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Spin Alignment in High-Spin Carbenes of Heteroatomic π-Conjugation; Invalidity of Simple Extension of "π-Topology Rule" for Homoatomic Systems

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Spin alignment of heteroatomic π-conjugated systems, 2,6-, 2,4-, and 3,5-pyridinebis(phenylmethylene) (3,5-PY), in which heterocycle plays a ferromagnetic or antiferromagnetic linker between carbenic units, has been studied by random orientation ESR spectroscopy. The electronic structures of the isomers are important for the understanding of spin alignment vs. topology of the heteroatomic π-electron networks. In 2,6-PY and 2,4-PY, the perturbing nitrogen atoms are in active positions, giving rise to a larger influence on their spin structure than in 3,5-PY. A simple application of molecular Hund's rule is invalidated.

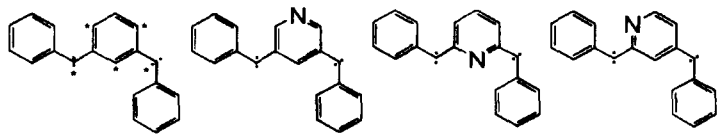
Keywords: organic magnetics; spin alignment; random orientation ESR spectroscopy; heteroatomic perturbation; π-topology rule

INTRODUCTION

Organic molecule-based magnetics has been the topic of increasing interest in many fields of both the pure and applied sciences for the last three decades. This research field is based on high-spin chemistry which can date back to the first detection of a quintet organic molecule, *m*-phenylenebis(phenylmethyl-

ene) (**I**) by K. Itoh[1] and E. Wasserman *et al.*[2] in 1967, demonstrating the importance of the topological nature of homoatomic (carbon) π-electron networks in generating high-spin ground states of organic systems[3-5].

We have studied the topological nature of the heteroatomic (nitrogen) π-electron networks in prototypical organic high-spin systems. We focus our attention on isomers in which the heterocycle plays the role of either a ferromagnetic or antiferromagnetic linker between carbenic units[6]. The electronic structures of the isomers are of fundamental importance for the understanding of spin alignment vs. topology of the heteroatomic π-electron networks in organic high-spin systems.



I 3,5-PY 2,6-PY 2,4-PY

In alternant hydrocarbons (AH) the carbon sites can be divided into two sets, • and non-*, such that no two members of the same set are connected. Note that in 3,5-PY the nitrogen atom is at a non-active (non-*) site of the corresponding AH, and in both 2,6-PY and 2,4-PY the nitrogen atom is at an active (*) site. In 2,6-PY and 2,4-PY the perturbing nitrogen atoms in active positions impose a larger influence on their spin structure than in 3,5-PY.

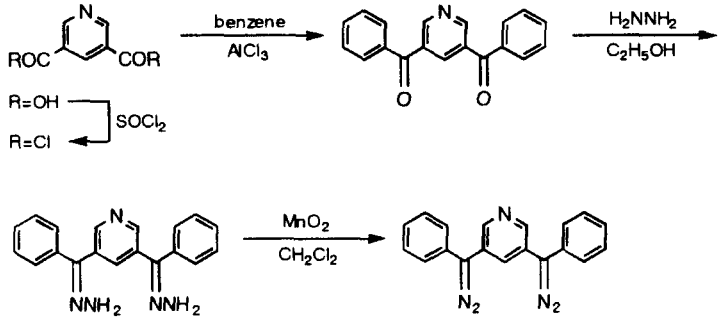
EXPERIMENTAL

The diazo precursors were prepared by the usual method as shown Scheme I. The corresponding pyridine dicarbonyl chlorides were reacted with benzene in the presence of aluminum chloride to give dibenzoyl pyridines, which were recrystalized from ethanol to give the colorless crystals in 50-60% yields. The dibenzoyl pyridines were treated with hydrazine to give corresponding

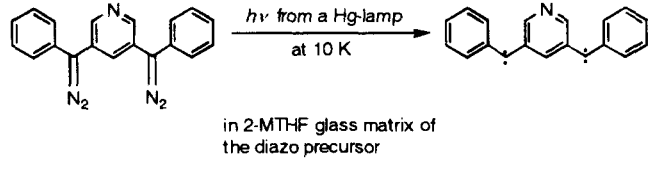
hydrazones as colorless oil, which were used for the following step without further purification. The hidrazones were oxidized with activated manganese dioxide to give diazo derivatives. The obtained crude compounds were recrystalized from pentane to give purple crystals in 40-50% yields.

