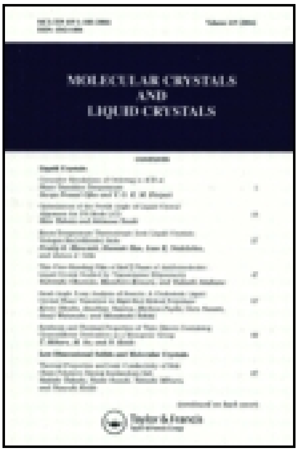

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Spin Polarization Effect in Organic High-Spin Molecules, as Studied By Single Crystal ESR and ^{1}H-ENDOR Spectroscopies

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SPIN POLARIZATION EFFECT IN ORGANIC HIGH-SPIN MOLECULES, AS STUDIED BY SINGLE CRYSTAL ESR AND ^{1}H-ENDOR SPECTROSCOPIES

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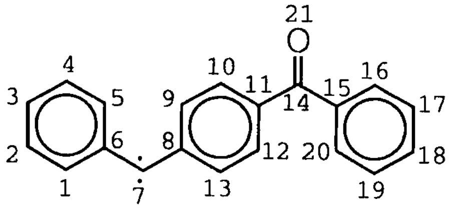
Abstract Single crystal ESR of ground-state triplet molecules, p- and m-benzoyldiphenylmethylene (p- and m-BDPM), was measured. From the angular dependence of the spectra the fine structure parameters were determined to be $D = +0.327\ \mathrm{cm}^{-1}$ and $E = -0.0056\ \mathrm{cm}^{-1}$ for p-BDPM and $D = \pm 0.428\ \mathrm{cm}^{-1}$ and $E = \mp 0.051\ \mathrm{cm}^{-1}$ for m-BDPM, respectively. It was shown that the effect of the benzoyl group on the spin alignment of the diphenylmethylene (DPM) unit is larger for the para position than for the meta position. Furthermore, in order to examine the effect by the introduction of the p-benzoyl group on the π-spin densities of the DPM unit, single crystal ^{1}H-ENDOR (Electron Nuclear DOuble Resonance) measurements of p-BDPM were performed. The ^{1}H-hyperfine couplings observed showed that relative to unsubstituted diphenylmethylene (DPM) the p-benzoyl substitution increased the absolute value of all the π-spin densities on the phenyl rings of the DPM unit. This result is attributable to the spin polarization enhancement induced by the introduction of the p-benzoyl group.

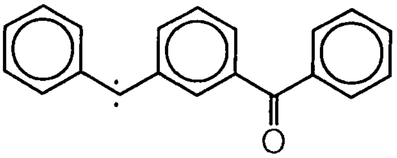
INTRODUCTION

Recently organic molecular based magnetism has been attracting wide interest from both pure and applied sciences.[1] As models for organic ferro- and ferri-magnets, we have been studying organic high-spin molecules since the detection of the first quintet organic molecule in 1967,[2,3] demonstrating the importance of the topological nature of π electron networks in generating high-spin ground states of organic systems.[4-8] In order to obtain bulk organic magnetism, it is necessary to construct organic polymers or molecular assemblages with two- or three-dimensional robust spin structures. Such spin structures are closely associated with molecular and crystal engineering in organic magnetic systems. As part of a basic study for the construction of robust spin structures, this paper deals with the enhancement effect on spin polarization by chemical modification of organic high-spin molecules. Control of spin polarization is recently an important issue in spin chemistry.

In the present work, single crystal ESR spectroscopy was applied to two ground-state triplet molecules with the benzoyl substituent, p- and m-benzoyldiphenylmethylene (p- and m-BDPM). Single crystal ^{1}H-ENDOR spectroscopy was also applied to p-BDPM. From the angular dependence of the ESR and ENDOR spectra we determined the fine structure parameters of both the molecules and the ^{1}H-hyperfine coupling parameters of p-BDPM, respectively, from which its π-spin densities were derived. Comparing the results for p- and m-BDPM with those of unsubstituted diphenylmethylene (DPM), we discuss the effect of the substituent on the spin delocalization and the spin polarization with the help of a generalized Hubbard calculation.[9,10,11]



