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ELECTRONIC AND MOLECULAR STRUCTURE OF ROOM-TEMPERATURE STABLE TRIPLET CARBENE AS STUDIED BY ESR SPECTROSCOPY

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Abstract A ground-state triplet diphenylcarbene derivative, 2,2',4,4',6,6'-hexabromodiphenylcarbene **1** was synthesized and generated to be a model for chemically stable organic high-spin molecules. Electron Spin Resonance spectroscopy showed that **1** was a triplet molecule in the ground state and survived up to room temperature in the crystal state. **1** is the first stable triplet carbene in fluid solution at low temperature and in the crystal state at room temperature.

INTRODUCTION

High-spin carbene is suitable as models for building blocks of high-spin molecular clusters and organic superpara- and ferro-magnets whose molecular designs are based on through-bond approach (topologically controlled π-spin polarization). A weakness of carbene, however, is that in general it is a highly reactive intermediate. Thus, the quest for stable organic high-spin systems with robust π-spin polarization has been an important issue for studying supramolecular functionalities of super high-spin molecules and their molecular assemblages. Among the diverse topics of organic molecular magnetism, syntheses and detection of room-temperature stable triplet carbene as a prototype of stable high-spin systems have been the focus of current topics in high spin chemistry.[1)]

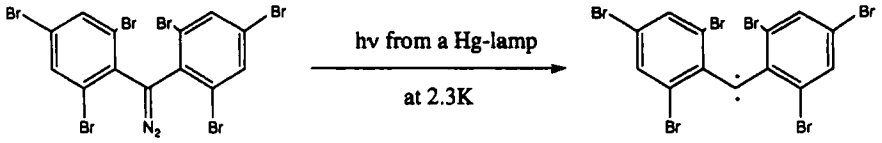
In this paper, we report ESR detection of the first triplet carbene, 2,2',4,4',6,6'-hexabromodiphenylcarbene **1** which is stable in solids at room temperature: **1** is stable even in fluid solution.[1m)] We have studied the chemical stability of **1** by monitoring the fine-structure ESR spectra of **1** from random orientation. From the fine-structure spectra observed in the neat crystal of the diazo precursor of **1**, it has been shown that **1** survives

at room temperature in the neat crystal upon exposure to air. The comparison of the experimentally derived fine-structure constants with the theoretically predicted ones for non-substituted diphenylcarbene has provided us with the molecular conformation responsible for the extreme stability of **1**.

EXPERIMENTAL

Sample Preparation

The preparation of the diazo precursor of **1** will be described elsewhere.[1m] The diazo precursor was fairly soluble in 2-MTHF. A solution of the diazo precursor of **1** was degassed by freeze-pump thaw cycles and sealed off on a vacuum line. 2-MTHF was purified according to usual methods. The solution yielded a dark red glass at 2.3K in the sample site of a cryostat. Upon irradiating the glassy sample with light of 405 nm wave length, several new peaks appeared in the ESR spectrum over a wide range of 0.05–0.75T, indicating the generation of **1**. **1** was generated by the photo-dissociation of the precursor diazomethane as follows:



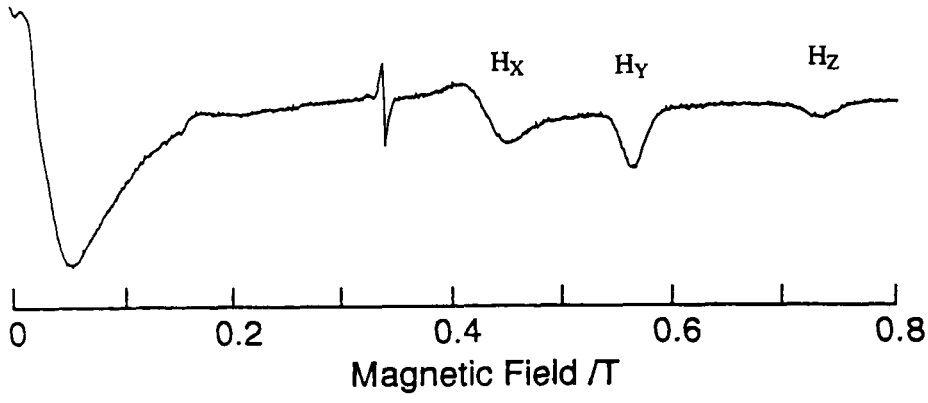
in 2-MTHF glass matrix or single crystal of the diazo precursor **1**

ESR Measurements

ESR measurements were carried out at X band microwave frequencies by use of magnetic field modulation of 100kHz. The temperature dependence of the ESR spectral intensity for the glassy sample was observed in the range of 2.5 to 110K. The temperature was controlled by an Oxford ESR 910 helium gas flow system.

