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Electronic and Molecular Structures of p-Phenylenebis(phenylmethylene) in its Thermally Excited Triplet State as Studied by Single-Crystal ^{1}H-ENDOR

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ELECTRONIC AND MOLECULAR STRUCTURES OF *p*-PHENYLENE-BIS(PHENYLMETHYLENE) IN ITS THERMALLY EXCITED TRIPLET STATE AS STUDIED BY SINGLE-CRYSTAL ^{1}H-ENDOR

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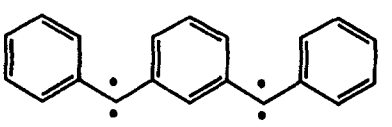
Abstract The thermally excited triplet state of *p*-phenylenebis(phenylmethylene) (*p*-PBPM) which is a topological isomer of the first organic high-spin molecule, *m*-phenylenebis(phenylmethylene) (*m*-PBPM, S=2), was examined using single-crystal ^{1}H-ENDOR (Electron-Nuclear DOuble Resonance) spectroscopy. From the ^{1}H-ENDOR spectrum of the triplet state we found that the absolute sign of the fine-structure parameter *D* was negative and that *p*-PBPM in the triplet state has eight negative π-carbon sites and six positive ones. The π-spin density distribution determined experimentally indicates that the carbon atoms of the central *p*-phenylene ring have negative π-spin density. The spin-spin interaction between the induced π-spins causes the fine-structure parameter D to be negative. It is concluded that the π-π spin interaction predominates in the triplet state of *p*-PBPM.

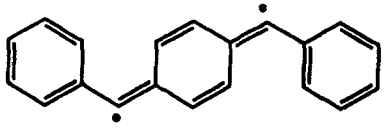
INTRODUCTION

Organic molecular based magnetism has attracted wide interest from both pure and applied sciences.[1,2,3] Organic high-spin molecules have been studied since the detection in 1967 of the first quintet organic molecule,[4,5] *m*-phenylene-bis(phenylmethylene) (*m*-PBPM, S=2), as models for organic molecular based magnetic materials.[6,7] In this paper we focus on *p*-phenylenebis(phenylmethylene) (*p*-PBPM) which is a topological isomer of the first organic high-spin molecule, *m*-PBPM. The spin states of organic high-spin molecules closely depend on the topology of their own π-electron network. In contrast to *m*-PBPM with topologically controlled robust spin polarization, the ground state and the first or the second excited state of *p*-PBPM are fairly close to each other. Even though the ground state of the isomer is singlet and silent for ESR measurements, the nearby excited triplet state is thermally accessible.

The electronic structure in the excited state of the isomer are of fundamental importance for the understanding of spin alignment vs. topology of the π-electron network in organic molecules. This paper describes the electronic structure of *p*-PBPM in terms of its π-spin density distribution, as studied by single-crystal ESR and ^{1}H-ENDOR spectroscopies.



m-PBPM



p-PBPM

A study of the electronic state of *p*-PBPM has been done so far by Wasserman's, Itoh's, and Sixl's groups. In 1963, Wasserman et al. have reported the ground state of *p*-PBPM to be triplet by ESR measurement using a powder sample where the diazo precursor of *p*-PBPM was incorporated into 1,4-dibenzoylbenzene glassy matrix.[8] Itoh et al. have carried out ESR measurements of *p*-PBPM using a host single crystal of 1,4-dibenzoylbenzene, reporting that the triplet state was thermally populated above the singlet ground state by 202cm^{-1}.[9] Sixl et al. have carried out ESR measurements of *p*-PBPM using benzophenone as host single crystals.[10] Although their result is qualitatively in agreement with Itoh's, the singlet-triplet energy gap ΔE_{ST}=120cm^{-1} reported is quite different. We have applied single-crystal ESR and ^{1}H-ENDOR spectroscopies to the triplet state of *p*-PBPM incorporated into benzophenone single crystals, determining the fine structure parameters, the singlet-triplet energy gap, and the π-spin density distribution of the triplet state.