The diazo precursors[7] of the isomers were fairly soluble in 2-MTHF (2-methyltetrahydrofuran). The solutions of these diazo precursors were degassed by freeze-pump thaw cycles and sealed off on a vacuum line. The sample tubes were set at the sample site of an Oxford ESR 910 cryostat at cryogenic temperature. The glassy samples were irradiated for 60 minutes at 10 K with 436 nm light selected by a glass filter (Toshiba KL440) placed in front of a SAN-EI UVF-351S 300W high-pressure mercury lamp. ESR measurements were made on a Bruker ESR 300 X-band spectrometer. The sample preparation was carried out in the dark (Scheme II).

SCHEME I Preparation of the 3,5-diazo precursor.



SCHEME II Formation of 3,5-PY.

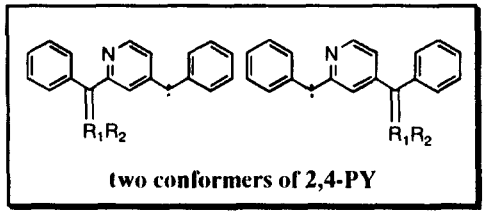


RESULTS AND DISCUSSION

Random Orientation ESR Spectra

We detected the quintet ESR signals after photolysis of 3,5-PY below 10K in 2-MTHF. However, both 2,6-PY and 2,4-PY showed only triplet ESR spectra after photolysis below 10K in 2-MTHF. The triplet signals were due to monocarbenes as by-products generated by side reactions. All the observed results suggest that the ground states of both 2,6-PY, and 2,4-PY are singlet while that of 3,5-PY is quintet.

We have detected for the first time the quintet ESR signals from the two conformers which coexist after photolysis of 3,5-PY below 10K in 2-MTHF (See Fig. 1). The best fit spin Hamiltonian parameters of the two spectra for 3,5-PY were found to be S = 2, g = 2.003 (isotropic), $|D_1|$ = 0.0719 cm^{-1}, $|E_1|$ = 0.0198 cm^{-1} (conformer 1) and S = 2, g = 2.003 (isotropic), $|D_2|$ = 0.1192 cm^{-1}, $|E_2|$ = 0.0063 cm^{-1} (conformer 2). The fine structure parameters and the |E/D| ratio for conformer 1 (*cis-trans* type) and conformer 2 (*trans-trans* type) of 3,5-PY were reproduced by a semiempirical calculation[8] assuming the bond angle (150°) of the divalent carbon atom and molecular conformations.



two conformers of 2,4-PY

On the other hand, both 2,6-PY and 2,4-PY showed only triplet ESR spectra[8] from monocarbenes after the photolysis. The observed fine-structure constants for 2,6-PY and 2,4-PY (two conformers) were |D| = 0.3341 cm^{-1}, |E| = 0.0155 cm^{-1}, and $|D_1|$ = 0.3811 cm^{-1}, $|E_1|$ = 0.0170 cm^{-1}, and $|D_2|$ = 0.3539 cm^{-1}, $|E_2|$ = 0.0194 cm^{-1}, respectively.