The chemical stability of **1** was investigated in the crystal state of the diazo precursor. **1** in the crystal state was obtained by irradiating the single crystal of the diazo precursor which was prepared at 20 C° by slowly evaporating the benzene solution of the diazo precursor. The temperature dependence of ESR spectra for **1** in the crystal state was observed in the range of 2.5 to 300K.

(a) Observed (2-MTHF; before annealing)



(b) Observed (2-MTHF; after annealing)

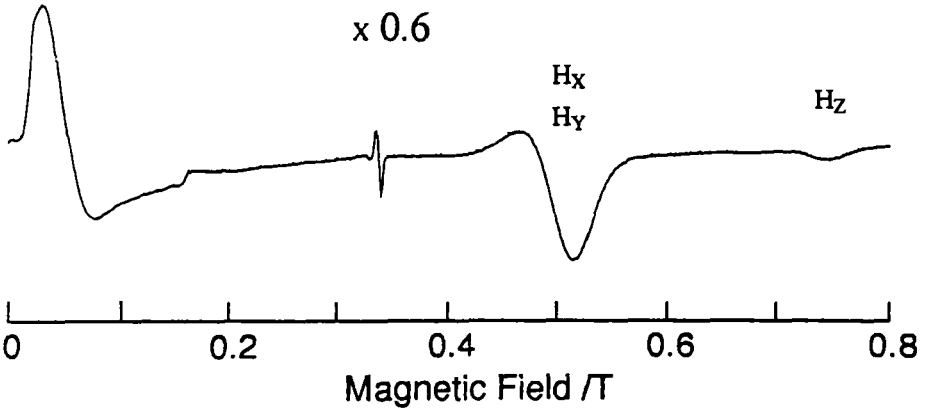


FIGURE1 X-band ESR spectra observed at 5K in a 2-MTHF glass from the triplet state of **1**. (a) before annealing (b) after annealing.

RESULTS AND DISCUSSION

Figure 1a shows the ESR spectrum observed at 5K after the irradiation of the diazo precursor of **1**. This ESR spectrum is typical for randomly oriented triplet molecules with the fine-structure constant D~0.4cm^{-1}, except for the signal observed at 0.34T. The signal at 0.34T originates from by-products during the sample preparation and/or photochemical decomposition of the diazo precursor. The values of D and E can be calculated exactly from the observed resonance fields denoted by H_X, H_Y, and H_Z in Figure 1a using the following equations

$$H_x^2=(g_e/g_{xx})^2[(H_0+D'-E')(H_0-2E')]$$

$$H_y^2=(g_e/g_{yy})^2[(H_0+D'+E')(H_0+2E')]$$

$$H_z^2=(g_e/g_{zz})^2[(H_0+D')^2-E'^2)]$$

where the g tensor was assumed to be isotropic and equal to 2.003 ($g=g_e=g_{xx},g_{yy},g_{zz}$), $H_0=h\omega/2\pi g_e\beta$, $D'=D/g\beta$, and $E'=E/g\beta$. The values of |D|, |E|, and |E/D| are summarized in Table I. The determinations of the signs of D and E by use of single-crystal ESR experiments are under way.

When the 2-MTHF glass was warmed to 150K for 10 seconds, there was a striking shift in the positions of the H_x and H_y lines, which moved closer together (Figure 1b), resulting in nearly zero E value. Re-cooling the sample did not reverse this change. Since the E/D depends on the magnitude of the central C-C-C angle, it indicates that, on warming, the carbene relaxes to a structure with an expand C-C-C angle presumably to gain relief from steric compression.[1,2] These observations are in accord with the UV/vis studies[1m] showing that **1** is kinetically stable and undergoes substantial geometrical changes upon annealing.