EXPERIMENTAL AND ANALYSIS

The diazo precursor of *p*-PBPM, 1,4-bis(α-diazobenzyl)benzene, was incorporated into perdeuterated benzophenone-d_{10} crystals by slowly cooling a diethylether solution. The mole fraction of the precursor to the host molecule was 0.0042 in the solution. Benzophenone-d_{10} was used in order to eliminate the ^{1}H-ENDOR transitions arising from protons of the surrounding host molecules. A partially deuterated diazo precursor was also synthesized to decrease the ^{1}H-ENDOR spectral density. *p*-PBPM was formed at 4K by the irradiation of the 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 (100g/cm^3, $CuSO_4 \cdot 5H_2O$, *l*=5cm) and a glass filter (TOSHIBA VY39) were used 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 dependences of the ESR and ^{1}H-ENDOR signals were measured by rotating the single crystal using a uniaxial goniometer.

The spin Hamiltonian used for analyses is given by

$$\begin{aligned} H &= H_{eZ} + H_D + H_{hf} + H_{nZ} \\ &= \beta_e \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} + \sum_i (\mathbf{S} \cdot \mathbf{A}_i \cdot \mathbf{I}_i - g_n \beta_n \mathbf{B} \cdot \mathbf{I}_i), \end{aligned} \tag{1}$$

where H_{eZ}, H_D, H_{hf}, and H_{nZ} stand for the electron Zeeman, fine structure, hyperfine coupling, and nuclear Zeeman terms, respectively. In the ESR analysis the hyperfine coupling and the nuclear Zeeman terms were omitted.

RESULTS AND DISCUSSION

Single-Crystal ESR Measurements of *p*-PBPM

The ESR transitions of the triplet state of *p*-PBPM were detectable above 35K, and the intensity grew stronger with increasing temperature. We observed irreversible conformational changes at 120K and just below 190K. The ESR spectrum of *p*-PBPM consisted of the ESR transitions due to two conformers (**I, II**) before the first conformational change. After the changes at 120K and 190K we observed the ESR spectra to be comprised of four (**III** ~ **VI**) and two (**VII, VIII**) sets of conformers, respectively. The triplet signals completely disappeared at 250K. The fine-structure tensors of the conformers were determined from the angular dependence of the ESR spectra using the least-square procedure. The fine-structure parameters of the conformers are listed in Table I with their singlet-triplet energy gap (ΔE_{ST}). ΔE_{ST} was determined from the temperature dependence of the ESR signal intensities using the following equation,

$$I(T) \propto \frac{1}{3 + \exp(\Delta E_{ST} / kT)} \times \frac{1}{T}, \tag{2}$$

which was derived under the high temperature approximation, $kT >> h\nu \sim 0.3$ cm^{-1}.

We discuss the electronic states of *p*-PBPM in benzophenone-d_{10} single crystals as compared with the results reported by the three groups, Wasserman's,[8] Itoh's,[9] and Sixl's.[10] The present result that the triplet state is a thermally excited state is in agreement with those reported by Itoh and Sixl, whereas not with that by Wasserman *et al.* in 1963. In order to show that the singlet state of *p*-PBPM is more stable than the

triplet state, we utilize the concept of spin polarization. This concept is closely related to spin correlation in the π electron network. Among the spin states of the molecule with delocalized π spins, the most stable is the state where the up and down spins are adjacent to each other. If two sites both with the up spin are adjacent, the molecule loses the spin correlation energy given by $-J_{ij}\ \rho_i \cdot \rho_j$, where J_{ij} (>0) is an effective exchange coupling constant between the i and j spins neighboring each other and ρ_i the spin density on the i site. In the case of *p*-PBPM, assuming that positive π spin densities are induced on both the para-substituted divalent carbon atoms in the triplet state, a spin structure where all the up and down spins are adjacent to each other could not occur owing to topology. Therefore, this molecule favors a singlet for the ground state of *p*-PBPM because the triplet state is destabilized by same amount of spin correlation energy.[11,12]

In the present work, we detected the triplet ESR signals of various conformers. Itoh *et al.* had observed only the one conformational change at 62K in the single crystal of 1,4-dibenzoylbenzene. On the other hand, Sixl *et al.* have reported three conformers in a benzophenone single crystal. Since the molecular size of the precursor of *p*-PBPM is very close to that of 1,4-dibenzoylbenzene, the precursor is expected to replace the

TABLE I. The observed fine-structure parameters and singlet-triplet energy gaps of the conformers of *p*-PBPM.

