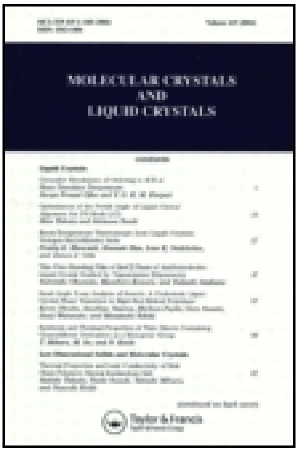

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Molecular Design, Synthesis, and Electron Spin Resonance Detection of a Ground-State Tridecet (S=6) Hydrocarbon as a Model for 2D Organic Ferro- and Superpara-Magnets

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MOLECULAR DESIGN, SYNTHESIS, AND ELECTRON SPIN RESONANCE DETECTION OF A GROUND–STATE TRIDECET (S=6) HYDROCARBON AS A MODEL FOR 2D ORGANIC FERRO– AND SUPERPARA–MAGNETS

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Abstract The electronic and molecular structures of a high-spin carbene oligomer, hexakiscarbene **B**, having a two-dimensional spin structure were investigated by single-crystal ESR spectroscopy. **B** was designed on the basis of π-topological symmetry argument, and generated by the photolysis of the corresponding hexakisdiazo precursor **A** oriented in benzophenone-d_{10} host single crystals at 2.3K. The observed ESR spectra from **B** were well reproduced by an exact diagonalization of the spin Hamiltonian with $g=2.003$, $D= +0.01909\ \mathrm{cm}^{-1}$, $E= -0.00193\ \mathrm{cm}^{-1}$, and $S=6$, proving **B** to be in the tridecet ($S=6$) state. The temperature dependence of the total intensity of the tridecet signals proved the observed tridecet state to be the ground state. A semiempirical calculation of the fine-structure tensor yielded the most probable molecular conformation of **B** in the host crystal.

INTRODUCTION

Recently, organic magnetism has become an important issue in both pure and applied sciences. A through-bond approach to organic magnetism can date back to the detection of m-phenylenebis(phenylmethylene), the first organic high-spin molecule ($S=2$) in the electronic ground state, by one of the authors (K.I.)[1] and by Wasserman et al.[2] in 1967. Since then, we have synthesized and detected various organic high spin molecules as models suitable for studying the spin alignment in organic systems.[1,3,4] The molecular design of these molecules has been based upon the topological nature of degenerate πnonbonding MO's and Hund's rule. On the basis of the unlimited degree of topological degeneracy, Mataga[5] and one of the authors (K.I.)[6] proposed the possible occurrence of organic ferromagnetism and the hypothetical ferromagnetic polymers such as one- or two-dimensional triarylmethyl π-radical based polymers and meta-connected polycarbens. Suitable synthetic materials, however, did not exist at that time and only high-spin units[1,2,7-9] or a small oligomer of a two-dimensional spin structure[8,9] was studied as models for such organomagnetic materials.

In the last five years, reports appeared on organic high-spin oligomers with $S \geq 5$, whose spin structures are similar to the above hypothetical polymers. The $S=5$ pentakiscarbene[4] as a model for a quasi one-dimensional organic ferromagnet and the $S=5$ decaradical[10] as a model for a two-dimensional triarylmethyl based ferromagnetic polymer have been documented. In this paper, as a model for the two-dimensional organic ferro- and superpara-magnets, we report the design, synthesis, and unequivocal characterization of a tridecet ($S=6$) high-spin carbene oligomer **B** by single-crystal ESR spectroscopy. As for this molecule, Iwamura's group has reported a magnetic susceptibility measurement.[11] From the viewpoint of a synthetic strategy, **B** is a key step to organic super high-spin macromolecules with extremely large spin multiplicities. Furthermore, **B** is important for studying the thermal stability of ferromagnetic polymers.

