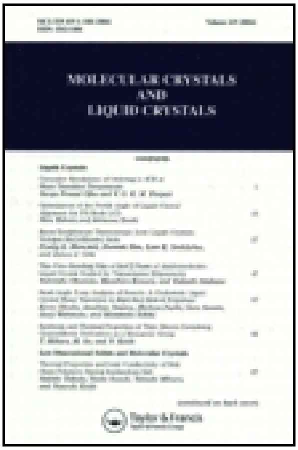

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Electronic and Molecular Structures of Room-Temperature Stable Triplet Carbene as Studied by ESR and X-Ray Crystal Analysis of the Diazo Precursor

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ELECTRONIC AND MOLECULAR STRUCTURES OF ROOM-TEMPERATURE STABLE TRIPLET CARBENE AS STUDIED BY ESR AND X-RAY CRYSTAL ANALYSIS OF THE DIAZO PRECURSOR

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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 the precursor obtained by X-ray diffraction at room temperature. The crystal is monoclinic with cell dimensions, $a = 9.993$Å, $b = 13.261$Å, $c = 12.743$Å, $\theta = 91.88°$, $Z = 4$, and the space group *P21/n*. The two phenyl rings of 2,4,6-bromo-substitution make bent perpendicular conformation with 139 degree 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.

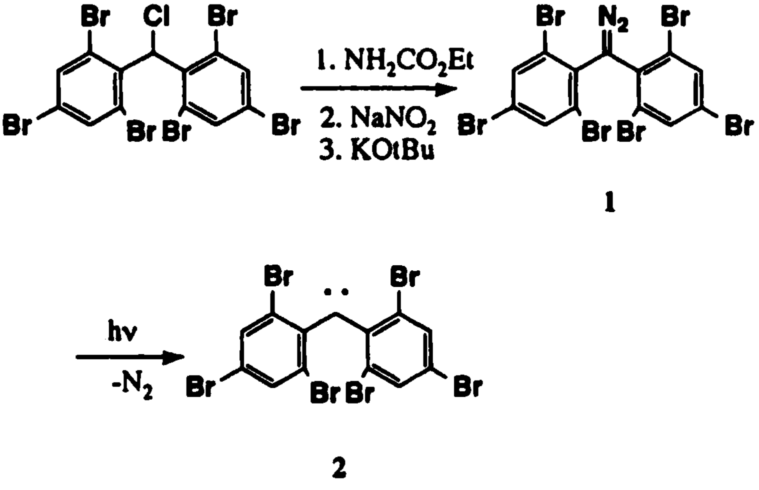
INTRODUCTION

The quest for stable molecular high-spin building blocks with robust π-spin polarization has been an important issue in the rapidly developing research field of organic molecule-based magnetism and spin chemistry.[1] The robust spin polarization is of essential importance for the underlying mechanism in both inter- and intramolecular 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 and sites in intriguing organic magnetic materials with supra functionalities of super high-spin molecules and their molecular assemblages. It is well known, however, that a common weakness of carbene and nitrene is that in general both are highly reactive intermediates. Thus, chemistry has been challenged to synthesize, particularly, stable triplet aryl-based carbene as a prototypical example of room-temperature stable high-spin organic systems. In this paper, we report the first room-temperature stable triplet carbene, 2,2',4,4',6,6',-hexabromodiphenylmethylene **2** in both the crystal state and fluid solution, describing ESR detection of 2 in crystals of the diazo precursor 1 and the molecular and crystal structure of the precursor analyzed by X-ray diffraction at room temperature.

EXPERIMENTAL

The diazo precursor 1 was synthesized by acyl cleavage of the corresponding N-alkyl-N-nitrosourethane by pottassium *tert*-butoxide as a rather stable red crystal which was purified by repeated chromatograhy (see below: Scheme 1).[2] The single crystals of the precursor 1 for X-ray analysis were grown in benzene solutions at room temperature. Fine-structure ESR spectra of 2 were obtained by the photolysis of the neat single crystal of the precursor 1 at liquid helium temperature.

Scheme 1



RESULTS AND DISCUSSION

The crystal data of the precursor 1 is as follows: the crystal is monoclinic with the cell dimensions, a = 9.933Å, b = 13.261Å, c = 12.743Å, θ = 91.88 degree, Z = 4 and the space group *P2i/n*.

Figure 1 shows the projection onto the crystallographic *bc* plane, depicting that between the nitrogen and bromine atoms of the nearest neighboring molecules there occur non-bonded contacts shorter than the van der Waals radii. The observed distance, which is denoted by broken lines in Figure 1, is 3.16Å, while the sum of