p-BDPM



m-BDPM

EXPERIMENTAL

Mixed single crystals of perdeuterated benzophenone-d_{10} incorporating the diazo precursor of p- or m-BDPM were prepared in a diethylether solution by slow cooling. Mole fraction of the precursors to the host molecule was 0.017 in the solution. Benzophenone-d_{10} was used in order to avoid the ^{1}H-ENDOR transitions arising from protons of surrounding host molecules. Both p- and m-BDPM were formed at 4K by the irradiation of the corresponding diazo precursor in the crystal with an XBO 500W high-pressure mercury lamp, after the crystal was mounted on a quartz wedge in an X-band TE_{102} or TM_{011} cavity for ESR or ENDOR measurements, respectively. An aqueous solution filter (100g/cm^3, $CuSO_4 \cdot 5H_2O$, l=5cm) and a glass filter (TOSHIBA VY39) were used in order to select the 405nm light from the mercury lines.

ESR and ^{1}H-ENDOR signals were detected on a Bruker ESP 300/350 spectrometer equipped with an Oxford helium gas flow variable temperature controller ESR910. The angular dependence of the ESR and ^{1}H-ENDOR signals was measured by rotating a single crystal using a uniaxial goniometer.

RESULTS AND DISCUSSION

Fine Structure Parameters of p- and m-BDPM

The fine structure parameters were determined from the angular dependence of the ESR spectra of BDPM. ESR transitions from two or more than two conformers were observed for both p- and m-BDPM. Only the parameters for the major conformers are listed in Table 1 together with those for diphenylmethylene (DPM) determined by Hutchison et al.[12,13] The absolute sign of the D value of p-BDPM was determined to be positive from the ^{1}H-ENDOR spectra of p-BDPM, as described below. A comparison with DPM indicates that the D value of p-BDPM is significantly smaller than that of DPM, whereas the D value of m-BDPM is similar to that of DPM. This is understandable considering the spin distribution in DPM: the interaction between the DPM unit and the benzoyl group in m-BDPM is not so significant as that in p-BDPM, since the meta position of DPM corresponds to the nodal carbon site of the singly occupied MO (SOMO) from the simple Hückel theory for alternant hydrocarbons.

TABLE I Experimentally determined fine structure parameters of p-BDPM and m-BDPM.

	D value /cm^{-1}	E value /cm^{-1}
p-BDPM	0.327	-0.0056
m-BDPM	±0.428	∓0.051
DPM	0.405	-0.019

The fine structure parameters of molecules without heavy atoms are predominantly determined by the electron spin-spin interaction, which is classified into π electron - π electron (π-π), n electron - π electron (n-π), and n electron - n electron (n-n) interactions.[14] As one-center n-π interaction on the divalent carbon atom predominates in the spin-spin interaction in organic high-spin carbenes,[14,15] their fine structure parameters are proportional to the product of the spin densities in the π SOMO and the σ nonbonding orbital (n) on the same divalent carbon atom. Hence, the decrease in the D value of p-BDPM indicates that the total spin density on its divalent carbon atom is diminished relative to that of DPM, leading to an increase in the delocalization of the net π-spin over the whole molecular frame.

^{1}H-ENDOR Measurements of p-BDPM

Figure 1 shows a typical ^{1}H-ENDOR spectrum of p-BDPM observed at 4K, where an $|M_S=0\rangle \leftrightarrow |M_S=+1\rangle$ ESR transition in the high-field limit was monitored with the magnetic field in the crystallographic bc plane. There are five and four transitions above and below the free proton NMR frequency ($\nu_n = g_n\beta_n H/h$), respectively, except for the transitions appearing very close to ν_n. The shift of a ^{1}H-ENDOR signal (ν_{ENDOR}) from ν_n is given by

$$\nu_{ENDOR} - \nu_n = -A_{zz}M_S/h, \tag{1}$$

in terms of the first-order perturbation treatment. The ^{1}H-ENDOR transitions observed were referred to five negative and four positive hyperfine couplings (hfc's) according to Eq.(1). They were thus assigned to the nine protons of the DPM unit from comparison with the hfc's of DPM.[12,13] ^{1}H-ENDOR signals near ν_n arise from the nuclear transitions belonging to the $|M_S=0\rangle$ and $|M_S=+1\rangle$ sublevels; they are attributable to the protons of the benzoyl group.

