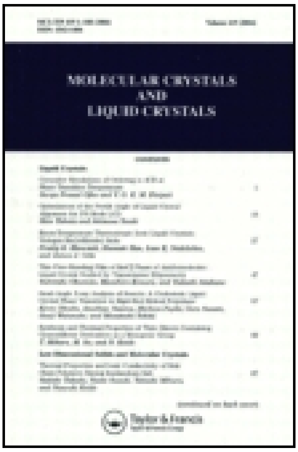

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Electronic and Molecular Structures of 2D Septet Tris(p-Methoxyphenylmethylene)Benzene as Studied by ESR: A Model for Discotic High-Spin Assemblages

Shigeaki Nakazawa [a], Kazunobu Sato [b], Takamasa Kinoshita [b], Takeji Takui [b], Koichi Itoh [a], Makoto Fukuyo [b], Tai-Ichiro Higuchi [b] & Ken Hirotsu [b]

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

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

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ELECTRONIC AND MOLECULAR STRUCTURES OF 2D SEPTET TRIS(*P*-METHOXYPHENYLMETHYLENE)BENZENE AS STUDIED BY ESR: A MODEL FOR DISCOTIC HIGH-SPIN ASSEMBLAGES

SHIGEAKI NAKAZAWA,[1] KAZUNOBU SATO,[2] TAKAMASA KINOSHITA,[2] TAKEJI TAKUI,[2] KOICHI ITOH,[1] MAKOTO FUKUYO,[2] TAI-ICHIRO HIGUCHI,[2] and KEN HIROTSU[2]
[1]Department of Material Science and [2]Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, Japan.

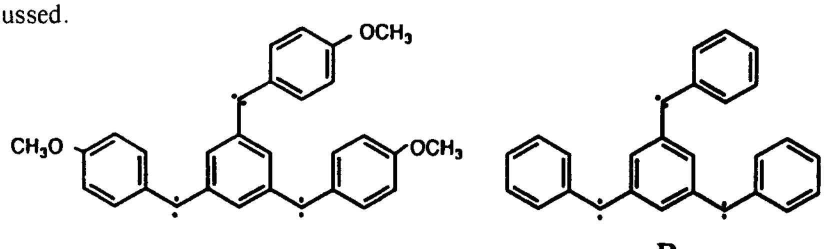
Abstract The electronic and molecular structures of a two-dimensional septet-state molecule (S=3), 1,3,5-tris(*p*-methoxyphenylmethylene)benzene **A**, were investigated by single-crystal ESR spectroscopy. **A** was designed for a prototype core model for discotic liquid crystalline organic high-spin molecules. Tris(α-benzoyl)benzene was adopted as the host crystal and its crystallographic parameters were determined by X-ray diffraction: the space group $P\bar{1}$ with Z=4, a=11.99 A, b=21.94 A, c=7.82 A, α=98.0°, β=90.9°, and γ=94.1°. The effect of the methoxy functional group on the fine-structure constants was found: the effect showed up in the significant reduction of the fine-structure constant D value, showing the modification of the topologically controlled robust π spin polarization. The observed finite E value is in accord with the molecular symmetry and crystal structure of the host molecule.

INTRODUCTION

Organic molecular based magnetism and syntheses of related magnetic materials with multifunctionality have been emerging as an interesting issue in materials science, pure sciences and interdisciplinary areas of research.[1] Among the diverse pertinent subjects, purely organic ferroelectric magnetic materials are an intriguing target because of their optical adaptabililty.[2] Thus, synthetic chemistry has been challenged and studies for fundamental bases to understand modified spin structures effected by functional groups introduced from synthetic necessity serve to identify underlying mechanisms in the spin alignment of novel functionality materials.

As part of our continuing project on organic magnetism, particularly, on ferroelectric organic ferromagnetism based on an elaborate design for liquid crystals with high-spin sites, we designed and synthesized a two-dimensional septet molecule (S=3), 1,3,5-tris(*p*-methoxyphenylmethylene)benzene **A**, which is a prototype core model for liquid crystalline organic high-spin molecules. Previously, we had investigated the electronic and molecular structure of 1,3,5-tris(phenylmethylene)-

benzene **B** as the first high-spin molecule characterized by two-dimensional spin structure by using single-crystal ESR spectroscopy.[3] It had turned out that the experimentally determined fine-structure constants, D= +0.04158cm^{-1} and E= 0.01026cm^{-1} arise from the dominant one-center nπ spin-spin interactions at the divalent carbons of the triarylcarbene **B**, revealing that the robust π-spin polarization takes place in **B** and the finite E value indicates a non C_3-symmetric molecular structure for **B** in the 1,3,5-tris(α-benzoyl)benzene host lattice. The results obtained in the present work are compared with those, and the modified spin structure by the methoxy group is discussed. Also, the molecular symmetry of **A** in the host lattice is discussed.



