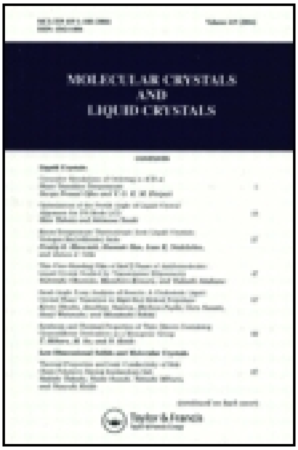

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Electronic and Molecular Structures of 1,3,5-Tris(Phenylmethylene)Benzene (S = 3) as Models for Discotic High-Spin Liquid Crystals: Single-Crystal ESR and X-Ray Diffraction Studies

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ELECTRONIC AND MOLECULAR STRUCTURES OF 1,3,5- TRIS(PHENYLMETHYLENE)BENZENE (S=3) AS MODELS FOR DISCOTIC HIGH-SPIN LIQUID CRYSTALS: SINGLE-CRYSTAL ESR AND X-RAY DIFFRACTION STUDIES

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Abstract The electronic and molecular structures of the two-dimensional septet-state molecules(S=3), 1,3,5-tris(*p*-methoxyphenylmethylene)benzene **A** and 1,3,5-tris(phenylmethylene)benzene **B**, were investigated by single-crystal ESR spectroscopy. **A** was designed for a prototypical core model for discotic liquid-crystalline organic high-spin molecules. We determined the fine-structure constants of **A** by the ESR spectroscopy and analyzed the crystal and molecular structures of **B** by X-ray diffraction. 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 for **A**, indicating the modification of the topologically controlled robust π spin polarization. The observed non-vanishing E value is in accord with the molecular symmetry and crystal structure of the host molecule, 1,3,5-tris(α-benzoyl)benzene.

INTRODUCTION

Organic molecular based magnetism and syntheses of related magnetic materials with multifunctionality have attracted increasing interest in materials science and interdisciplinary areas of research.[1] Among the diverse pertinent subjects, purely organic ferroelectric magnetic materials are an intriguing target because of their optical adaptability[2].

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 prototypical 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.[3,5] 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 non-vanishing 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. The neat single crystal of the diazo precursor of **B** was prepared and the crystal parameter and molecular structure of **B** were determined by X-ray diffraction analysis. The high-spin species generated in the neat crystal by photolysis were investigated by ESR spectroscopy.

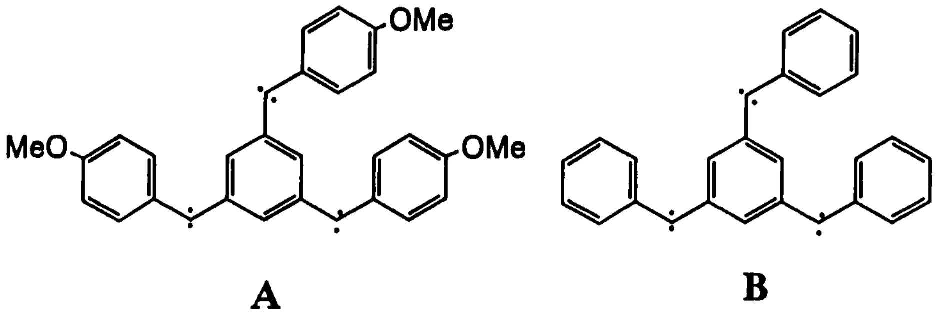

FIGURE 1 Organic high-spin molecules with two -dimensional spin structure. **A**: 1,3,5-tris(*p*-methoxyphenylmethylene)benzene. **B**: 1,3,5-tris(phenylmethylene) benzene.

EXPERIMENTAL

The syntheses of the diazo precursor of **A** will be published elsewhere.[4] The diazo precursor was diluted in the 1,3,5-tris(α-benzoyl)benzene host crystal whose crystal parameter are triclinic, $P\bar{1}$, and Z=4 with unit cell dimensions, *a*=11.99Å, *b*=21.94Å, *c*=7.82Å, 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 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, 5cm 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 100kHz 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//c axis) defined in reference to the crystal.

The synthesis of the diazo precurson of **B** was previously reported.[5] The neat single crystals of the diazo precursor were grown in CH_2Cl_2 at -20°C. The X-ray diffraction analysis of the neat crystal was carried out by Rigaku AFC 7R diffractometer whose source of radiation was MoKα (λ=0.71069Å). The photolysis of the neat single crystal was carried out at 3K using a high-pressure mercury lamp equipped with a glass filter and a solution filter (100g of $CuSO_4 \cdot 5H_2O$/L, 5cm light-path length). ESR measurements were made on a Bruker ESP 300 X-band spectrometer equipped with an Oxford ESR910 variable-temperature controller.

