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Takeji Takui [a], Shuichi Kita [a], Shinji Ichikawa [a], Yoshio Teki [a], Takamasa Kinoshita [a] & Koichi Itoh [a]

[a] Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka, 558, Japan

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SPIN DISTRIBUTION OF ORGANIC HIGH-SPIN MOLECULES AS STUDIED BY ENDOR/TRIPLE

TAKEJI TAKUI, SHUICHI KITA, SHINJI ICHIKAWA, YOSHIO TEKI, TAKAMASA KINOSHITA, and KOICHI ITOH
Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

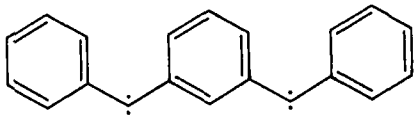
Abstract Single-crystal ^{1}H-ENDOR and TRIPLE resonance spectroscopies have been applied to the first organic high-spin molecule, m-phenylenebis(phenylmethylene), **1** in its quintet ground state. Both the magnitude and absolute sign of all the proton hyperfine coupling constants have been determined from the ENDOR/TRIPLE data, yielding crucial information on the spin density distribution of its pi-electron network. The spin distribution thus determined demonstrates the important role of topological symmetry in organic high-spin molecules. Spin densities on carbon atoms of other typical high-spin molecules such as 3,4'-diphenylmethylenebis(phenylmethylene), **2** have also been determined for their ground states or low-lying excited states. Spin-prediction theories have been tested in terms of the spin density distribution, showing a UHF generalized Hubbard model Hamiltonian to be appropriate for the evaluation of spin densities in macromolecules with large spins and those in organic high-spin molecules which are unit moieties of organo-magnetic materials.

INTRODUCTION

Organic high-spin molecules[1,2] have attracted increasing intense interest from both experimental[3-20] and theoretical sides[18,21-38] as models for purely organic ferro- or ferrimagnetism. Recently, syntheses of organo-magnetic materials and experimental evidence for their ferromagnetic properties have been reported.[39-44] Only a few reports, however, have claimed that the magnetic behavior originates from molecular/organic based moieties and their cooperative nature. Mechanisms responsible for the ferromagnetic behavior are still being quested. For both elucidation of such mechanisms and molecular designs of organo-magnetic materials, it is indispensable to study the spin density distribution in their unit

moieties such as high-spin molecules or radical sites. Experimental determination of spin density distribution serves to interpret inter- as well as intramolecular spin alignment and provides a direct test for the validity of the spin-prediction theory for their ground and low-lying excited states.[18,30-32,34-36]

As part of a project for spin ordering in chemistry and experimental realization of organic magnetism, we have applied single-crystal ^{1}H-ENDOR(Eelectron-Nnuclear-DOuble Resonance) and TRIPLE(electron-nuclear-nuclear-TRIPLE resonance) techniques to the first organic high-spin molecule, m-phenylenebis(phenylmethylene), **1**(m-PBPM) in its quintet ground state.[1,2] Both the magnitude and absolute sign of all the proton hyperfine coupling constants (hfcc's) for the quintet molecule provide crucial knowledge of its pi-electron network associated with the spin alignment as well as with the molecular structure. For the other typical organic high-spin molecules such as 3,4'-diphenylmethylenebis(phenyl-methylene), **2**(3,4'-DPBPM), we have also determined the spin density distribution in their ground state or low-lying excited states. Both the UHF generalized Hubbard and Heisenberg models, which have successfully applied to spin-prediction for organic high-spin molecules, have been tested in terms of spin density distribution.



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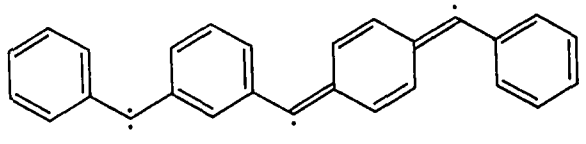

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EXPERIMENTAL

The high-spin molecules adopted here were formed by the photolysis of corresponding diazo precursors. The precursor of **1**, 1,3-bis(α-diazobenzyl)benzene and perdeuterated benzophenone-d_{10} were synthesized according to the usual procedure. Deuterium labeled trisdiazo precursors of **2** were prepared to reduce ^{1}H-ENDOR spectral density and to facilitate correct assignment of ^{1}H-ENDOR transitions to thirty-six protons of **2**. All the deuterated compounds were synthesized from perdeuterated benzene-d_{10}(>99.6 atom%D; Merk Sharp & Dohme Co., Inc.) as a starting material.