A **B**

FIGURE 1 Organic high-spin molecules with two-dimensional spin structure. **A**: 1,3,5-Tris(*p*-methoxyphenylmethylene)benzene. **B**: 1,3,5-Tris(phenylmethylene)benzene.

EXPERIMENTAL

Host Single Crystals for Single-Crystal ESR Spectroscopy

Host crystals for single-crystal ESR spectroscopy must satisfied the following requirements: (i) host molecules are diamagnetic and unreactive to guest molecules, (ii) guest molecules are substitutionally incorporated into the host lattice, so that they preferably exhibit the space-group symmetry of the host crystal, (iii) sizable crystals with well-developed crystal planes are available, (iv) colorless crystals are desirable for photo-irradiation purposes. We examined aryl α-ketones and found two candidates, benzophenone and 1,3,5-tris(α-benzoyl)benzene. The former satisfied the three requirements, (i), (iii), and (iv), but not completely satisfied (ii). The latter met all the above requirements. Thus, we adopted 1,3,5-tris(α-benzoyl)benzene as the host molecule.

Crystal Data and Crystal Structure of the Host Molecule

The detailed structure of the host crystal was determined by X-ray analysis. The crystal is triclinic, P1̄, and Z = 4 with unit cell dimensions, a = 11.99A°, b = 21.94A°, c = 7.82A°, and α = 98.0°, β = 90.9°, and γ = 94.1°. Figure 2 shows the projection onto the *bc* plane of the host crystal in a unit cell. The dihedral angles between the central benzene and benzoyl rings range from 40° to 55°. The triangles, the three corners of which are formed by the carbonyl carbon and its two nearest carbon sites, make dihedral angles of 19~32° with the central benzene or three surrounding phenyl rings. It is worth noting that the host molecule itself does not have C_3 symmetry, but an aymmetric structure. The details will be published elsewhere.[4]

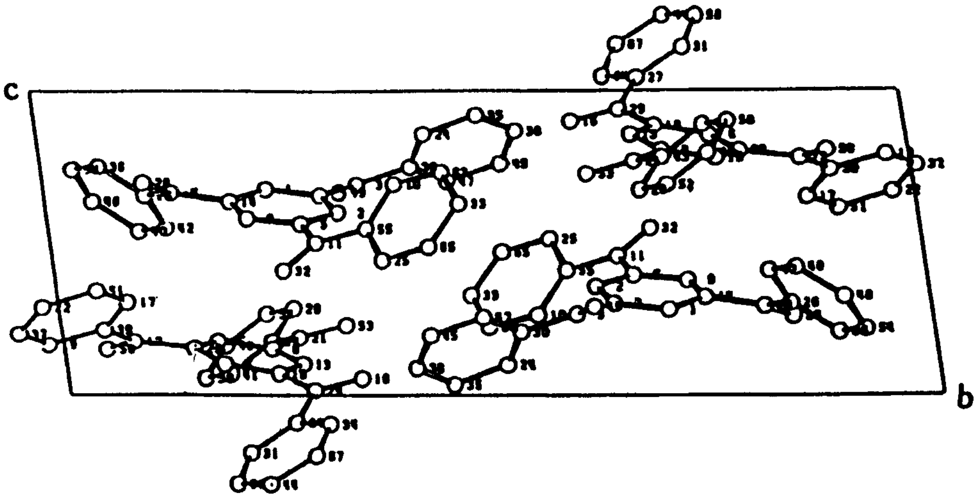


FIGURE 2 Projection of the host molecules in a unit cell onto the *bc* plane of the host crystal.

Synthesis

A was generated by the photolysis of the corresponding diazo precursor, 1,3,5-tris(*p*-methoxy-α-diazobenzyl)benzene. The diazo precursor was synthesized from trimesic acid via the following sequence of reactions: chlorination with thionyl chloride, Friedel-Crafts with methoxybenzene, hydrazonization, and oxidation with activated MnO_2.