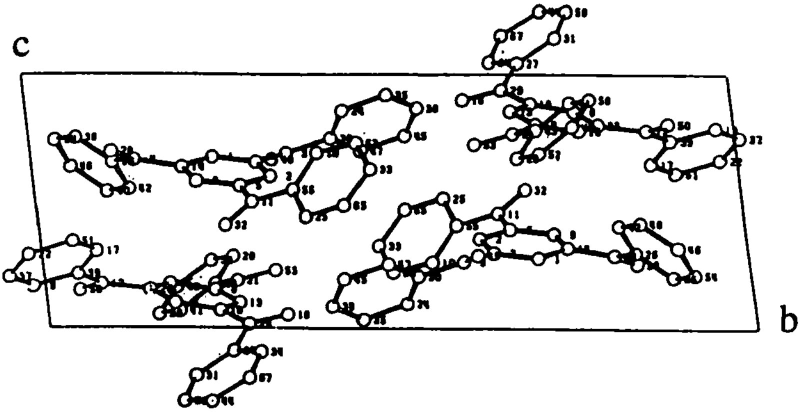

FIGURE 2 Projection of the host molecules in a unit cell onto the *bc* plane of the host.

RESULTS AND ANALYSIS

ESR Measurement of A

Figure 3 shows a typical fine-structure spectrum of A observed with the static magnetic field B_0 in the pq plane of the crystal. Figure 4 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 six lines corresponding to the $\Delta M_S = \pm 1$ allow transition were observed for all the orientation of B_0, showing that A in the host lattice maintains the space-group symmetry of the host crystal. The observed spectrum is characteristic of a fine structure expected from septet high-spin states in the high field limit.

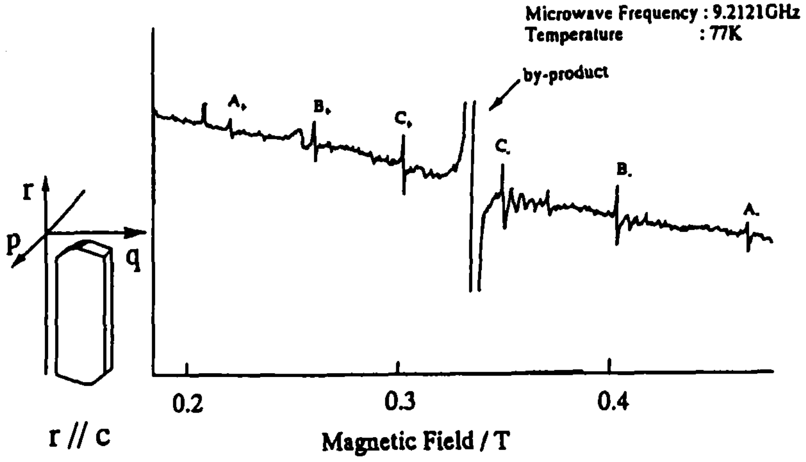

FIGURE 3 Typical fine-structure spectrum of A observed with the static magnetic field in the pq plane of the host crystal.

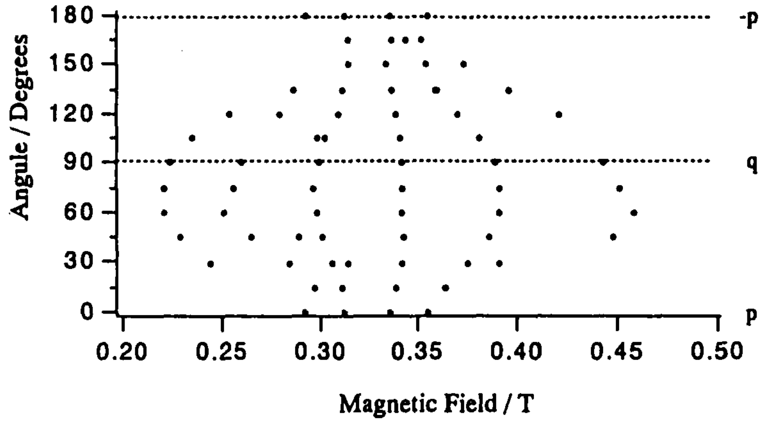

FIGURE 4 Angular dependence of the resonance fields of the six transitions observed with the static field in the pq plane.