EXPERIMENTAL

Materials

Hexakisketone was prepared from 3-benzoylbenzoic acid via the following sequence of reactions: chlorination with thionyl chloride, Friedel-Crafts with bis(trimethylsilyl)acetylene, reduction with "borax",[12] and trimerization[13] of ketoacetylene in DMF. The hexakisdiazo compound **A** was synthesized by oxidation with activated MnO_2 of hexakishydrazone which was prepared from hexakisketone by condensation with dry hydrazine in ethanol. A detailed synthetic procedure of **A** will be published elsewhere.[14]

Sample Preparation

Benzophenone-d_{10} was chosen as a host molecule, since its crystal was found to incorporate well the diazo precursor **A** in spite of their large difference in molecular size. The crystal structure has been determined by X-ray diffraction[15], the space group being $P2_12_12_1$ with Z=4. Benzophenone-d_{10} was purified by repeated recrystallizations from ethanol. The single crystals containing **A** as a guest were obtained as follows. A diethylether solution containing benzophenone-d_{10} and 0.00144 mol. fraction of **A** was prepared at 13 °C. Single crystals were grown in the dark by slowly cooling the solution in a thermostated bath. Light-red crystals of a desired size in the rectangular form were obtained from the wine-red solution.

Electron Spin Resonance Measurements

The single crystal was mounted on a quartz wedge or sample holder in an ESR cavity in such a manner that the crystallographic plane of the host crystal rotates in the static magnetic field H_0. **B** was formed at 2.3 K by the photolysis of **A** in the host crystal with the 405-nm line from an XBO 500-W high-pressure mercury lamp (OSRAM) equipped with a glass filter (Toshiba UV39) and a 5-cm solution filter of 100 g of $CuSO_4 \cdot 5H_2O/dm^3$.

ESR measurements were carried out at X-band microwave frequencies. We used a Bruker ESP300 ESR spectrometer. The angular dependence of the ESR spectra was measured by rotating the single crystal. The temperature dependence of the ESR spectra was observed in the range of 1.9 to 210K. The temperature was controlled by an Oxford ESR910 variable temperature controller.

RESULTS AND DISCUSSION

Feature of the X-band ESR Spectra at 2.3K

Figure 1 shows the ESR spectrum of **B** observed at 2.3K with the static magnetic field along the crystallographic *b* axis of the host crystal. The spectrum is composed of twelve absorption peaks expected for the fine structure of tridecet spin states. The observed absorption lines of the fine structure are assigned to the $\Delta M_S \cong \pm 1$ allowed transitions as $A_\pm : M_S \cong \pm 6 \leftrightarrow \pm 5$, $B_\pm : M_S \cong \pm 5 \leftrightarrow \pm 4$, $C_\pm : M_S \cong \pm 4 \leftrightarrow \pm 3$, $D_\pm : M_S \cong \pm 3 \leftrightarrow \pm 2$, $E_\pm : M_S \cong \pm 2 \leftrightarrow \pm 1$, $F_\pm : M_S \cong \pm 1 \leftrightarrow \pm 0$. The ratio of the observed relative separations of those pair signals is $A_- - A_+ : B_- - B_+ : C_- - C_+ : D_- - D_+ : E_- - E_+ : F_- - F_+ = 11.41 : 9.00 : 6.98 : 4.91 : 2.92 : 1.00$, which is close to the ratio of 11 : 9 : 7 : 5 : 3 : 1

theoretically obtained for S=6 in the high field limit. The integrated absorption intensities observed were also close to the values calculated for the fine structure of the tridecet states where the Boltzmann factor at 2.3K was taken into account.