Preparation of Mixed Single Crystals and ESR Measurements

The mixed single crystals for ESR measurements were prepared in the following manner. In a 1 ml solution of purified benzene 40 mg of 1,3,5-tris(*p*-methoxyl-α-diazobenzyl)benzene and 350 mg of 1,3,5-tris(α-benzoyl)benzene were dissolved at room temperature. The wine-red colured solution was placed in a thermostatic bath and left to cool down slowly in the dark. Several fairly well-grown light red crystals were obtained at 10°C by seeding the solution.

The mixed single crystal was mounted on a quartz rod with silicon grease.

The photolysis of the mixed single crystal was carried out at 77K using a high-pressure mercury lamp equipped with a glass filter and a solution filter (100g of $CuSO_4 \cdot 5H_2O$/L, 5 cm light-path length). ESR measurements were made on a JEOL FE-2XG ESR spectrometer operating at X-band equipped with a TE_{011} cylindrical cavity. The microwave magnetic field in the cavity was always polarized perpendicular to the static magnetic field, which was modulated at a frequency of 100 kHz with coils placed inside the cavity. Angular dependences of fine-structure ESR spectra from the septet state of **A** were measured at 77K by rotating the single crystal around the three mutually orthogonal axes pqr ($r \parallel c$ axis) defined in reference to the crystal (see the inset of Figure 4).

RESULTS AND DISCUSSION

A Fine-Structure Spectrum Expected for a Septet State (S=3)

For the analysis of fine-structure ESR spectra from high-spin hydrocarbons such as **A**, we used the effective spin Hamiltonian given by

$$\begin{aligned} H &= H_{eZ} + H_D \\ &= \beta S \cdot g \cdot \mathbf{B}_0 + S \cdot D \cdot S \\ &= \beta S \cdot g \cdot \mathbf{B}_0 + D[S_Z^2 - S(S+1)/3] + E(S_X^2 - S_Y^2) \end{aligned}$$

where H_{eZ} and H_D stand for the electron Zeeman term, and the fine-structure term, respectively, and D and E are fine-structure constants. In our analysis we neglected the higher order fine-structure terms such as B_0S^3 and S^4 which are allowed group-theoretically, since they are negligibly small for high-spin hydrocarbons.

Figure 3(a) shows the energy sublevel diagram for a septet state as a function of the applied static magnetic field $\mathbf{B}_0$. The double arrows in Figure 3(a) indicate $\Delta m_S=\pm1$ allowed ESR transitions in the high field limit when an X-band microwave frequency is used. A positive D value is assumed. Figure 3(b) shows the fine-structure theoretical stick spectrum corresponding to the allowed transition appearing in Figure 3(a). The six allowed transitions are designated by $A_\pm$: $m_S=\pm3 \leftrightarrow m_S=\pm2$, $B_\pm$: $m_S=\pm2 \leftrightarrow m_S=\pm1$, and $C_\pm$: $m_S=\pm1 \leftrightarrow m_S=0$. The ratios of the transition probabilities for $A_\pm$, $B_\pm$, and $C_\pm$ are 3 : 5 : 6 in the first order. The splittings A_+-A_-, B_+-B_-, and C_+-C_- are of approximately 5 : 3 : 1 in the second order. The above spectral features hold in any direction of the static magnetic field $\mathbf{B}_0$ in reference to the coordinate-axis system pqr defined in the present work, as far as the high field limit is satisfied in our experimental setup.