conformer	$\lvert D \rvert$ /cm^{-1}	$\lvert E \rvert$ /cm^{-1}	$\lvert E/D \rvert$	ΔE_{ST} /cm^{-1}
I	0.0494	0.0024	0.0486	159
II	0.0491	0.0019	0.0387	159
III	0.0615	0.0081	0.1317	196
IV	0.0613	0.0071	0.1158	178
V	0.0766	0.0071	0.0927	202
VI	0.0768	0.0066	0.0859	202
VII	0.0616	0.0047	0.0763	174
VIII	0.0622	0.0042	0.0675	174
Wasserman et. al.[8]				
	0.0521	< 0.002	< 0.0384	
Itoh et. al.[9]				
1	not reported			
2	0.05005	0.00159	0.0318	202
Sixl et. al.[10]				
1,2	not reported			
3	0.0650	0.0050	0.0769	120

host molecule in the single crystal, giving a lesser amount of strain in the mixed single crystals. In the case of the single-crystal ESR measurements for organic high-spin molecules, we have often observed many conformers in benzophenone single crystals. Since the precursor of *p*-PBPM seems to replace two host molecules in the benzophenone single crystal, *p*-PBPM immediately after photolysis at liquid helium temperature presumably takes a strained molecular conformation, which is then relaxed into a more stable one in a cooperative manner with host lattice vibrational modes. This is an irreversible process.

The observed conformers are classified into four groups, (**I** and **II**), (**III** and **IV**), (**V** and **VI**), and (**VII** and **VIII**), from the E/D value. By comparing the E/D values for the conformers to those reported by Wasserman, Itoh, and Sixl, the molecules reported by Sixl *et al.* corresponds to conformers **VII** and **VIII**. Although the matrix used by Wasserman's or Itoh's group is different from the present matrix, the structure of the molecule observed by them must be very close to conformers **I** and **II**.

Single-Crystal ^{1}H-ENDOR Measurements of *p*-PBPM

Part of the ^{1}H-ENDOR experiment described here has been already reported in our previous paper.[11] A ^{1}H-ENDOR spectrum of the thermally excited triplet state of *p*-PBPM can be detected above 35K when the allowed ESR transition with a higher resonance field is pumped. We show the typical ^{1}H-ENDOR spectrum of *p*-PBPM in Figure 1 which was observed at 60K for the magnetic field oriented in the

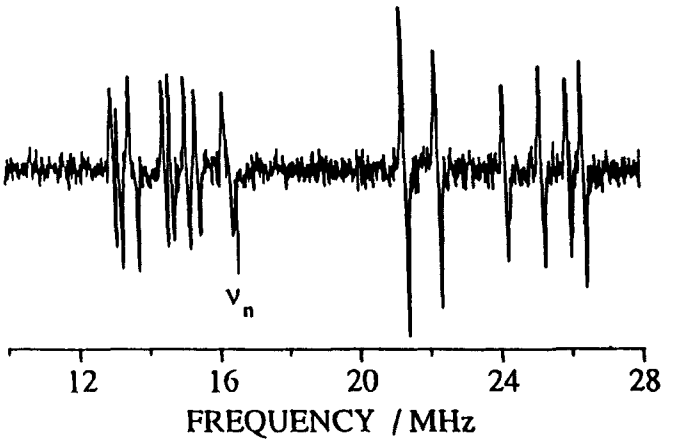


FIGURE 1. ^{1}H-ENDOR spectrum of *p*-PBPM in benzophenone-d_{10} single crystals, with the magnetic field oriented in the crystallographic ***ab*** plane.

crystallographic ***ab*** plane of the benzophenone-d_{10} single crystal. There are six and eight transitions, respectively, above and below the transition near the free-proton NMR frequency ν_n ($=g_n\beta_n H/h$) attributed to an $|M_S=0\rangle$ sublevel. The fourteen transitions should be attributed to either the $|M_S=+1\rangle$ or $|M_S=-1\rangle$ sublevel. Noticing that the shifts of the six transitions from ν_n are larger in magnitude than those of the eight transitions, it was concluded that the six protons have negative hyperfine couplings (hfc's) leading to positive spin densities on the adjacent carbon atoms. Since the shift $\Delta\nu$ of the ^{1}H-ENDOR frequency ν_{ENDOR} from ν_n is given by

$$\Delta\nu = \nu_{ENDOR} - \nu_n = -A_{ZZ}M_S/h, \quad (3)$$

in terms of the first-order perturbation theory for the spin Hamiltonian, Equation (1), the ESR transition pumped for the ^{1}H-ENDOR measurement was assigned to that between the $|M_S=0\rangle$ and $|M_S=+1\rangle$ sublevels. It is, therefore, expected that the absolute sign of the fine structure parameter (D) of *p*-PBPM is negative because the present ESR transition pumped was at the higher-field.