Single crystals of benzophenone-d10 ($P2_12_12_1$, space group with Z=4) containing the corresponding diazo precursor were prepared and irradiated at 4.2K with a 500 W high-pressure mercury lamp.

^{1}H-ENDOR/TRIPLE measurements were made on a home-made X-band spectrometer equipped with a TE_{011} rectangular ENDOR cavity.

RESULTS and DISCUSSION

High-spin Multiplet ^{1}H-ENDOR/TRIPLE of m-PBPM

Figure 1 shows a typical ESR spectrum of m-PBPM observed at 4.2K with the external magnetic field applied parallel to the crystallographic b axis of the benzophenone host crystal. The strong lines B+ and weak lines A+ correspond to the $|M_s=0\rangle \leftrightarrow |M_s=\pm1\rangle$ and $|M_s=\pm1\rangle \leftrightarrow |M_s=\pm2\rangle$ ESR transitions, respectively, where Ms refers to a spin sublevel of the quintet spin state in the high field limit.

Figure 2(a) and 2(b) show ,respectively, the ^{1}H-ENDOR and TRIPLE spectra of 1 observed when the line B+ in Figure 1 was monitored. The figures in Figure 2 denote the positions of fourteen protons belonging to **1**. The lines labeled by the figures were attributed to the ENDOR transitions assigned to the Ms=+1 manifold, while most of the unlabled lines were attributable to the

the Ms=0 manifold. The Ms-assignment straightforwardly reveals that the ENDOR spectrum comprises five protons with positive hfcc's and nine protons with negative hfcc's. The polarity of the

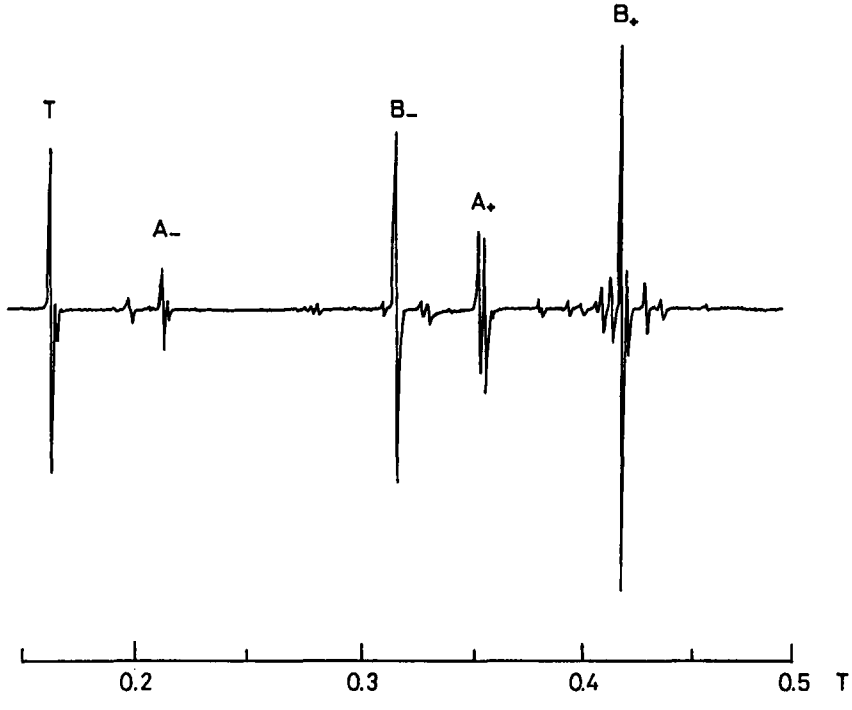

FIGURE 1. An ESR spectrum of m-PBPM observed at 4.2K with the external magnetic field along the b axis of the benzophenone-d_{10} host crystal.

TRIPLE signal exclusively determined the Ms-assignment of the ENDOR transitions, therefore, the absolute sign of the hfcc's, as shown in Figure 2(b), where the ν_{N+} line was the observer. The TRIPLE transitions belonging to the same Ms-manifold (Ms=0 in Figure 2(b)) as that of the observer diminish their intensity, while those belonging to another Ms-manifold (Ms=+1 in Figure 2(b)) gain their intensity.

