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# ROOM-TEMPERATURE STABLE GROUND-STATE TRIPLET CARBENE AS MODELS FOR ORGANIC HIGH-SPIN UNITS WITH ROBUST π-SPIN POLARIZATION; ESR STUDY AND X-RAY ANALYSIS

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Abstract we report the first room-temperature stable triplet π-aryl based carbene, 2,2',4,4',6,6',-hexabromodiphenylmethylene **2** in both crystals and fluid solutions. This paper describes ESR detection of **2** in the crystal of the diazo precursor **1** and the molecular and crystal structure of **1** obtained by X-ray diffraction at room temperature. ESR spectroscopy showed that **2** was a triplet molecule in the ground state and survived up to room temperature in the crystal state. The crystal of **1** is monoclinic with cell dimensions, $a$=9.933Å, $b$=13.261Å, $c$=12.743Å, $\beta$=91.88° , $Z$ =4 and the space group $P2_1/n$. The two 2,4,6-bromo-substituted phenyl rings make bent perpendicular conformation with 139° of the bond angle at the diazo methane. Non-bonded contacts shorter than the van der Waals radii were found between the nitrogen and bromine atoms of the nearest neighboring molecules. The correlation between the chemical stability and the molecular structure of **2** is discussed.

## INTRODUCTION

The quest for persistent molecular high-spin building blocks with robust π-spin polarization has been an important issue in the rapidly developing research field of purely organic molecule-based magnetism.[1)] The robust spin polarization is of essential importance for the underlying mechanism in both inter- and intra-molecular spin alignment of organic systems and their assemblages. Among organic open-shell systems the robust spin polarization features in high-spin aryl-based carbene and nitrene. Thus, they are suitable as models for building spin blocks in intriguing organic magnetic materials with supra functionalities. It is well known, however, that a common weakness of carbene and nitrene is that in general they are highly reactive intermediates. Thus, chemistry has been challenged to design and synthesize, particularly, persistently stable triplet aryl-based carbene as a prototypical example of room-temperature stable organic high-spin units.

This paper deals with the first room-temperature stable triplet carbene in both the crystal state and fluid solution, describing the electronic and molecular structures as studied by ESR spectroscopy and X-ray crystal analysis.

## EXPERIMENTAL

The preparation of **1** will be described elsewhere.[2] The single crystal of **1** for the single crystal ESR experiments and the X-ray analysis were grown in benzene solutions at room temperature. **2** was generated by the photo-dissociation of **1** in the single crystal.

ESR measurements were carried out at X band microwave frequencies by use of magnetic field modulation of 100kHz. The temperature dependence of ESR spectra for **2** in the crystal state was observed in the range of 2.5 to 300K.

The structures of **1** was determined by X-ray diffraction and details are given in Table I. All measurements were made on Rigaku AFC7R diffractometer with graphite monochromated Cu-$K\alpha$ radiation and a 12Kw rotating anode generator. The data were collected at a temperature of 20 ± 1 C using the $\omega$–$2\theta$ scan technique to a maximum $2\theta$ value of 120.2°. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. All calculations were carried out with the teXsan crystallographic software package of Molecular Structure Corporation.[3]

TABLE I Details of Space Group, Cell Parameters, Data Collection and Structure Refinement for **1**.

| | |
|---|---|
| space group | $P2_1/n$ |
| cell parameters | |
| $a$, Å | 9.933 |
| $b$, Å | 13.261 |
| $c$, Å | 12.743 |
| $\beta$, Å | 91.88 |
| radiation | Cu$K\alpha$($\lambda$=1.54178 Å) graphite monochromated |
| no. of reflections used for unit cell determination ($2\theta$ range) | 20 (79.0-79.9° ) |
| intensity data reflections | 2742 |
| unique reflections | 2577 |
| significant reflections | 1963 |
| Residuals: $R$; $Rw$ | 0.072; 0.105 |

## RESULTS AND DISCUSSION

Figure 1(a) and (b) show the ESR spectra observed from a single crystal at 2.5K and 300K respectively, indicating that the signals occurred at 2.5K in the crystal of **1** survived up to room temperature without loss of intensity, considering the effect of Boltzmann factor. The observed triplet spectra showed the crystal site splitting corresponding to the crystal symmetry. The signals have still survived at room temperature in a nitrogen gas atmosphere for a year. These facts indicate the remarkable chemical stability of **2** in comparison with the other diphenylcarbene derivatives.