TABLE II. The experimentally determined ^{1}H-hyperfine coupling tensors and π-spin densities on the carbon sites bonded to the α-protons of *p*-PBPM in benzophenone-d_{10} single crystals. The tensors for the proton sites of *p*-PBPM were not assigned.

Isotropic Term	Anisotropic Term /MHz			π-spin density
Aiso /MHz	Bxx	Byy	Bzz	ρ_π
-7.991	-5.023	0.301	4.723	0.238
-9.814	-3.714	-1.873	5.587	0.293
-6.884	-3.242	-0.079	3.321	0.205
-6.395	-3.668	0.422	3.245	0.191
-7.526	-2.300	0.416	1.884	0.225
-7.402	-2.603	0.954	1.649	0.221
2.405	-1.804	0.507	1.298	-0.072
2.699	-0.814	-0.113	0.927	-0.081
2.581	-1.907	0.264	1.643	-0.077
2.320	-0.613	-0.472	1.086	-0.069
2.595	-2.417	-0.434	2.851	-0.077
1.463	-0.553	-0.452	1.004	-0.044
0.350	-2.379	-0.066	2.444	-0.010
0.413	-1.019	-0.558	1.576	-0.012

The ^{1}H-ENDOR signals were observable only in the several directions around the crystallographic ***a*** axis. After determining the hyperfine tensor by the least-square procedure, we refined all the elements of the tensors by comparing the observed frequencies with those calculated by numerically diagonalizing the spin Hamiltonian of Equation (1). The ^{1}H-hyperfine coupling tensors determined are summarized in Table II. From the isotropic term of the ^{1}H-hyperfine tensor, $A_{iso} = (A_{aa} + A_{bb} + A_{cc})/3$, the π-spin densities ρ_π on carbon atoms in Table II were calculated using the generalized McConnell equation:[11,13]

$$A_{iso} = Q\,\rho_\pi / 2S, \tag{4}$$

where 1/2S is a projection factor which normalizes the total spin density to unity. We used -66.9 MHz for the Q value which was determined for the excited triplet state of naphthalene.[14]

π-Spin Density Distribution of the Thermally Excited Triplet State of *p*-PBPM

The ^{1}H-ENDOR spectrum of *p*-PBPM indicates that the eight and six atoms of the fourteen carbon atoms adjacent to protons have negative and positive π-spin densities, respectively. The π-spin density distribution of *p*-PBPM is expected to be the one shown in Figure 2, judging from the numbers of positive and negative sites. It should be noted that all the π spin densities on the central phenyl ring have been assigned negative values.[11] In order to confirm this assignment for the central phenyl ring, we measured ^{1}H-ENDOR spectra of a partially deuterated molecule *p*-PBPM-d_{10}. The partial deuteration removes the signals attributed to the protons of the end phenyl groups from the ENDOR spectrum. Figure 3 shows the ^{1}H-ENDOR spectrum of *p*-PBPM-d_{10} which was observed for the magnetic field with the same direction as that in

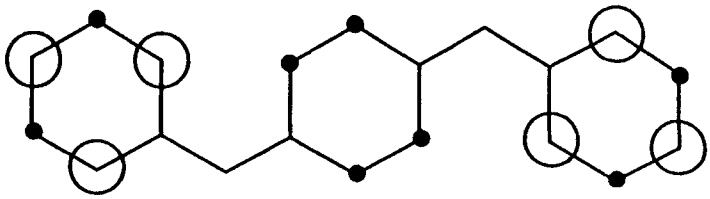


FIGURE 2. π-Spin density distribution of the triplet state of *p*-PBPM obtained from the ^{1}H-ENDOR experiments. Six positive and eight negative spin densities were observed. Open and shaded circles denote positive and negative spin sites, respectively.

Figure 1. Since there appears no ^{1}H-ENDOR signal above ν_n except for the signals due to the $|M_S=0\rangle$ sublevel, all the remaining protons of *p*-PBPM-d_{10} have positive hfc's. Therefore the four carbon atoms having the adjacent protons in the central phenylene ring have negative π-spin densities. In addition, these negative spin densities are smaller in magnitude than those of the end phenyl groups. The present measurements of ^{1}H-ENDOR spectra of *p*-PBPM-d_{10} conclusively support the π-spin density distribution shown in Figure 2.