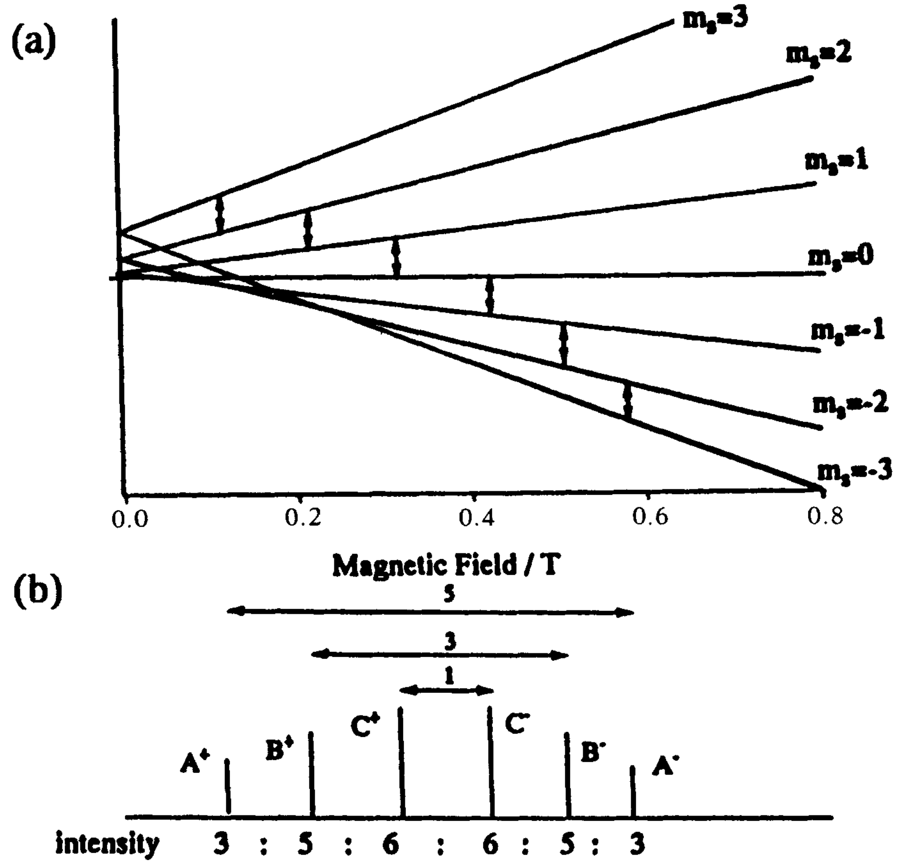


FIGURE 3 Energy sublevel diagram of a septet state as a function of the applied static magnetic field B_0 (a) and fine-structure theoretical stick spectrum (b). The double arrows in (a) denote the allowed ESR transitions.

Spectral Analysis of the Observed ESR Spectra

Figure 4 shows a typical fine-structure spectrum of A observed with B_0 in the pq plane of the crystal. The six lines denoted by $A_\pm$, $B_\pm$, and $C_\pm$ correspond to the allowed transitions, $A_\pm$, $B_\pm$, and $C_\pm$, defined above, respectively. The observed intensity ratios of the six lines and fine-structure splittings A_+-A_-, B_+-B_-, and C_+-C_- agree precisely with the features described above for the septet state, unequivocally showing that the observed spectrum arises from the septet state of A. Furthermore, only one set of the six lines was observed for all the orientation of B_0, showing that A in the host lattice maintains the space-group symmetry of the host crystal. Figure 5 shows the angular dependence of the resonance fields of the six lines observed with B_0 rotated in the pq plane, i.e., with the crystal rotated around the r||*c* axis. The detailed measurements in the pq, qr, and rp planes are under way.

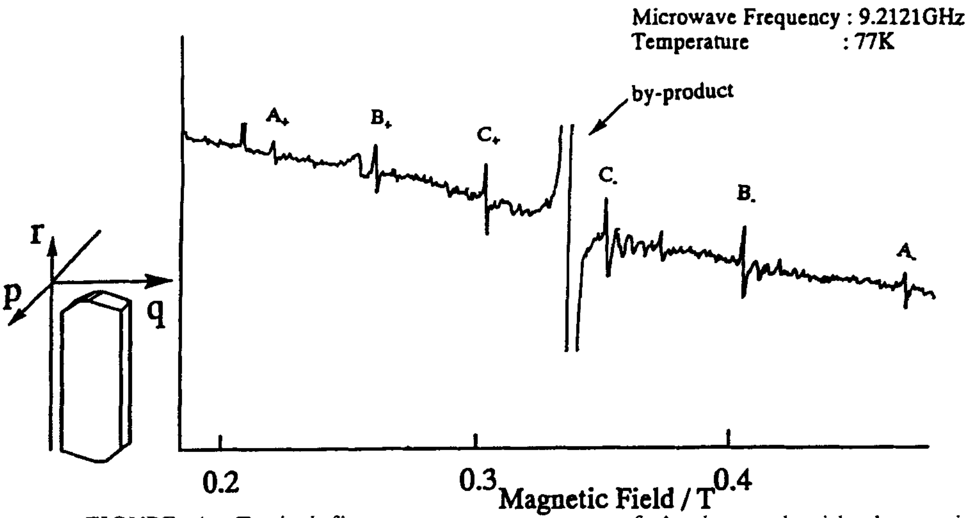


FIGURE 4 Typical fine-structure spectrum of A observed with the static magnetic field in the pq plane of the host crystal.