In 1971 Higuchi predicted the relation between the fine-structure constants and molecular conformations of non-substituted diphenylcarbene on the basis of LCAO-MO calculations.[3] Figure 2 shows the calculated D and E values of non-substituted diphenylcarbene as a function of the central C-C-C bond angle (θ) assuming the planar structure (α=0°) and the structure with the two phenyl groups perpendicular to the plane of the central C-C-C triangle (α=90°). It is well known that this result coincides with the observed values[4] of D=0.4050cm^{-1} and E=0.01918cm^{-1} for non-substituted diphenylcarbene. Because molecular conformation changes affect the fine-structure constants more than functional group substitutions do,[5] it seems reasonable that the relation shown in Figure 2 applies to the case of **1**. According to Higuchi's model, θ and α of **1** are 140° and 90°, respectively. On the other hand, the X-ray crystal

TABLE I Fine-structure constants and E/D of **1**

matrix	temp,K	|D|,cm^{-1}	|E|,cm^{-1}	|E/D|
before annealing				
2-MTHF	5	0.3598	0.0295	0.0820
after annealing (T_a=150K)				
2-MTHF	5	0.3656	< 0.0002	≒ 0

analysis of the diazo precursor of **1** showed that θ and α are 131° and 85°, respectively.[6] Higuchi's model considered only the dipolar interaction between the two unpaired electrons for the estimation of the molecular conformation of non-substituted diphenylcarbene. The model does not expect any significant effect of electron-donating substituent functional groups on the fine-structure tensor. The calculations incorporating such effect of the substituent groups are under way. A direct intramolecular interaction between the substituted bromines and non-bonding MO's is considered. In a semi-quantitative sense the feature of the molecular conformation of **1** before annealing is close to θ and α obtained by the X-ray crystal analysis of the diazo precursor of **1**.

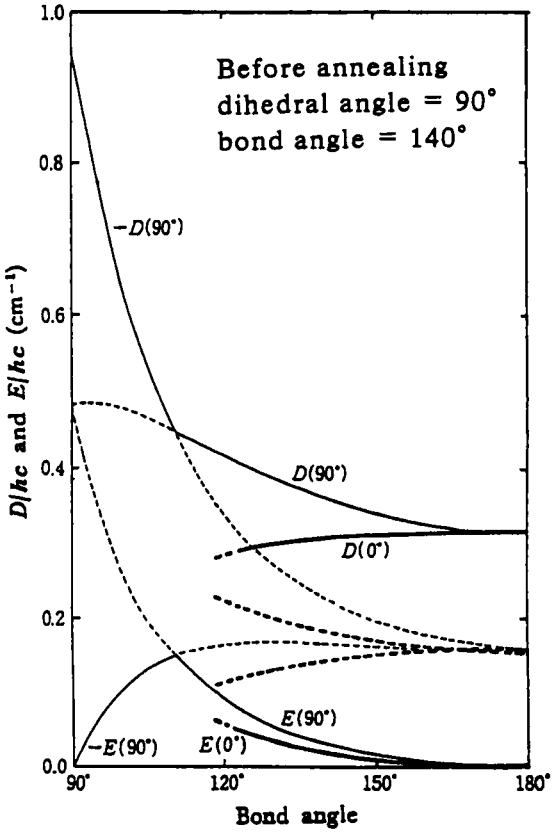


FIGURE 2 Relation between the fine-structure constants and molecular conformations.[3]