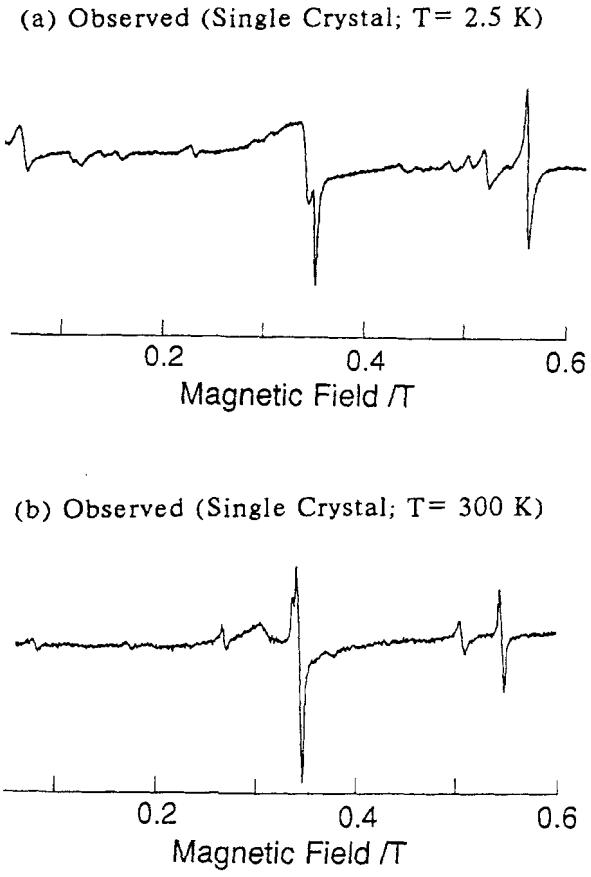


FIGURE 1 X-band ESR spectra from the triplet state of **2** in the crystal of **1**. (a) T=2.5K (b) T=300K.

Figure 2(a) and (b) show the projections of molecular conformations of **1** onto the crystallographic *bc* plane and the *ab* plane of the crystal of **1**, respectively. There occur non-bonded contacts shorter than the van der Waals radii between the nitrogen and bromine atoms of the nearest neighboring molecules. The observed distance, which is denoted by broken lines in Figure 2(a), 3.16Å, while the sum of the van der Waals radii is 4.10Å. The dihedral angle between the two phenyl rings is 85.3 degree and the bond angle at the diazomethane is 139 degree, which corresponds to a bent perpendicular molecular conformation. This conformation prevents other molecules from approaching the reaction center, resulting the extraordinary stabilization of **2** in the triplet ground state.

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.[4] It is well known that this result coincides with the observed values for non-substituted diphenylcarbene[5] and most of diphenylcarbene derivatives.[1a] The values of $|D|$, $|E|$, and $|E/D|$ obtained in randomly oriented ESR experiments are summarized in Table II, indicating an increase in the $D$ value by annealing.[1c] The results suggest the possible occurrence of the enhancement in the one-center spin-spin interaction at the divalent carbon site, which shows the limitation of Higuchi's prediction for the relation between the fine-structure constants and molecular conformations. The occurrence is presumably explained by the effects of pseudo orthogonal π-MO degeneracy of the two phenyls due to the perpendicular conformation and spin influx from electron-donating substituent functional groups at ortho positions of the divalent carbon atom. The calculations incorporating the two effects are under way.