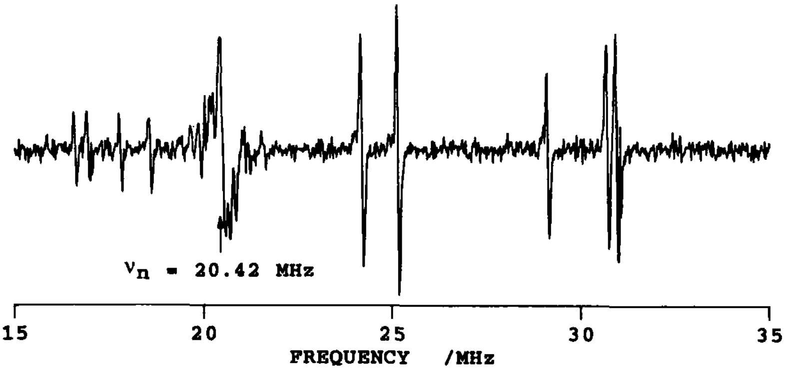


FIGURE 1 A typical ^{1}H-ENDOR spectrum of p-BDPM observed at 4K, with an $|M_S=0\rangle \leftrightarrow |M_S=+1\rangle$ ESR transition monitored in the crystallographic bc plane. The magnetic field employed is 0.47964 Tesla.

Let us consider the sign of the D value of p-BDPM that has been determined to be positive. Figure 1 shows that the ^{1}H-ENDOR transitions ($A_{zz}M_S<0$) appearing at the frequency above ν_n correspond to the hfc's larger in magnitude than those ($A_{zz}M_S>0$) appearing at the frequency below ν_n. This indicates that the ^{1}H-ENDOR transitions above

ν_n arise from α-protons bonded to the carbon atoms possessing positive π spins. In the strict sense, the contribution from anisotropic interaction should be considered for the angular dependence of the ^{1}H-ENDOR signals. As the isotropic hfc (A_{iso}) of a proton bonded to a carbon atom with a positive π spin gives a negative hfc for the α-proton via the spin polarization of the paired electrons of the C-H bond,[16] the ESR sublevel to which these ^{1}H-ENDOR signals belong is assigned to the $|M_S=+1>$. We can, therefore, conclude that the $|M_S=0> \Leftrightarrow |M_S=+1>$ transition was pumped for the ^{1}H-ENDOR detection shown in Figure 1.

The angular dependence of the ^{1}H-ENDOR signals was also examined in order to determine the ^{1}H-hfc tensors of p-BDPM. As the ^{1}H-hfc's of the benzoyl group are too small to be determined, only their maximum value was estimated. The principal values of the ^{1}H-hfc tensors obtained from the best fitting procedure are listed in Table II. They were assigned to each proton sites with the help of the direction cosines observed. The protons are denoted by the site numbers of neighboring carbons.

TABLE II Experimentally determined ^{1}H-hyperfine coupling tensors of p-BDPM.

Site No.	Isotropic Term A_{iso} /MHz	Anisotropic Term /MHz B_{xx}	B_{yy}	B_{zz}
1	-8.706	-3.020	-0.870	3.891
2	3.952	-1.713	-0.242	1.955
3	-9.249	-5.025	-0.272	5.297
4	4.423	-1.694	0.085	1.609
5	-7.541	-2.795	-0.930	3.725
9	-8.554	-2.884	-1.362	4.246
10	4.170	-1.429	-0.036	1.465
12	3.539	-1.655	0.144	1.511
13	-8.588	-3.657	0.270	3.387
16 - 20	$\lvert A\rvert < 1.3$	——	——	——