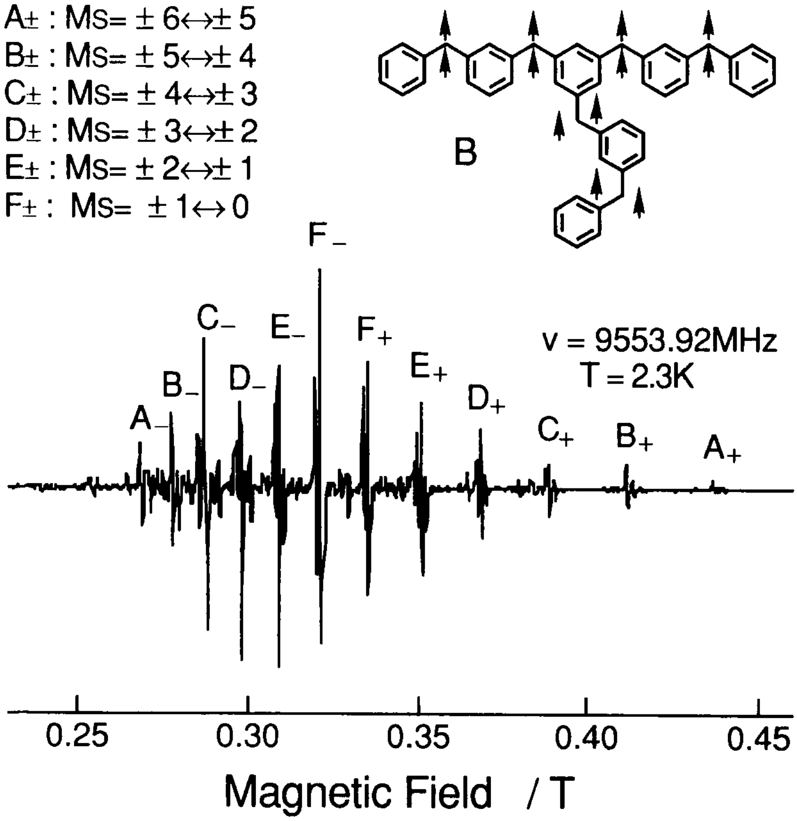


FIGURE 1 The X-band ESR spectrum from **B** observed at 2.3K with the static magnetic field along the crystallographic *b* axis of the host benzophenone-d_{10} crystal.

Analysis of the Spectra at 2.3K

Numerical calculations based on the following effective spin Hamiltonian

$$\begin{aligned}\mathcal{H} &= g\beta \mathbf{H}\cdot\mathbf{S} + \mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S} \\ &= g\beta \mathbf{H}\cdot\mathbf{S} + D[S_Z^2 - S(S+1)/3] + E(S_X^2 - S_Y^2)\end{aligned}$$

with g= 2.003 (isotropic), $D = +0.01909\ \mathrm{cm}^{-1}$, $E = -0.00193\ \mathrm{cm}^{-1}$ and $S = 6$ reproduced well the observed resonance fields and intensities shown in Figure 1 as well as their angular dependence in the *ab*, *bc* and *ca* crystallographic planes. The calculated values were obtained by means of an exact numerical diagonalization of the above spin Hamiltonian matrices. The absolute sign of the fine structure parameter D was determined to be positive considering the effect of the Boltzmann distribution on the signal intensities of the spectra. As a result, it was unequivocally concluded that the observed fine structure and angular dependence were not attributable to the superposition of spectra from more than one paramagnetic species with S=1, 2, 3, 4 and 5. Consequently, the observed paramagnetic species is undoubtedly in the tridecet state. ESR transitions due to the by-products of photolysis with lower spin multiplicities were distinguishable from the tridecet signals; their weak signal intensities indicates that the by-products were minor species.

Determination of the Lowest Energy Level

It was proved in the following manner[3] that the tridecet state is the ground state. To determine the lowest energy level, we observed the temperature dependence of the ESR signal intensity. The ESR spectra were recorded in the range from 1.9 to 210K. For a system with twelve unpaired electrons, seven different spin multiplicities corresponding to S=0, 1, 2, 3, 4, 5 and 6 are allowed. Figure 1 shows that the ESR spectrum of the tridecet state only was observable at 2.3K. Moreover, no thermally populated triplet, quintet, septet, nonet and undecet signals were detected up to a temperature where **B** decomposed, i.e., 210K. Given the sensitivity of the spectrometer, it was estimated that the spin states other than the tridecet state are located at least 300 cm^{-1} above the ground state except the singlet state being ESR silent. As for the singlet state, one can estimate its location from the temperature dependence of the total intensity of the tridecet signals. Assuming the singlet–tridecet energy separation ΔE, the total intensity of the tridecet signals at a given temperature, $I_6^{\mathrm{calcd.}}(T)$, can be calculated by the equation,

$$I_6^{\mathrm{calcd.}}(T) = A \sum_m \left| \langle m+1 \,|\, S_x \,|\, m \rangle \right|^2 N(T,m,m+1)$$

$$N(T,m,m+1) = \left|\xi_m(H_m) - \xi_{m+1}(H_m)\right| / \left[\sum_i \xi_i(H_m) + \xi_s\right]$$

$$\xi_m(H_m) = \exp[-(E_m - E_0) / kT] , \xi_s = \exp[-\Delta E / kT]$$

where E_0 stands for the ground state energy, E_m the energy of the state |m⟩, N(T,m,m+1) the Boltzmann factor and A a constant to normalize the total