To determine the hyperfine coupling tensors of the fourteen

protons, we measured the angular dependence of the ENDOR transitions for the rotation of the external magnetic field in the three crystallographic planes.

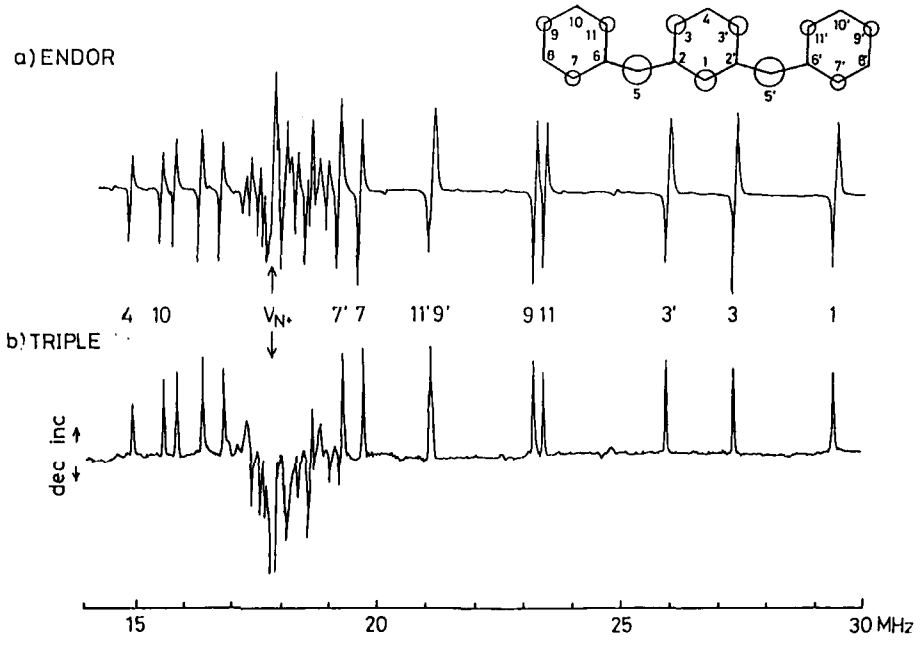

FIGURE 2. ^{1}H-ENDOR (a) and TRIPLE (b) spectra of m-PBPM observed at 4.2K when the ESR line B+ was monitored with the external magnetic field parallel to the b axis of the benzophenone-d_{10} host crystal. The free proton NMR frequency ν_{N+} was 17.7607 MHz.

pi-Spin Density Distribution and Molecular Structure of m-PBPM

Figure 3 (b) depicts the pi-spin density distribution on the carbon atoms of 1 obtained from the experimentally determined isotropic hfcc (a_i), where the total spin density is normalized to two in harmony with the number of the pi-unpaired electron. The pi-spin density (ρ_i^π) was obtained using the McConnell equation in its simple form, $a_i = Q\rho_i^\pi$, where Q is a constant value of -33.45 MHz.[45] Since the spin density on the ring carbon bonded to the

divalent carbon atom could not be determined, a half of the residual value $2-\Sigma \rho_i\pi$ was assigned to each divalent carbon atom. Figure 3(a) shows the pi-spin density distribution calculated by the Longuet-Higgins non-bonding MO theory (the simple MO theory).