For the analysis of the fine-structure ESR spectra from A, we used the effective spin Hamiltonian given by

$$\begin{aligned}\mathcal{H} &= \mathcal{H}_{eZ} + \mathcal{H}_D \\ &= \beta S\cdot g\cdot B_0 + S\cdot D\cdot S \\ &= \beta S\cdot g\cdot B_0 + D[S_Z^2 - S(S+1)/3] + E(S_X^2 - S_Y^2),\end{aligned}$$

where $\mathcal{H}_{eZ}$ and $\mathcal{H}_{D}$ stand for the electron Zeeman term and the fine-structure term, respectively, and D and E are fine-structure terms. We omitted the higher order terms such as B_0S^3 and S^4 which are allowed group-theoretically, since they are negligibly small for high-spin hydrocarbons. In order to derive the spin Hamiltonian parameters for A the least-square-fitting procedure was exploited, giving S=3, g=2.003, $|D| = 0.037\,\mathrm{cm}^{-1}$, $|E| = 0.005\,\mathrm{cm}^{-1}$. The maximum fine-structure splitting, which corresponds to the orientation of $\mathbf{B}_0$ along the nearby Z axis of the fine structure tensor, was observed with $\mathbf{B}_0$ in the pq plane.

X-Ray Analysis of B

The molecular and crystal structures of the neat crystal of **B** were determined by X-ray analysis. The crystal is triclinic, $P\bar{1}$, and Z=2 with cell dimensions, a=11.568Å, b=13.488Å, c=7.946Å, and α=105.21°, β=95.66° and γ=111.49°. Figure 5 shows the projection onto the *bc* plane. The dihedral angles between the central benzene and the other phenyl rings range from 44° to 56°. The triangles, the three corners of which are formed by the diazo carbon and its two nearest carbon site, make dihedral angles of 17.96°, 26.09° and 45.48° with the central benzene.

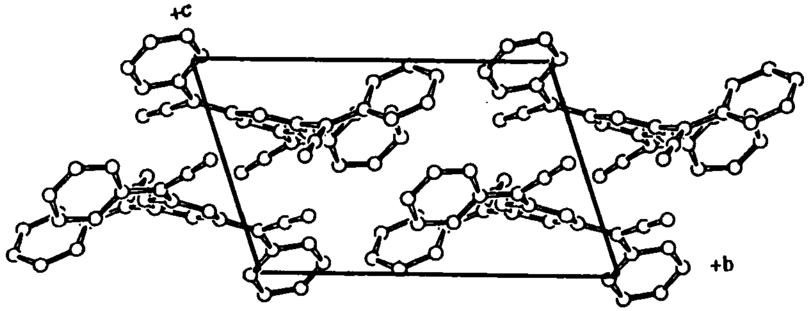

FIGURE 5 Projection of **B** molecules in two unit cells onto the *bc* plane of the crystal.

ESR Measurement of the Neat Crystal of B

The ESR measurement of the neat crystal of the diazo precursor of **B** showed the appearance of high-spin species. The detailed analysis is under way.

DISCUSSION

The Molecular Structure of A

The principal Z axis lies approximately in the *ab* plane because of the result that the maximum fine-structure splitting was observed with B_0 in the pq plane. Figure 6 showed the fine-structure constants, the principal axes, and molecular configuration obtained by semiempirical calculation. The D tensor for A was calculated by the following equation.[5]

$$D_{ij} = [S(2S-1)^{-1}\sum_k \frac{\rho_k}{\rho_{DPM}}(U_k \cdot D_{DPM} \cdot U_k^{+})_{ij} \;, \quad i,j = X,Y,Z$$

The calculated |D| and |E| values and calculated |D/ E| ratio satisfactorily agree with those observed for A. Considering the host crystal structure, this shows that the principal Z axis of the D tensor nearly lies in the ab plane. 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. The non C_3-symmetric molecular structure of A interprets the observed non-vanishing E value. Temperature dependence of 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.

