts have been made to observe carbenes crystallographically.

Here we report the successful characterization of a transient triplet carbene (**2**) trapped in the crystal of a diphenyldiazomethane derivative (**1**) by X-ray crystallography at low temperatures.

Results and Discussion

Single-Crystal X-ray Diffraction Study. A crystal of **1** was mounted on a CCD area-detector diffractometer and cooled below 80 K using the cold-nitrogen gas-flow method. Three-dimensional intensity data were collected and the structure of **1** was determined (Figure 2a). Then, the crystal was irradiated with 365-nm light at the same temperature. Although the crystal turned from yellow to red, there was no evidence for deterioration of the crystal quality. The difference electron density map after irradiation showed new peaks around the molecule of **1**. These new peaks were assigned to a dinitrogen molecule and the carbene **2** as shown in Figure 2b. The occupancy factors of the product **2** and the original molecule **1** are 0.197(5) and 0.803(5), respectively. Crystallographic data of **1** and **2** are summarized in Table 1. The most interesting geometrical parameters are the carbenic angle θ and the bond distances between the carbenic carbon and the phenyl carbons. The θ is obtained as 142(2)°, while the distances between C1A and C11A and C1A and C21A are 1.437(15) and 1.423(16) Å, respectively. These values are significantly different from the corresponding values for **1** (127.1(1)° and 1.477(1) and 1.480(1) Å, respectively).

Further photolysis ($\lambda > 300$ nm) of a single crystal containing both **1** and **2** resulted in a loss of crystallinity. When the carbenes

---

(15) Srajer, V.; Teng, T.; Ursby, T.; Pradervand, C.; Ren, Z.; Adachi, S.; Schildkamp, W.; Bourgeois, D.; Wulff, M.; Moffat, K. *Science* **1996**, *274*, 1726.

(16) Genick, U. K.; Soltis, S. M.; Kuhn, P.; Canestrelli, I. L.; Getzoff, E. D. *Nature* **1998**, *392*, 206.

(17) Wilmot, C. M.; Hajdu, J.; McPherson, M. J.; Knowles, P. F.; Phillips, S. E. V. *Science* **1999**, *286*, 1724.

(18) Doetschman, D. C.; Hutchison, C. A, Jr. *J. Chem. Phys.* **1972**, *56*, 3964.

(19) Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Chim. Phys.* **1964**, *61*, 1003.

(20) Shin, S. H.; Cizmeciyan, D.; Keating, A. E.; Khan, S. I.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **1997**, *119*, 1859.

Table 1. Crystallographic Data for Bis(2,4,6-trichlorophenyl)diazomethane Before and After Irradiation

	before irradiation	after irradiation ($\lambda_e = 365$ nm)
crystal system, space group	monoclinic, $P2_1/n$	
temp, K	80(2)	80(2)
a, Å	9.6777(16)	9.731(2)
b, Å	12.760(4)	12.813(4)
c, Å	12.248(2)	12.254(3)
β	90.975(14)	90.55(2)
V, Å^3	1512.3(6)	1527.9(6)
Z	4	4
d_{calcd}, mg/m^3	1.761	1.743
abs coeff, mm^{-1}	1.127	1.115
crystal dimens, mm	0.35 × 0.15 × 0.06	0.20 × 0.15 × 0.06
no. of reflns measd	50227	26715
no. of symm-unique reflns ($2\theta_{max} = 65.0$)	5471	5405
merging $R(I)$, R(sigm)	0.0396, 0.0180	0.0754, 0.0634
no. of retained reflns with $I > 2\sigma(I)$	4735	3526
population of photoproducts	0	0.197(5)
no. of variables	190	323
no. of restraints	0	158
$R1(F)$ ($I > 2\sigma$(I))	0.0218	0.0418
w$R2(F^2)^a$(all data)	0.0567	0.0949
GOF	1.070	1.004

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

produced in the crystal were irradiated with >300-nm light, the two carbenes should come close together to form dimer **3**, releasing dinitrogen molecules. Because the distance between the two carbenic carbons (7.2 Å) is too large for retention of the orderly molecular array, it is not surprising that the crystallinity gradually deteriorates as dimer **3** is produced.