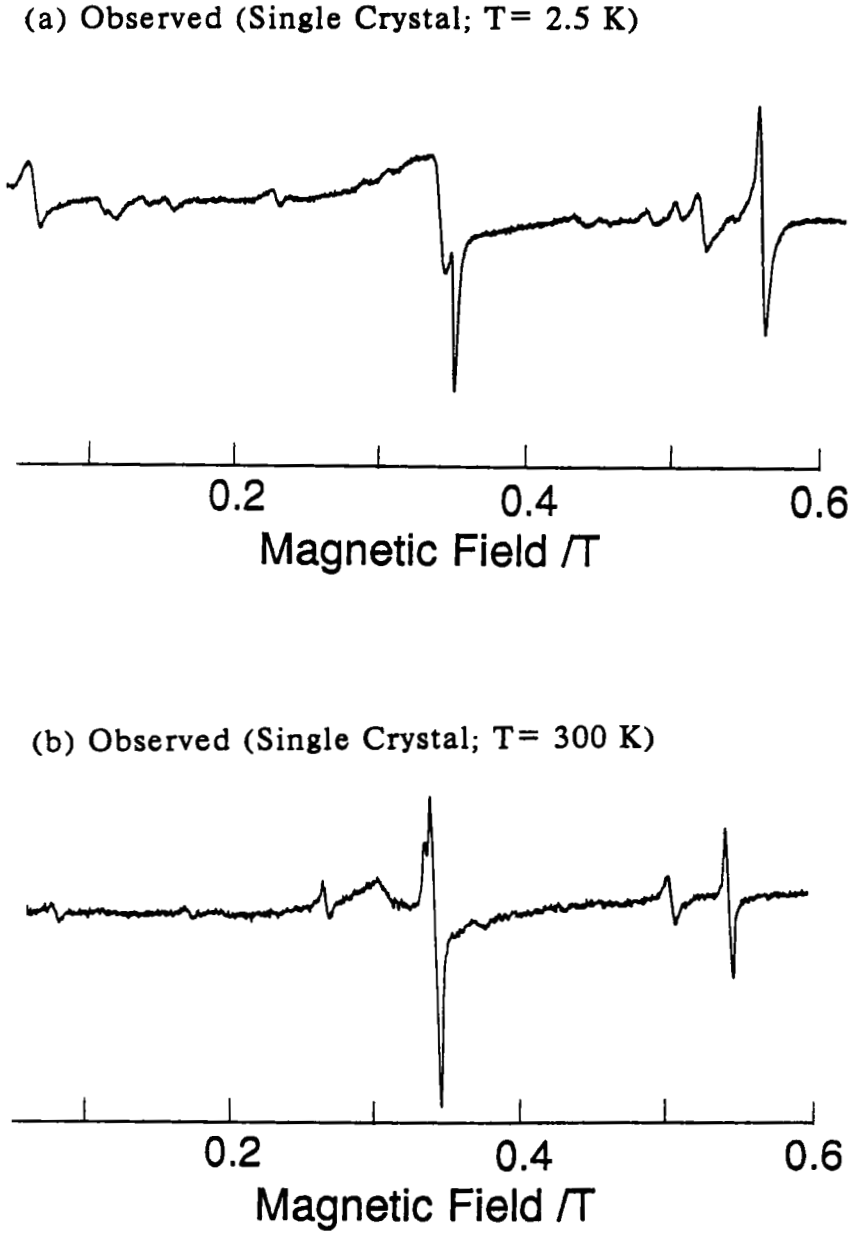


FIGURE 3 X-band ESR spectra from the triplet state of **1** in the neat crystal of the diazo precursor. (a) T=2.5K (b) T=300K.

The remarkably reduction in E by annealing shows an increase of axial symmetry of **1**, indicating that the central C-C-C bond angle becomes expanded and the dihedral angle of the two phenyl rings becomes closer to 90°. Thus, the phenyl rings are perpendicular to each other and the reactive center (divalent carbon atom) is protected by the six bromo groups of the two phenyl rings in this conformation.

Figure 3 shows the ESR spectra observed from a single crystal [(a) at 2.5K, (b) 300K], indicating that the signals occurred at 2.5K in the neat crystal of the diazo precursor survived up to room temperature without loss of intensity, considering the effect of Boltzmann factor. The signals have still survived at room temperature in a nitrogen gas atmosphere for half a year. These facts indicate the remarkable chemical stability of **1** in comparison with the other diphenylcarbene derivatives. In conclusion, triplet diphenylcarbene derivative **1** regarded as highly reactive intermediates can be stabilized by the substitution of 2-, 4-, and 6-position of the two phenyl rings, causing the bent perpendicular molecular conformation.

CONCLUSION

The electronic structure and the chemical stability of **1** were investigated by ESR spectroscopy, and the molecular conformation responsible for this stability was shown LCAO-MO calculations of the fine-structure constants and the X-ray crystal analysis of the diazo precursor of **1**. The observed fine-structure constants were $|D|=0.3598cm^{-1}$, $|E|=0.0295cm^{-1}$ before annealing, $|D|=0.3656cm^{-1}$, $|E|<0.0002cm^{-1}$ after annealing in 2-MTHF glass. The single-crystal ESR experiment showed that **1** survived up to room temperature without loss of intensity in the neat crystal. The LCAO-MO calculations and the X-ray crystal analysis of the diazo precursor of **1** indicated that the stability of **1** was due to the perpendicular conformation.

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