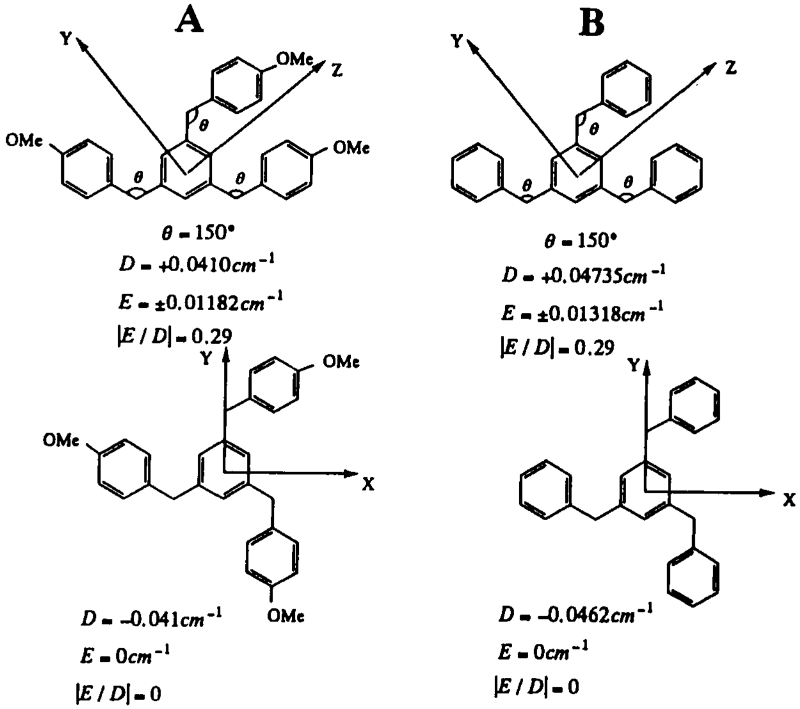

FIGURE 6 Fine-structure tensors for A and B determined by semiempirical calculation.

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

It turned out that introduction of the p-methoxy group gives rise to an intriguing effect on the electronic spin structure of the high-spin state of **B**. Comparison of the observed D value for **A** with that of **B** directly indicates a significant reduction of the D value of **B**. This reduction 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 have large weight 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 the semiempirical calculation based on the tensorial property of addition assuming the 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 7 depicts the π spin densities at the 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.

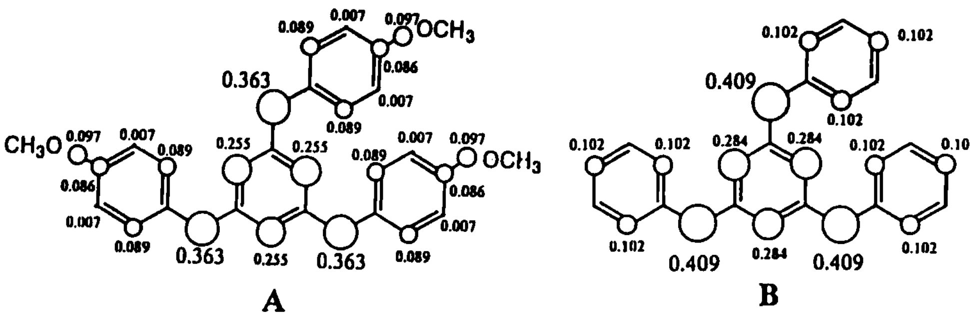

FIGURE 7 π Spin densities of the septet molecule **A** and **B**.

Possibility of the Intermolecular Interaction in the Neat Crystal of B

The observation of the intermolecular triplet-triplet ferromagnetic interaction in the neat crystal of p,p'-dimethoxyphenylmethylene was reported.[6] The distance between the benzene rings of nearest neighboring molecules in the crystal of the diazo precursor of p,p'-dimethoxyphenylmethylene is 4.0Å. The occurrence of the intermolecular ferromagnetic interaction between arylcarbene-based high-spin systems requires suitable molecular packing modes in the crystal: intermolecular pseudo spin density wave propagates itself from one high molecule to another in such a way as electron repulsions are minimized. The relative molecular conformation and intramolecular spin density distribution of high-spin molecules as building block units in the crystal is of crucial importance. This is due to tensorial nature of electronic exchange interaction. An important attempt from the theoretical side was mode by Yamaguchi et al. to expound intermolecular ferro or antiferro-magnetic interaction between arylcarbene-based high-spin systems.[7] The photo-irradiated neat crystal of **B** gave complex fine-structure spectra, suggesting the possible occurrence of intermolecular interactions in the crystal. Analyses are under way assuming intermolecular distances based on the crystal structure of **B** determined by X-ray diffraction.

CONCLUSION

The two-dimensional septet-state molecules, 1,3,5-tris(p-methoxyphenylmethylene) benzene A and 1,3,5-tris(phenylmethylene)benzene **B** were synthesized and the electronic and molecular structures were examined by X-ray diffraction 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, i.e a significant decrease in the π-spin densities at the carbene sites. The observed septet spin state for A shows that the topologically controlled robust spin polarization predominates in the system. p-Methoxy can be one of 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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