Infrared Spectroscopy. The reaction was also observed in the solid state by infrared spectroscopy in a KBr matrix at 7−300 K. Irradiation of **1** at 365 nm from a high-pressure mercury lamp below 80 K drastically weakened the band (2079 cm^{-1}) of ν(N═N) and the related bands (1456, 1436 cm^{-1}) to a precarbenic carbon atom and produced several isosbestic points, confirming the direct transformation of **1** to a single product ascribable to **2**. It is noteworthy that photolysis at 365 nm in a KBr matrix generated **2** in ca. 100% yield, possibly because of good light penetration through the microcrystals in a KBr matrix. Further irradiation with longer wavelength light ($\lambda > 365$ nm) of the sample containing **2** caused no spectral change, but either irradiation with shorter wavelength light (λ_> 300 nm) at 7−80 K or warming the sample to >120 K led to the disappearance of **2** and the formation of dimer **3**.

Spin State of 2 in a Crystal. A subsidiary question is whether the spin state of product **2** is singlet (S0) or triplet (T1). First, we note that triplet diarylcarbenes are usually known to be thermodynamically more stable than the singlet counterpart.[8] ESR measurements on a single crystal of **1** irradiated with 365-nm light at 77 K showed no clear signal ascribable to the triplet carbene but a weak doublet signal. This has been occasionally observed in crystalline samples of triplet carbenes possibly because of a strong exchange coupling of the triplet states and/or antiferromagnetic interactions.

Theoretical Calculations. To explore further the assignment of the spin state of **2** in the crystal, theoretical calculations were carried out. First, the molecular geometries of **1** and singlet (^{1}**2**) and triplet (^{3}**2**) carbenes were optimized at the DFT (U)B3LYP/6-31G* level of theory. The calculated bond distances of **1** are in excellent agreement with the experimental values within ±0.004 Å (4σ) except for a C═N$_2$ bond distance (the observed distance of 1.323(1) Å versus the calculated one of 1.313 Å) and C−Cl bond distances (the calculated distances are by ca. 10σ longer than the observed one). The calculated θ of 126.3° is close to the observed one of 127.1(1)°. The observed structure is different from the optimized structures of either ^{1}**2** or ^{3}**2**. The observed θ of 142(2)° is between that of ^{1}**2** (131°) and that of ^{3}**2** (160°). Such a perturbation caused by the steric effect in a crystalline lattice is also observed in a dihedral angle of C26−C21−C11−C16 (obsd 75.6° versus calcd 97.6°).

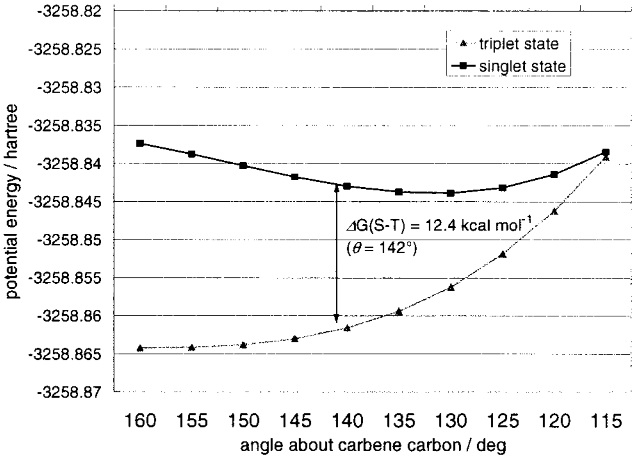

Figure 3. A potential energy surface calculation as a function of θ in the range of 115−160°.