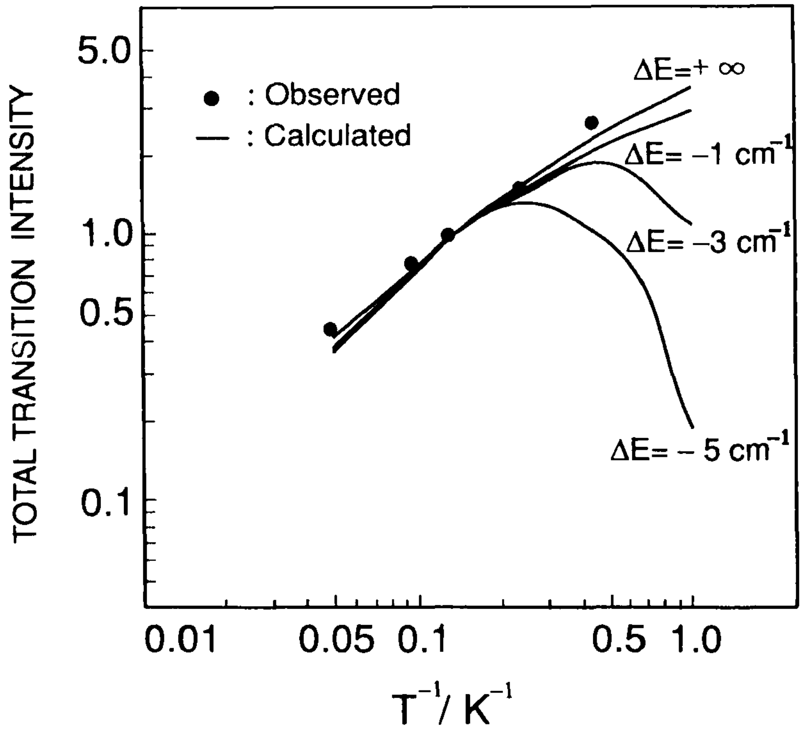


FIGURE 2 Plots of the total intensity for the tridecet signals. The energy separation between the singlet and tridecet states is given by ΔE.

intensity to unity at 4K. In Figure 2 the total signal intensities obtained experimentally and theoretically are plotted as a function of reciprocal temperature in the range from 1.9 to 20K. The points denote the values observed with the magnetic field along the crystallographic *a* axis of the host crystal. The solid curves are plots of the total intensity calculated from the above equations for ΔE= +∞, −1, −3 and $-5\ \mathrm{cm}^{-1}$. If the singlet state was located lower than the tridecet state, a considerable decrease in the total intensity would be expected below ca. 2K. Since no decrease is observed as shown in Figure 2, it is safely concluded that the observed tridecet state is the electronic ground state.