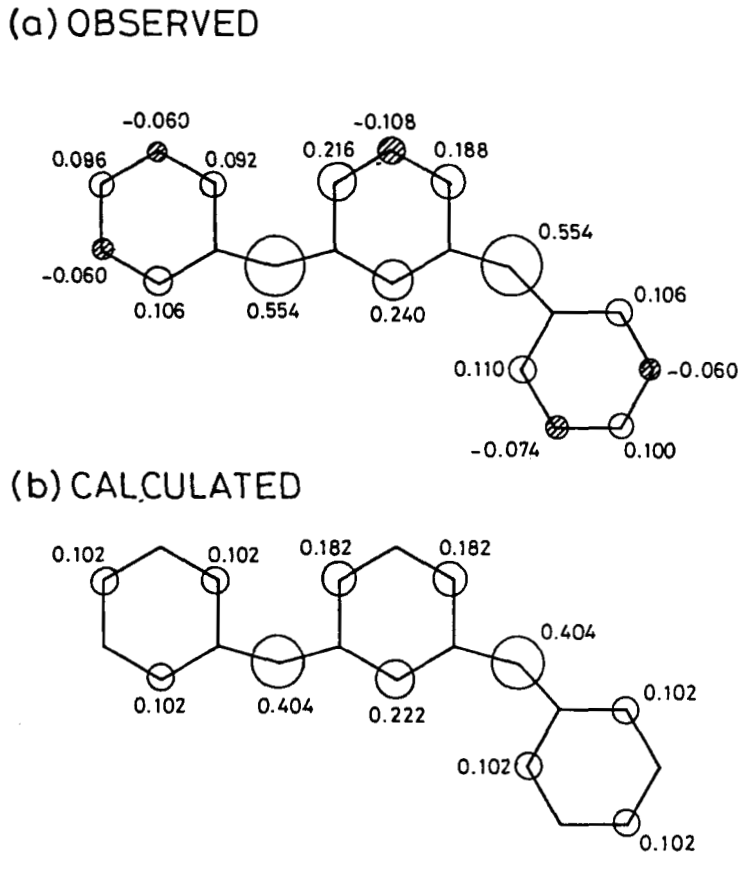

FIGURE 3. pi-Spin density distribution of m-PBPM: (a) calculated by the Longuet-Higgins theory, (b) obtained using the McConnell equation, $a_i=Q\rho_i\pi$.

The calculated positive spin densities are in good agreement with the experimental values given in Figure 3 (b). This is because the Longuet-Higgins theory deals with the essence of pi topological symmetry of alternant hydrocarbons such as m-PBPM. The ob-

served nine positive p_i's, and five negative p_i's assigned show that the pi-spin changes its sign alternately from one carbon site to another and that the pi-spin ferromagnetically-exchange couples the n-spin in the orbital localized on the divalent carbon site.

The non-equivalence of the observed spin densities on the 3- and 3'- carbon sites and the negative spin density can not be explained by the simple MO theory. The molecular structure of 1 may not be entirely planar. Hence, it seems most appropriate to adopt an all-electron or all-valence-electron method to interpret the non-equivalence and the negative spin density. Advanced calculations of the ab initio level for open-shell systems have been extended to a larger one,[46] but extension to large high-spin molecules such as m-PBPM is still limited. We chose the INDO calculation as a more tractable and spin-polarized SCF method which has widely been applied to semi-empirical calculations of spin densities. The INDO calculation reproduces the observed hfcc's and show the asymmetric molecular structure as shown in Figure 2. The most probable non planar molecular structure was determined.

^{1}H-ENDOR Study of Other Typical High-spin Molecules such as 3,4'-DPBPM

High-spin molecules are characterized by many open-shell electrons in both the delocalized pi orbitals and the localized n orbitals. Furthermore, they have large molecular sizes. For these reasons, conventional MO and VB theories are difficult to apply to high-spin molecules for prediction of their electronic states. Recently, we have reported a UHF generalized Hubbard model as a spin-prediction theory for the ground states of larger molecular systems[18] and a Heisenberg model as a more reliable method[34]. Both model Hamiltonian approaches, however, have not been tested in terms of spin densities.

3,4'-DPBPM is a model compound suitable for studying spin alignment of the n and pi electrons as well as the role of topology in organic high-spin molecules, since 3,4'-DPBPM is in its triplet ground state with a thermally accessible quintet state[19] in con-

trast to its topological isomer, 3,3'-DPBPM, in the septet ground state[12]. ^{1}H-ENDOR measurements were successfully carried out for the triplet ground state of 3,4'-DPBPM and all the hyperfine coupling tensors of the eighteen protons were experimentally identified. The observed pi-spin densities on the ring carbon sites were compared with the calculated ones by the generalized Hubbard model and by the exact numerical diagonalization of the Heisenberg Hamiltonian. The Hubbard calculation, in a quantitative sense, reproduces well the experimentally obtained spin densities, while the Heisenberg calculation gives overestimates for both the negative and positive spin densities on the ring carbon sites.

The ^{1}H-ENDOR technique has applied also to thermally accessible low-lying excited states of other typical organic high-spin molecules and their complete analyses are under way. Furthermore, the Hubbard calculation has been carried out for the hyperfine coupling tensors of macromolecules in order to identify radical sites of organic based magnetic materials[44] and to interpret their powder-pattern ^{1}H-ENDOR spectra.

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