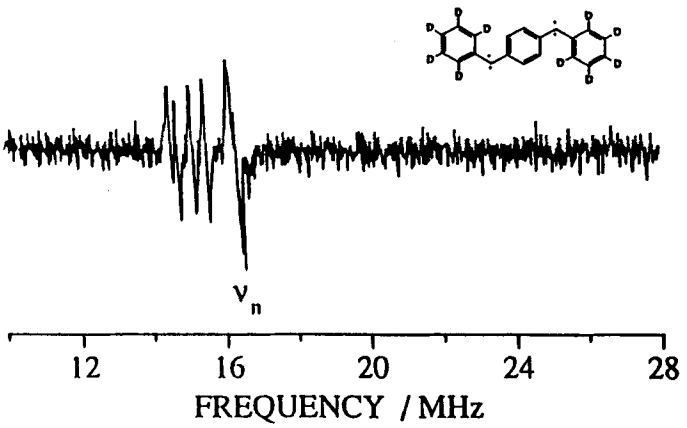


FIGURE 3. ^{1}H-ENDOR spectrum of *p*-PBPM-d_{10} in a benzophenone-d_{10} single crystal with the magnetic field oriented to the same direction with the spectrum of *p*-PBPM in Figure 1.

We compare the spin density distribution observed for the triplet state of *p*-PBPM with that calculated on the basis of a Heisenberg model.[15,16] The model Hamiltonian is given by

$$H = -2\sum_{<i,j>} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j, \tag{5}$$

where J_{ij} is an effective exchange coupling constant between the i and j sites and $\mathbf{S}_i$ a spin operator on the i site. For polycarbenes, $J_{\pi\pi'}$ between the π spins on adjacent carbon atoms and $J_{n\pi}$ between the n and π spins on a divalent carbon atom are antiferromagnetic and ferromagnetic, respectively. We adopted -0.2 as a semiempirical factor for $J_{n\pi} / J_{\pi\pi'}$, a value successfully applied to organic high-spin molecules.[15] The π-spin density distribution of *p*-PBPM calculated in terms of this model is depicted in Figure 4.

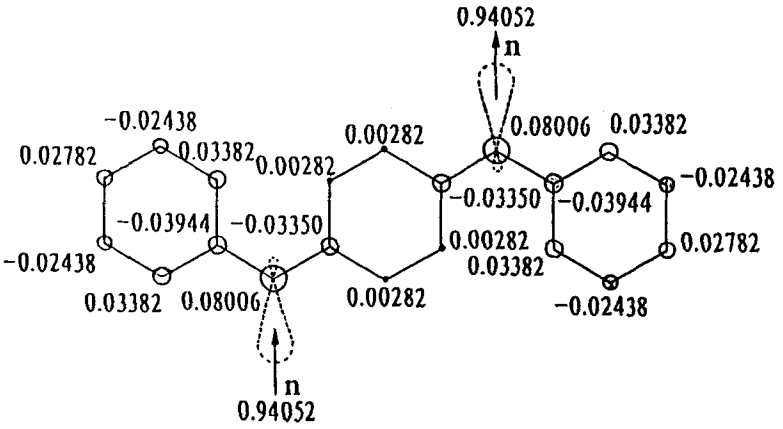


FIGURE 4. π-Spin density distribution of *p*-PBPM calculated in terms of the Heisenberg model.

Figure 4 shows that the up- and down-spins were alternately distributed on the end phenyl rings in agreement with the experiment. On the ither hand, small *positive* π-spin densities are induced by spin polarization on the four carbon atoms adjacent to the protons in the central phenylene ring contrary to the experiment where the opposite sign was observed. In addition, these positive π-spin densities are one order of magnitude smaller than the spin densities on the end phenyl rings. Although the Heisenberg model has successfully interpreted the π-spin density distribution of many organic high-spin molecules so far, it fails to reproduce the π-spin densities of the excited triplet state of *p*-PBPM especially for the central phenylene ring. The difficulty arises from the fact that the π-spin densities themselves are those induced by the spin polarization due to the large n spins, since no spins are expected without spin polarization judging from its π electron structure. For predicting the π-spin density distribution of *p*-PBPM, the introduction only of the spin correlation between the π and n spins is insufficient and a more sophisticated treatment of the spin polarization effect should be considered.