π-Spin Density Distribution of p-BDPM and Spin Polarization

The π-spin density (ρ_π) on a carbon atom is related to the isotropic hfc term (A_{iso}) of the ^{1}H-hfc tensor of the adjacent α-proton by a generalized McConnell's equation,[8] $A_{iso}=Q\rho_\pi/2S$, where $1/2S$ is a projection factor in order to normalize the spin density per one electron to be unity. We used -66.9 MHz for Q value which was determined for the triplet excited state of naphthalene.[17] The π-spin densities determined from the isotropic hfc's are shown in Table III together with those calculated from the unrestricted Hartree-Fock (UHF) procedure of the generalized Hubbard Hamiltonian.[9,10,11] The π-spin densities for DPM are shown in Table III for comparison. The table also contains the spin densities of DPM reported by Hutchison et al.[13] The table shows that all the π-spin densities on the carbon atoms in the phenyl rings of the DPM unit (site No. 1-13) observed are larger in magnitude than those of the parent DPM. This indicates that the delocalization of unpaired electron from the divalent carbon site to the phenyl rings of the DPM unit is induced by the introduction of the p-benzoyl group, giving rise to the increase in the π-spin densities on the phenyl rings of the DPM unit. This delocalization effect leads to the decrease in the π-spin densities on the divalent carbon atom in accordance with the decrease in the D value of p-BDPM.

TABLE III π-Spin densities of p-BDPM and DPM.

Site No.	p-BDPM		DPM	
	Obsd.	Calcd.	Obsd.	Calcd.
1	0.260	0.227	0.243	0.231
2	-0.118	-0.153	-0.076	-0.155
3	0.277	0.207	0.222	0.210
4	-0.133	-0.153	-0.078	-0.155
5	0.225	0.227	0.202	0.231
6	—	-0.154	-0.044	-0.156
7	—	0.579	0.590	0.589
8	—	-0.161	-0.044	-0.156
9	0.256	0.229	0.202	0.231
10	-0.125	-0.164	-0.078	-0.155
11	—	0.188	0.222	0.210
12	-0.106	-0.164	-0.076	-0.155
13	0.257	0.229	0.243	0.231
14	—	-0.089		
15	—	0.032		
16	$\|\rho_\pi\|<0.04$	-0.037		
17		0.026		
18		-0.033		
19		0.026		
20		-0.037		
21(O)	—	0.173		

The Hubbard calculation has partially reproduced the experimental result for both p- and m-BDPM. Thus, as shown in Table III the calculation indicates that the delocalization from the DPM unit to the benzoyl group is very small for p-BDPM and that the up- and down-spins are adjacent with each other over the whole molecule, in consistent with the present ENDOR result. It failed, however, to interpret the decrease in the D value and the increase in the π-spin densities on the phenyl rings of the DPM unit.

The reason for the above failure is presumed as below. The spin density in the RHF method consists of two contributions which arise from the spin delocalization (SD) and spin polarization (SP) mechanisms.[18] The former means the direct delocalization of unpaired electrons in the SOMO's of the best restricted wavefunction, while the latter means the mechanism owing to the correlation between electron spins in the MO's of the wavefunction, i.e. configuration interaction. The UHF method based on a spin-polarized single-determinant wavefunction[19] by the SCF procedure gives the spin density arising from the sum of both contributions. Thus the present UHF Hubbard calculation is expected to provide the spin density including both contributions within the π electron approximation. The calculation, nevertheless, failed to account for the experiment. As the present calculation explicitly treats the SD contribution which is associated with the orbitals near frontier MO's, the failure indicates the insufficient treatment of the SP under the present approximation. From these consideration, it is inferred that the SP effect from the inner shell must be considered for the decrease in the D value as well as the increase in the π-spin densities (i.e., SP enhancement) on the phenyl rings of the DPM unit.

CONCLUSIONS

The triplet ground states of p- and m-BDPM were studied in terms of the fine structure parameters obtained by single crystal ESR measurements as well as the π-spin density distribution of p-BDPM obtained by single crystal ^{1}H-ENDOR measurements. The results for p-BDPM showed that the π-spin densities of the phenyl rings of the DPM unit increase in magnitude relative to DPM. An attempt to interpret the spin structure of p-BDPM has been made with the help of the generalized Hubbard calculation. It was shown that the introduction of the p-benzoyl group leads to the enhancement of the spin polarization on the phenyl rings of the DPM unit. This finding suggests that control of the spin polarization by the substituent group is feasible for the design and construction of higher-dimensional robust spin networks.

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