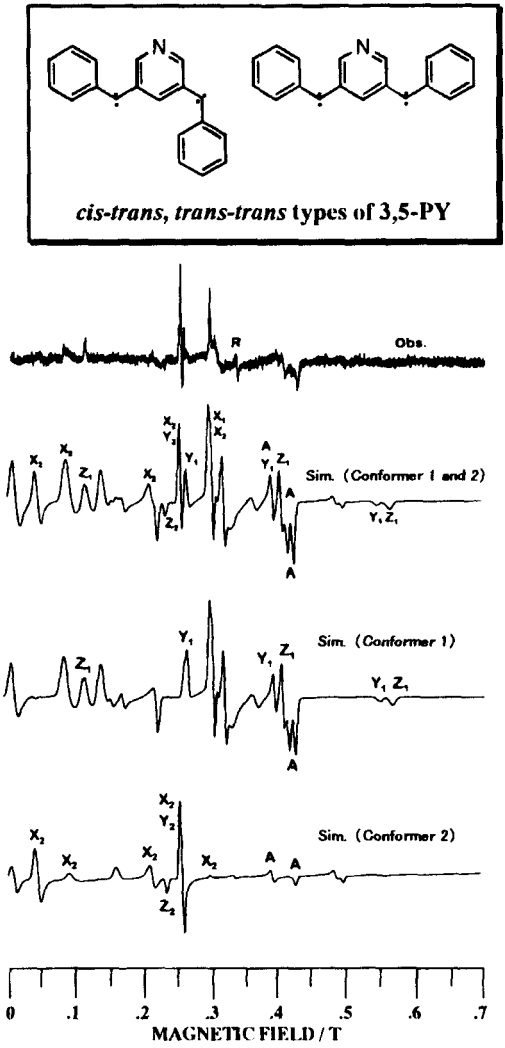


FIGURE 1 Observed (top) and simulated random orientation ESR spectra for the quintet state of 3,5-PY in 2-MTHF at 10K. The symbol A in the simulated spectrum denotes the off axis extra lines. The symbol R designates doublet species as by-products. The symbol $\mathbf{X}_i$, $\mathbf{Y}_i$, and $\mathbf{Z}_i$ designate the canonical orientation.

Molecular Orbital Theory

The prominent effect of the heteroatomic replacement appears in the energies of two degenerate π-NBMOs (non-bonding molecular orbital Ψ_{10} and Ψ_{11}) for 3,5-PY and of two quasi degenerate π-MO's appearing nearby zero energy in units of β for 2,6- and 2,4-PY. In 3,5-PY where the nitrogen atom is at a non-active site, the electronic structure of 3,5-PY is quite similar to **I** and the energy gap between Ψ_{10} and Ψ_{11} is zero. However, in 2,6- and 2,4-PY where the nitrogen atoms are at active sites, the heteroatomic perturbation imposes a larger influence on their spin structures than on that of 3,5-PY; as a result the energy gaps become non-zero. We obtained in terms of a simple molecular orbital calculation that the energy gap of 3,5-PY as well as of **I** is zero whereas those of 2,6- and 2,4-PY are 0.107β and 0.088β, respectively (See Fig. 2). These tendencies favor parallel spins for 3,5-PY and **I** but antiparallel spins for 2,6- and 2,4-PY in the ground state. The tendencies are due to the weakening of robust π-spin polarization. As mentioned above, all the observed and calculated results show that the ground state of 3,5-PY is quintet whereas those of 2,6- and 2,4-PY are singlet[8].

Valence Bond Approach in Terms of the MO Calculation

We illustrate the valence bond (VB) approach[9-11] for the interpretation of the open-shell electronic structure and spin alignment of organic high-spin systems. It should be noted that the numerical results obtained here depend on the level of MO calculations. An advantage of this methodology is that the spin structure associated with spin alignment can be described in a systematic and quantitative manner and that a translation from the MO to the VB is free from the method in the MO calculation. The relative contributions of dominant local spin structures (S=1) of wavefunctions obtained by the simple MO calculations for **I**, 3,5-PY, 2,6-PY and 2,4-PY are 1.95, 1.92, 1.88, and 1.89, respectively (See Fig. 3). The results clearly demonstrate that the

progression **I** > 3,5-PY > 2,4-PY > 2,6-PY represents a preferential stabilization of the triplet relative to the singlet.