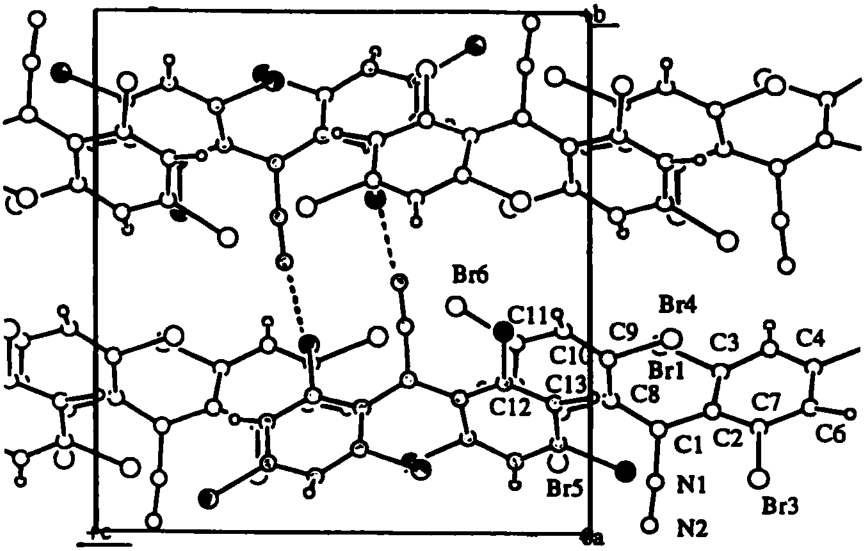


FIGURE 1 Projection onto the crystallographic *bc* plane of the crystal 1.

the van der Waals radii is 4.10Å. The two phenyl rings are planar and the substitution of bromine does not give rise to significant departure from the planarity: each carbon atom of the phenyl rings deviates only by less than 10^{-2}Å from the complete mean plane.

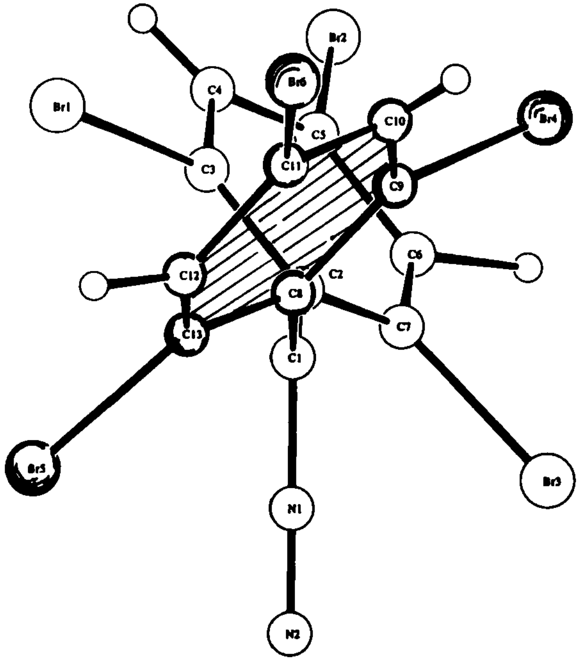


FIGURE 2 Molecular structure of the room-temperature stable triplet carbene 2: the bent perpendicular conformation.

One of the most salient features obtained from the X-ray analysis is a bent perpendicular conformation of the precursor, as shown in Figure 2. The dihedral angle between the two phenyl rings is 85.3 degree. The bond angle at the diazo methane is 139 degree, which corresponds to the bent angle of the phenyl rings. This perpendicular conformation is responsible for the extraordinary stabilization of 2: photolyses of the single crystal of 1 generated fine-structure ESR spectra due to typical triplet diarylcarbene with a large D value (D~ 0.4 cm^{-1}). The ESR signals survived up to room temperature without loss of itensity, considering the effect of the Boltzmann factor, for months.

It should be noted that the perpendicular conformation suggests the possible occurrence of the enhancement in the one-center spin-spin interaction at the divalent carbon site of 2. This effect arises from electron-donating substituent functional groups at *ortho* positions of the divalent carbon atom. A direct intramolecular interaction between the substituted bromines and the two non-bonding MO's may intensify the one-center interaction, leading to an increase in the D value. For the perpendicular conformation of non-substituted diphenylmethylene in the triplet ground state, the D value is expected to be minimized.[3] A significant delocalization of the non-bonding MO's into the π-conjugated system of the phenyl rings gives a rationale for the minimization. The ground-state triplet of 2 is not the case. In order to expound any significant effect of the substituted bromines on the fine-structure tensor of 2 theoretical calculations are under way.

A direct determination of the crystal and molecular structures of 2 in the triplet ground state has emerged as a challenging target. X-ray diffraction experiments on 2 at low temperature as well as room temperature are going on after the photolysis of the precursor 1 at low temperature. Also both the elaborate analyses of the fine-structure ESR spectra of 2 observed in the single crystal of the precursor 1 and the powder-pattern fine-structure spectra are under way in order to determine precisely whether the E value is vanishing. If the E value is vanishing, the ground-state triplet of 2 undergoes the strict requirement of axial molecular symmetry. Otherwise, sp^2 hybridization at the divalent carbon site may dominates in stabilizing 2, as an *ab initio* calculation predicts.[1] The molecular symmetry obtained from ESR spectroscopy will be compared with that from the X-ray analyses.

CONCLUSION

This paper dealt with the determination of the molecular and crystal structures of the diazo precursor of 2,2',4,4',6,6'-hexabromodiphenylmethylene **2** in the triplet ground state by X-ray diffraction. Since the isolation of carbene in the singlet state has been realized very recently,[4-6] the stabilization of a triplet carbene has emerged as a challenging target. The aryl-based carbene **2** is the first which is persistently stable in the crystal state at room temperature and in fluid solutions.[2] One of the most salient features of the molecular structure of the precursor is the bent perpendicular conformation, giving rise to steric protection against reactions of the carbenic site of **2**. Molecule **2** is a prototypical example of persistently stable high-spin building blocks with robust π-spin polarization, which is viable as models for building spin blocks and sites in intriguing organic magnetic materials with potential supra functionalities.

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