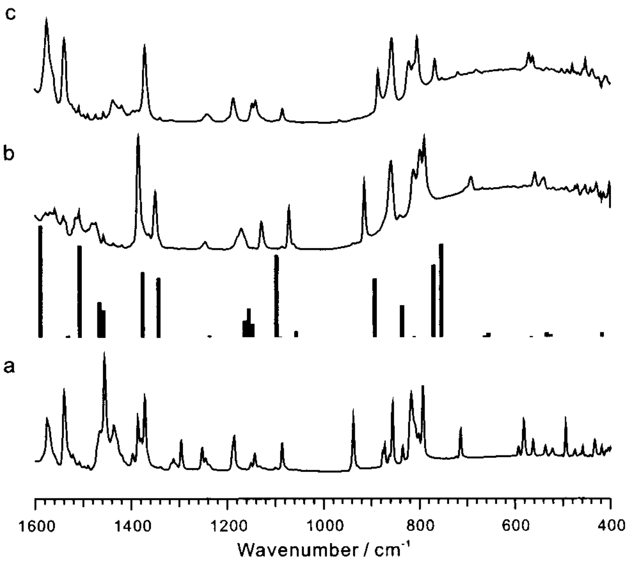

Figure 4. IR spectra before and after irradiation at 7−60 K in a KBr matrix: (a) before irradiation of **1** at 60 K and (b) after 365 nm irradiation of **1** at 60 K. A single product of **2** was produced. Bar: the simulated spectrum of ^{3}**2** at the UB3LYP/6-31G* level. The broad band in the lower wavenumber is attributed to water on the KBr window of the cryochamber. (c) After >300 nm additional irradiation at 7 K. This spectrum agrees with that of **3** independently prepared. At low temperatures below 80 K the photolysis of **1** generated the same product as at 80 K.

A potential energy surface calculation as a function of θ in the range of 115−160° was performed for both states, which indicates that in the range of 130−160° at θ, ^{3}**2** is always more stable in energy than ^{1}**2** and that both ^{3}**2** and ^{1}**2** have very shallow potentials (Figure 3): the calculated singlet−triplet energy gap, ΔG(S−T), between the singlet and triplet of their energy-minimum structures is 12.8 kcal mol^{-1}, while ΔG(S−T) between the optimized structures for ^{1}**2** and ^{3}**2** at a fixed

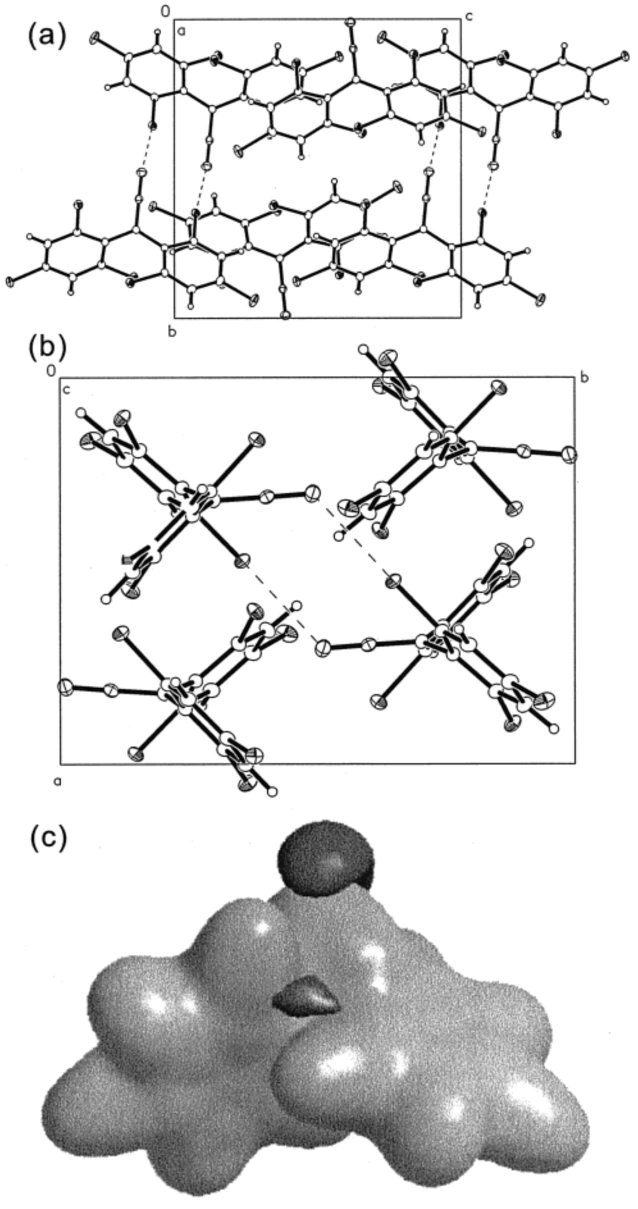

Figure 5. Packing diagram of **1** ((a) *bc* plane (b) *ab* plane) and its electrostatic potential map ((c) isopotential: 0.35 au; dark gray, positive charge; light gray, negative charge).