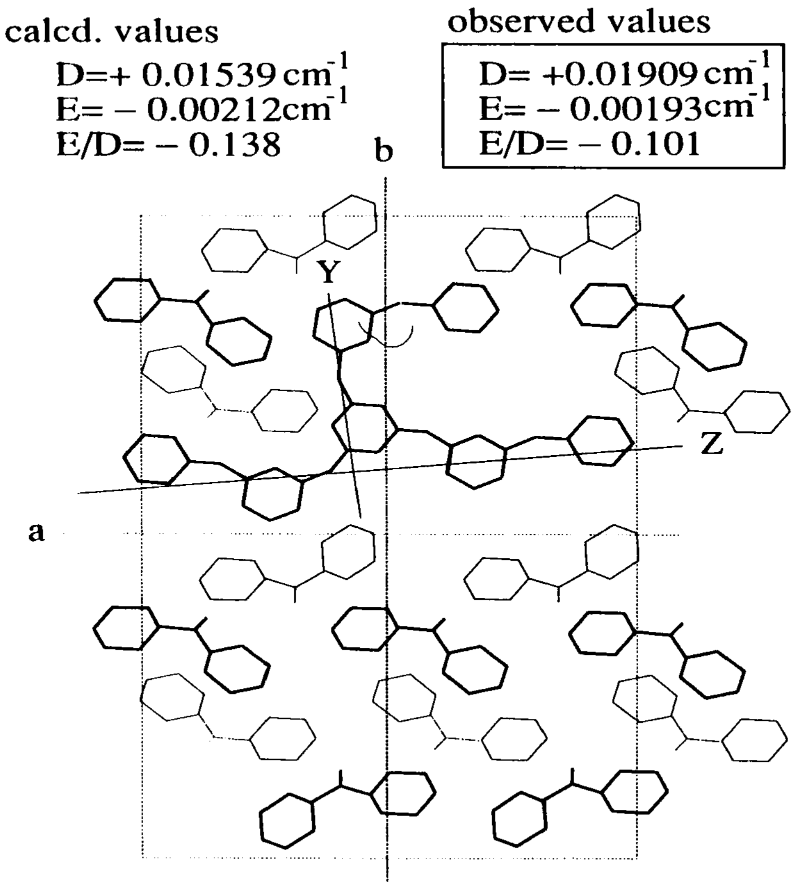
Probable Molecular Conformations of B

To obtain information about the molecular conformation of **B**, we carried out a semiempirical calculation of the fine structure tensor. Since the spin-orbit interaction is expected to be negligibly small for the hydrocarbon **B**, the dipole-dipole interaction between the electron spins is responsible for the fine structure tensor. For hydrocarbons with electronic structures similar to **B**, there are three types of spin-spin interactions, i.e., π-π, n-n, and n-π. It has been shown that the spin-spin interaction in such hydrocarbons arises predominantly from the one-center n-π interaction at divalent carbon atoms.[16a,16b] Assuming that only the one-center n-π interaction contributes to the spin-spin interaction and that n-electrons are localized on the divalent carbon atoms, the ij component of the fine structure tensor for such a hydrocarbon is given by the expression,[3]

$$D_{ij}=[S(2S-1)]^{-1}\sum_{k}(\rho_k / \rho_{DPM})(\mathbf{U}_k\cdot\mathbf{d}_{DPM}\cdot\mathbf{U}_k^{\dagger})_{ij}$$
$$(\ i, j = X, Y, Z\ )$$

where $\mathbf{d}_{DPM}$ is the fine structure tensor observed with diphenylmethylene (S=1).[17] ρ_{DPM} is the π-spin density on the divalent carbon atom of diphenylmethylene (DPM), and ρ_k is the π-spin density on the kth divalent carbon atom of **B**. Both ρ_{DPM} and ρ_k were estimated from a generalized Hubbard calculation.[18] Finally, $\mathbf{U}_k$ is a unitary matrix which transforms the local symmetry axes for the kth divalent carbon moiety to the principal X, Y, Z axes of the fine structure tensor **D** referred to the molecular frame.

Using the above equation, we have determined probable molecular conformations for **B** considering the consistency with the lattice structure of the benzophenone-d_{10} host crystal. The E/D ratio is a useful measure in determining the molecular structure of this type of hydrocarbons.[16c] **B** can take 204 different molecular conformations even when planar structures are assumed. We calculated the fine structure tensors for all the molecular conformations assumed and compared the calculated D, E and E/D values with the observed values. Figure 3 shows the projection of one of the most probable molecular conformations of **B** onto the *ab* plane of the host crystal; the observed and calculated D, E and E/D values of that conformation are also given. The Z axis is nearly along the molecular long axis and the X axis is perpendicular to the molecular plane. In addition, this orientation requires four substitutional sites of the benzophenone-d_{10} host molecule over the two unit cells. The 4 : 1 ratio is the minimum demanded by substitution of **B** with its molecular size.



calcd. values

$D = +0.01539\,\mathrm{cm}^{-1}$
$E = -0.00212\,\mathrm{cm}^{-1}$
$E/D = -0.138$

observed values

$D = +0.01909\,\mathrm{cm}^{-1}$
$E = -0.00193\,\mathrm{cm}^{-1}$
$E/D = -0.101$

FIGURE 3 The crystal structure of benzophenone-d_{10} and the projection of one of the most probable molecular conformations of **B** onto the *ab* plane.

CONCLUSION

The electronic and molecular structures of a high-spin carbene oligomer hexakiscarbene **B** having a two-dimensional spin structure were investigated by single crystal ESR spectroscopy, enabling us to unequivocally characterize the spin structure of **B**. All the resonance fields, the signal intensities, and their angular dependence were well interpreted by the effective spin Hamiltonian with $S=6$, $g=2.003$ (isotropic), $D= +0.01909$ cm^{-1} and $E= -0.00193$ cm^{-1}. The temperature dependence of the total signal intensity proved the tridecet state to be the ground state. In addition, the most probable conformations for **B** in the host crystal were determined with the help of a semiempirical calculation of fine structure tensors using Hubbard model.

B is an organic molecule with the highest spin multiplicity documented so far. Recently, a magnetic susceptibility measurements of the nonacarbene ($S=9$) has appeared.[19] The detection of **B** shows that the molecular design based upon the topological nature of degenerate π-nonbonding MO's in organic systems is essential for obtaining super high-spin polymers, organic superpara- and ferro-magnets.

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