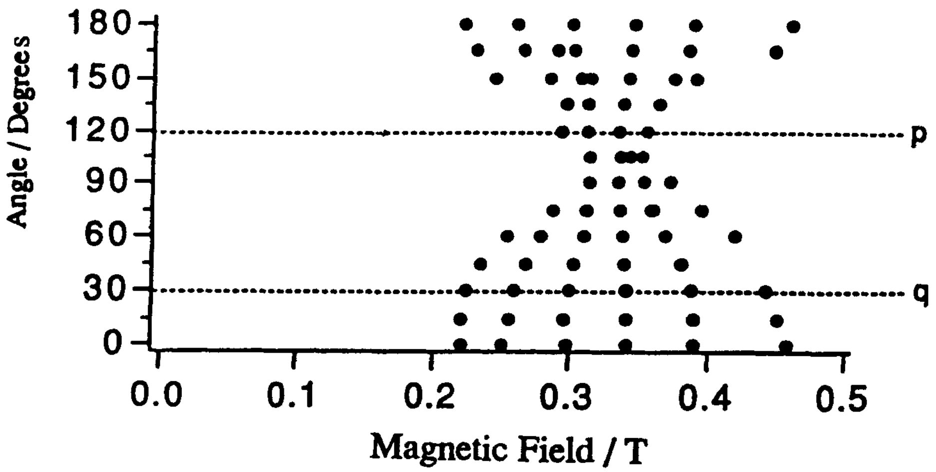


FIGURE 5 Angular dependence of the resonance fields of the six transitions observed with the static magnetic field in the pq plane.

Preliminary results from least-squares-fitting procedure of the observed resonance fields as a function of the orientation of B_0 gave $|D| = 0.037\ \text{cm}^{-1}$, $|E| = 0.0052\ \text{cm}^{-1}$, and three sets of the direction cosines for the **D** tensor. It turned out that the principal Z axis lies approximately in the *ab* plane. The preliminary results agree with the observation that the maximum fine-structure splitting was observed with B_0 approximately in the pq plane. Considering the host crystal structure (see Figure 2), this shows that the principal Z axis of the **D** tensor lies inthe molecular plane of A and thus the septet molecule A does not have C_3 molecular symmetry, because the principal Z axis is perpendicular to the molecular plane of A if A is C_3-symmetric.[5] The non C_3-symmetric molecular structure of A interprets the observed finite E value. The asymmetric molecular symmetry of A shown in Figure 1 results in the positive D value.[5] Temperature dependence of the signal intensity in the range of liquid helium temperature enables us to determine the absolute sign of the D value. The low temperature experiment is now planned.

The Effect of the *p*-Methoxy Group on the Electronic Spin Structure

Introduction of the *p*-methoxy group gives rise to an intriguing effect on the electronic spin structure of the high spin state of tris(phenylmethylene)benzene. Comparison of the observed D value for **A** with that of **B** directly shows a significant reduction of the D value of **B**. This effect originates not from difference in molecular structure between A and B but from modification in electronic spin structure of **B**. In carbene-based high-spin hydrocarbons, one-center nπ spin-spin interactions predominate in the contribution to the D value. Thus, their similar molecular structures with the same spin multiplicity give similar D values because of the tensorial property of addition if the hydrocarbons are multi-centered of carbene sites. Since a close resemblance is expected for the molecular structure between A and B as shown above, the difference in the observed D value between A and B arises from the spin structure modified by the introduction of the *p*-methoxy groups.