X-ray diffraction experiments on **2** at low temperature as well as room temperature have been attempted after the photolysis of **1** at low temperature to determine the crystal and molecular structure of **2** in the triplet ground state directly. Also the analysis of the powder-pattern fine-structure spectrum is under way in order to determine precisely whether the $E$ value is zero. If the E value is zero, the ground-state triplet of **2** undergoes the strict requirement of axial molecular symmetry. The molecular symmetry obtained from ESR spectroscopy will be compared with that from the X-ray analyses.

## CONCLUSION

This paper describes ESR detection of 2,2',4,4',6,6',-hexabromodiphenylmethylene **2** in the crystal of the diazo precursor **1** and the molecular and crystal structure of the precursor obtained by X-ray diffraction at room temperature. ESR spectroscopy showed

that **2** survived up to room temperature without loss of intensity in the crystal of **1**. One of the most salient features of the molecular structure of **1** obtained from the X-ray analysis is a bent perpendicular conformation. It can be concluded that the remarkable stabilization of **2** in the triplet ground state is responsible for the bent perpendicular conformation.

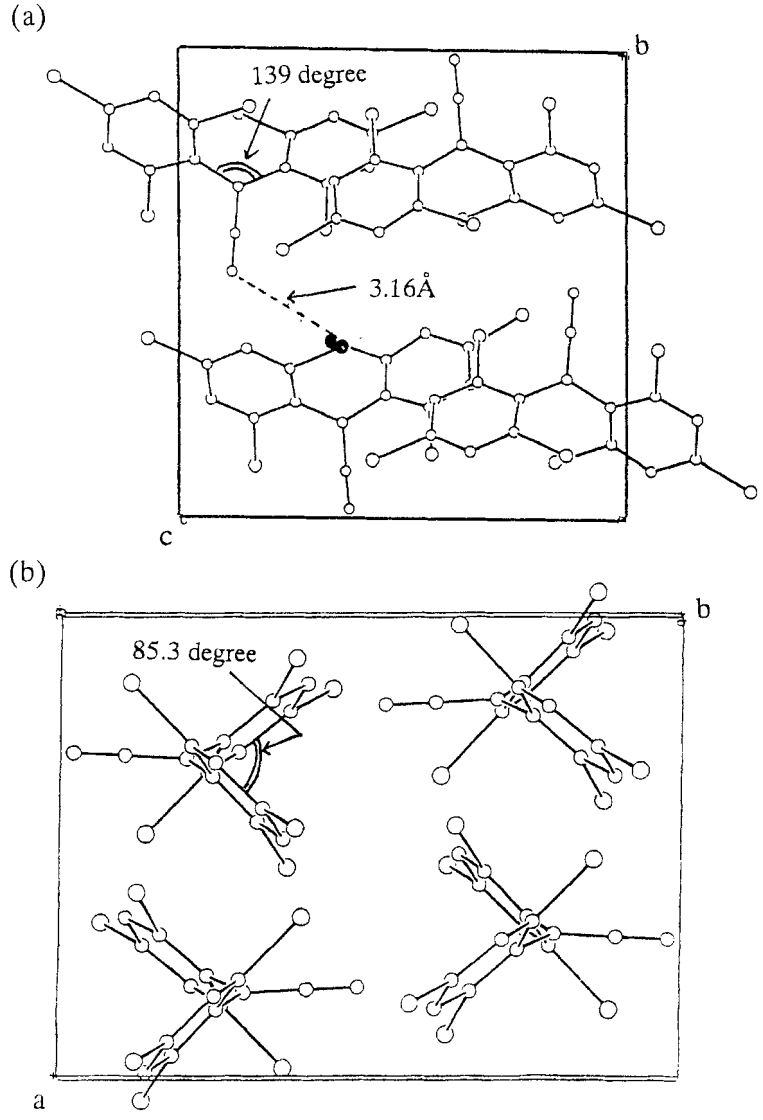


FIGURE 2 Projections of molecular conformations of **1** onto (a) the crystallographic *bc* plane and (b) the crystallographic *ab* plane of the crystal of **1**.

TABLE II Fine-structures constants and *E/D* of **2**

| 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 |

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