angle of 142° is 12.4 kcal mol^{-1}. Thus the two values are essentially the same. The ΔG(S$-$T) at 142° obtained for **2** is large enough to ensure that the spin state could be the triplet state.[21−23] In addition, the infrared spectrum of **2** in a KBr matrix fit the simulated spectrum of ^{3}**2** rather than ^{1}**2** (Figure 4).[24]

Molecular Array of 1. Figure 5 shows packing diagrams of **1** and its electrostatic potential map. After performing an ab initio geometry optimization using the 6-31G* basis set, we performed single-point-energy calculations. An independent molecule is present in the unit cell. A molecule and its inversion-center related one form a dimer in a crystal with dipole interactions between the diazo groups (positively charged) and the chlorine atoms (negatively charged). The shortest intermolecular distance between them (the broken line in Figure 5) is 3.01 Å, which is shorter than the sum of the van der Waals radii (3.30 Å). There are $\pi-\pi$ stacking interactions between the phenyl rings of the neighboring dimers (the interplane distance: ca. 3.5 Å). A side view of the packing diagrams (Figure 5b) shows a channel extending along the *b* axis, through which dinitrogen molecules might be able to get out of the crystal.

Concluding Remarks

We have been successful in observing the transient structure of a carbene and the reaction process of photolysis of a diazo compound by X-ray crystallography combined with a cryotrapping method, and the combined evidence is consistent with the assignment of the carbene as the triplet state. This method will provide useful information for materials design and insight into reaction mechanisms, particularly when coupled with time-resolved X-ray diffraction techniques.[25,26]

Experimental Section

General Considerations. Bis(2,4,6-trichloropheny)diazomethane and the chlorinated tetra(phenyl)ethylene were prepared by the method described in ref 9. Samples were irradiated with a high-pressure mercury lamp (SAN-EI UVF-352S) in combination with a band-path filter. The maximum power at 365 nm via the band-path filter was ca. 5 mW/cm^2.

Fourier transform infrared spectra were recorded on a JASCO FT/IR-5300 instrument. A sample dispersed in a KBr pellet was attached to the coldfinger of a helium cryogenic refrigerator system (DAIKIN PS24SS) equipped with KBr windows. ESR spectra were recorded at 77 K on a JEOL JES-TE 200 spectrometer (x-band microwave unit, 100 kHz field modulation) using a single crystal.

Single-Crystal X-ray Diffraction Analysis. (a) Sample Preparation. Crystals obtained by a slow evaporation of benzene solution were mounted on the tips of glass fibers with epoxy or paratone oil and cooled to low temperatures (80 K) controlled by a Rigaku cryostat system equipped with a N_2 generator. To proceed with the crystalline-state photoreaction, a crystal that was slowly rotated on a goniometer was irradiated with a high-pressure mercury lamp at 80 K for 2 h. The photoreaction and crystal quality were monitored by the total intensities of selected frames and shapes of Bragg diffractions. Different crystals were used for the structure determination of the initial photodimer and photoproducts.

(b)Data Collection and Reduction. Data were collected on a Siemens SMART CCD X-ray diffractometry system controlled by a Pentium-based PC running the SMART software package. Graphite-monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation was used with a Rigaku rotating anode generator (50 kV, 250 mA). A series of 25 frames measured at 0.3° increments of ω were collected with three different ϕ (0, 90°, 180°) values at two 2θ values of $-26°$ and 26° to calculate the matrix parameters. The data collection strategy is as follows: four sets of 606 frames, 5 s per frame, detector arm at $\theta = -32°$, $\phi = 0$, 90°, 180°, 270°. For the data collection before irradiation, an additional

---

[21] DFT UB3LYP tends to overestimate triplet energy. For example, in the case of a CH_2 carbene, UB3LYP overestimates the stability of the triplet by approximately 4 kcal mol^{-1}. This means that at a 142° angle a better estimate of ΔG(S$-$T) is 8.4 kcal mol^{-1}.

[22] Irikura, K. K.; Goddard, W. A., III; Beauchamp, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 48.