The fine-structure constants of **B** had been well reproduced in terms of a semiempirical calculation based on the tensorial property of addition assuming the

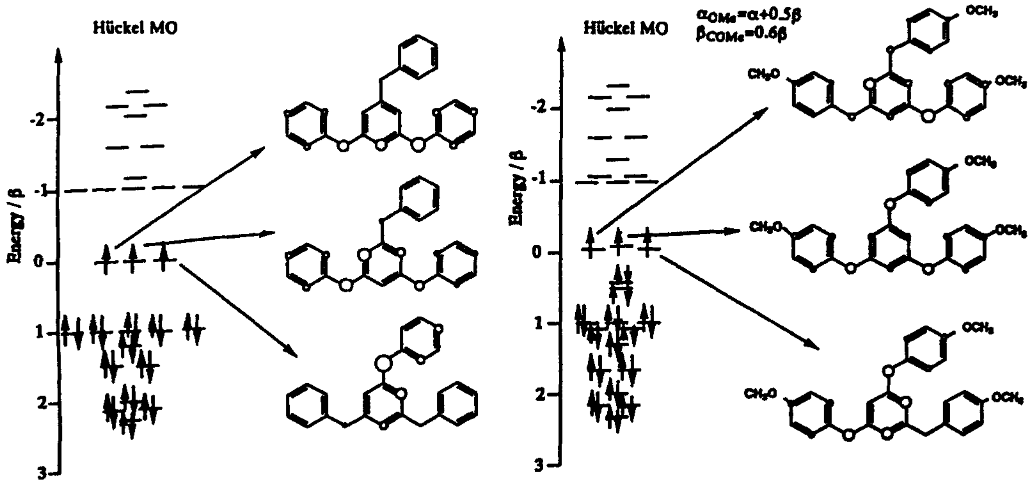


FIGURE 6 MO energy diagrams of the π system and pictorial non-bonding MOs for the septet molecules **B** (left) and **A** (right).

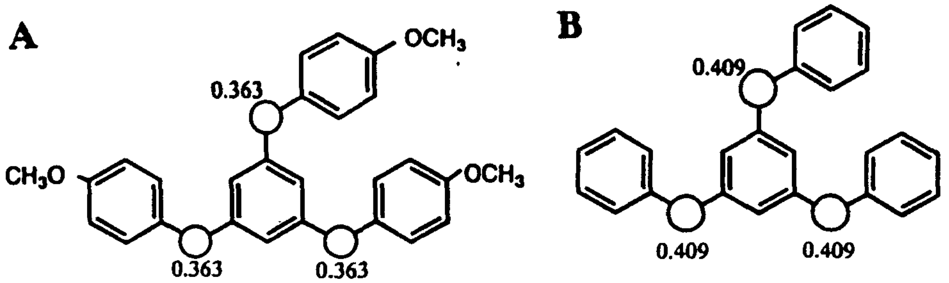


FIGURE 7 π Spin densities at the three divalent carbon sites of the septet molecule A (left) and B (right).

molecular structure.[5] The semiempirical nature of the method arises from the use of the calculated π-spin densities at the three divalent carbon sites. For carbene-based alternant high-spin hydrocarbons, the simple MO calculation is sufficient enough to reproduce the experimentally determined fine-structure constants.

Figure 6 shows the MO energy diagrams and electronic configurations for A and B. Figure 6 also depicts the simplified pictorial non-bonding MOs corresponding to the π spin populations at the carbon sites. Figure 7 depicts the π spin densities at the three divalent carbon sites obtained from the simple MO calculations for A and B. According to the semiempirical method, the D value is scaled proportional to the π spin densities at the divalent carbon sites for the same molecular structure. The introduction of the three *p*-methoxy groups gives rise to 90 % of the scaling factor of the calculated π-spin densities, i.e., a 10 % reduction in the D value. The reduction agrees well with the decrease in the D value observed for A. Thus, the *p*-methoxy substitution is capable of the prominent modification of the topologically controlled robust π-spin polarization of carbene-based high-spin hydrocarbons. The septet state in the electronic ground state, however, is expected for A. The detailed discussion in terms of both MO and VB pictures will be published elsewhere.

CONCLUSIONS

A two-dimensional septet-state molecule, 1,3,5-tris(*p*-methoxyphenylmethylene)-benzene A was synthesized and the electronic and molecular structures were examined by X-ray crystal structure analysis and single-crystal ESR spectroscopy. A significant reduction of the D value due to the *p*-methoxy substitution was found. It was concluded that the reduction arises from a decrease in the one-center nπ spin-spin interaction at the divalent carbon site, a significant decrease in the π spin densities at the carbene sites. The septet spin state is still expected for the electronic ground state of **A** because the topolocically controlled robust spin polarization predominates in the system. *p*-Methoxy can be one of the key functional groups for synthesizing variant intriguing functionality materials. Syntheses of molecule **A**-based high-spin core models for discotic liquid crystalline magnetic materials are under way.

ACKNOWLEDGMENT

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