Electronic Structure of the Thermally Excited Triplet State

In the early stage of the study of the electronic structures of several high-spin carbenes, *p*-PBPM was known as a typical n-n type triplet molecule. According to the calculation by Higuchi,[16,17] the D value for the n-n type triplet state of *p*-PBPM is expected to be $-0.013cm^{-1}$ and $-0.007cm^{-1}$, respectively, for a coplanar molecular conformation and for a conformation with the central phenylene ring perpendicular to the two end phenyl rings. The model of predominant dipole-dipole interaction in the n-n type triplet state can not interpret the experimental D values, indicating that the calculated values by Higuchi are underestimated.

The present ^{1}H-ENDOR measurements provide us with a clue to the interpretation of such large D values. The ^{1}H-ENDOR results indicate that spin polarization leads to π spin density in the thermally populated triplet state of *p*-PBPM. Since the actual *p*-PBPM molecule is expected to have a twisted conformation, the n-π and π-π spin-spin interactions must be considered in addition to the n-n interaction assumed in the calculation by Higuchi.[16,17] Such spin-spin interactions qualitatively explain the large D value observed. Thus the n spins localized on the divalent carbon atoms interact with each other through the delocalized π spins induced in the triplet state as well as the one-center n-π interaction on the divalent carbon sites. Moreover, the major contribution is the π-π interaction rather than the one-center n-π interaction because a positive D value is expected when the n-π interaction is dominant. Whether the π-π interaction leads to a positive D value or a negative one depends on the electronic structure of the triplet state. In the case of *p*-PBPM, the fine structure tensor, *i.e.*, the spin dipolar interaction tensor, is expected to be prolate if the π spins are induced and delocalized over the whole molecule, leading to a negative D value.

We have carried out UHF and ROHF/AM1 calculations[19,20,21] in order to qualitatively interpret the triplet state in terms of molecular orbital theory. The calculation was performed using MOPAC version 3.0 on the HITAC M680H computer. After optimizing the molecular structure of *p*-PBPM by a UHF calculation, we carried out an ROHF CI calculation for the optimized structure. The optimization was performed for the bond angles of the two divalent carbon atoms and the dihedral angles corresponding to the twisting angle between the phenyl rings. Configuration mixing was calculated within the n, n, π, and π^* orbitals shown in Figure 5. Because semiempirical CI calculation was performed with only four orbitals, the negative π spin density was not obtained. It was, however, shown that the configuration mixing induced a finite amount of spin in the π system, and that several configurations made significant contribution to the triplet state of *p*-PBPM in addition to the ^{3}nn configuration. Therefore we can conclude that configurational mix-

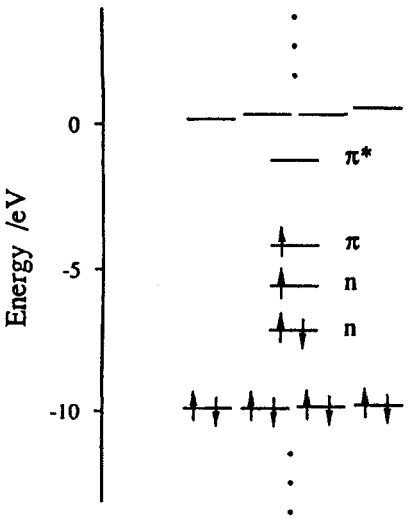


FIGURE 5. Schematic orbital energy of *p*-PBPM by an ROHF/AM1 calculation.

ing results in the induced spin in the π spin system in view of molecular orbital theory, giving a large D value through the π-π interaction.

CONCLUSIONS

The electronic structure of the thermally excited triplet state of *p*-PBPM was studied by single-crystal ESR and ^{1}H-ENDOR spectroscopies. The fine structure parameters of the triplet state were too large to be explained by an n-n type dipole-dipole interaction. The π-spin density distribution of the triplet state as determined by ^{1}H-ENDOR measurements showed that part of the triplet spin is induced in the π system and that the negative spin densities were distributed on the carbon atoms having the adjacent proton in the central phenylene ring. It is shown that the fine structure parameters are interpretable in terms of the spin-spin interaction between the π spins induced by the large n spins at the divalent carbon atoms as well as between the induced π spins and the n spins at the divalent carbon atoms. The π-π interaction is considered to be dominant rather than the one-center n-π interaction.

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