[23] Griller et al. have investigated a series of methylated diphenylcarbens by ESR and product analysis methods r to investigate the relationships between structure and the triplet−singlet energy gap and showed that increasing ortho substitution at the aryl groups led to an expansion of the carbene bond angle and an increase in the triplet−singlet energy gap. Gilbert, B. C.; Griller, D.; Nazran, A. S. *J. Org. Chem.* **1985**, *50*, 4738. Nazran, A. S.; Lee, F. L.; Gabe, E. J.; Northcott, D. J.; Park, J. M.; Griller, D. *J. Phys. Chem*. **1984**, *88*, 5251.

[24] The simulated IR spectrum of **1** at the B3LYP/6-31G* level reasonably agrees with the observed spectrum (Figure 1S). Figure 1S also includes the simulated spectrum of ^{1}**2**.

[25] Srajer, V.; Teng, T.; Ursby, T.; Pradervand, C.; Ren, Z.; Adachi, S.; Schildkamp, W.; Bourgeois, D.; Wulff, M.; Moffat, K. *Science* **1996**, *274*, 1726.

[26] Perman, B.; Srajer, V.; Ren, Z.; Teng, T.; Pradervand, C.; Ursby, T.; Bourgeois, D.; Schotte, F.; Wulff, M.; Kort, R.; Hellingwerf, K.; Moffat, K. *Science* **1998**, *279*, 1946.

four sets of 606 frames were measured at $\theta = -52°$, $\phi = 45°$, 135°, 225°, 315°, but reflections ($2\theta < 65°$) were used for the structural refinement.

(c) Structure Refinement. All structures were solved by use of the direct method program XS, part of the SHELXTL program package. Structure refinements were carried out with Shelxl-97.[27] All least-squares refinements minimized the function $\sum w(|F_o|^2 - k|F_c|^2)^2$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \mathrm{Max}(F_o^2,0)]/3$. Anisotropic temperature parameters were applied to all non-hydrogen atoms. Crystallographic data before and after irradiation were summarized in Table 1.

(1) Before Irradiation. The initial structure of **1** was refined by full-matrix least-squares with anisotropic temperature parameters for all non-hydrogen atoms. Thermal ellipsoid plots of the structure are shown in Figure 1. The final agreement factors were $R_1 = 0.0218$, $wR_2 = 0.0567$. The highest residual peak in the difference Fourier synthesis was 0.497 (0.69 Å from C11) e/Å^3, and the deepest minimum was −0.569 (0.03 Å from CL3) e/Å^3.

(2) After 365-nm Irradiation. The initial structure was treated as a rigid group in which its thermal parameters were refined anisotropically. The first least-squares refinement for the rigid group of the initial structure was performed to give agreement factors of $R_1 = 0.0910$, $wR_2 = 0.2761$ and subsequent difference Fourier maps showed several new residual features ranging from 3.96 (0.35 Å from CL2) to −3.23 (0.32 Å from CL2) e/Å^3. Salient changes were found around a $\rangle C{=}N{=}N$ group. New peaks were assigned to a single divalent species and a dinitrogen molecule. Chemical restraints were applied to the phenyl rings of the divalent species because of their severe overlapping with the diazo species. The final least-squares refinement for a disordered model of the initial structure and photoproducts with an occupancy factor of 0.197(5) was performed to give final agreement factors of $R_1 = 0.0\ 418$, $wR_2 = 0.0949$ and subsequent difference Fourier calculation resulted in reasonable residual features ranging from 0.38 (0.95 Å from CL6) to −0.44 (0.82 Å from CL2) e/Å^3.

Computational Procedures. Ab initio molecular orbital calculations were carried out using the GAUSSIAN 98 program.[28] Optimized geometries were obtained at the (U)B3LYP/6-31G* level of theory. Vibrational frequencies obtained at the (U)B3LYP level of theory were scaled by 0.97.

Acknowledgment. We are grateful to Professor A. Nicolaides (University of Cyprus) for profitable discussion about theoretical calculations and to Professor K. D. Harris (University of Berminghan) for fruitful comments. This work was supported by CREST from JST.

Supporting Information Available: An X-ray crystallographic file (CIF) and simulated IR spectra of **1**, ^{3}**2**, and ^{1}**2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0106366

---

[27] *SHELXL-97*, Crystal Structure Analysis Program, UNIX version; George M. Sheldrick, 1993−7, Release 97-2.

[28] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.