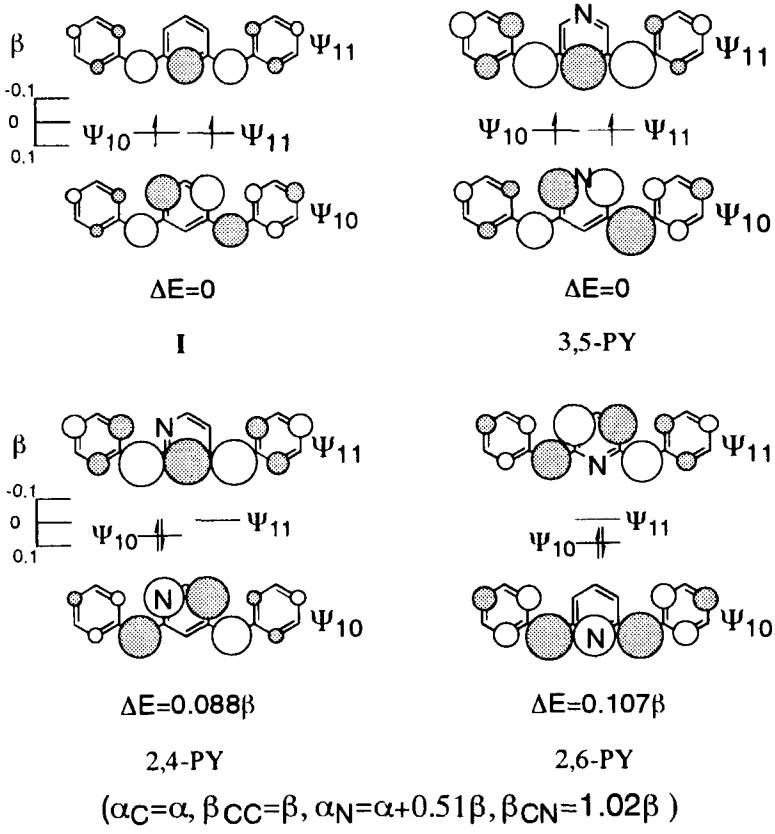


FIGURE 2 Zero and nearby zero orbital energy diagram for **I**, 3,5-, 2,6- and 2,4-PY calculated by the simple MO theory.

As is generally the case with biradical systems, both VB and MO arguments can be developed. Arguments based on MO theory emphasize the

role of the NBMOs. In 3,5-PY, nitrogen atom is introduced at a position where there are negligible coefficients of atomic orbitals in both NBMOs. Hence, very little perturbation occurs, and 3,5-PY behaves like **I**. In both 2,6-PY and 2,4-PY, however, nitrogen atom is at a site that has a large coefficient in one NBMO, and a negligible coefficient in the other.

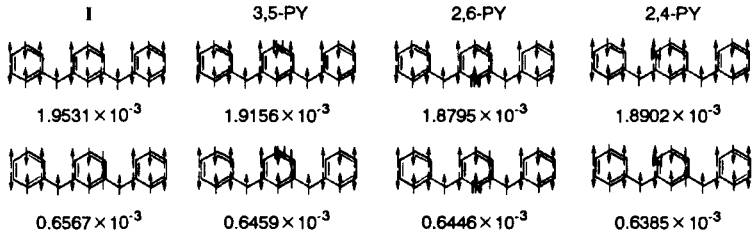
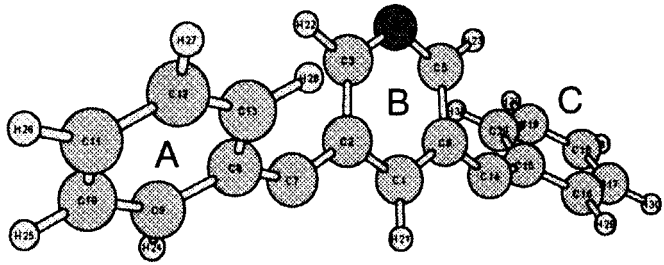


FIGURE 3 Relative contribution of dominant spin structures calculated by a VB approach in terms of the simple MO calculation.

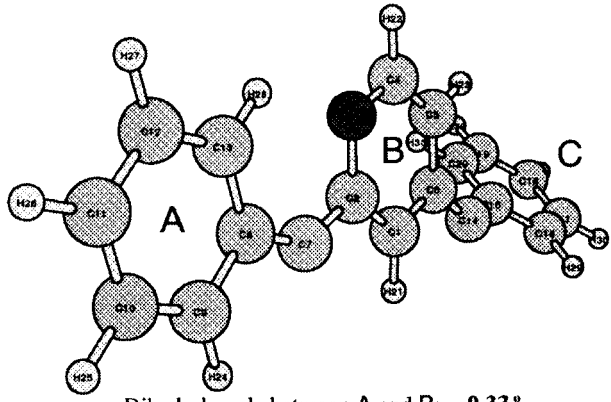
***Gaussian 94* (DFT methods) Calculations for Molecular Conformations**

We calculated the singlet (excited state)-quintet (ground state) [abbreviated to S-Q] gaps of the three isomers as well as **I** using geometry optimizations. The calculations were performed with the *Gaussian 94* package of *ab initio* programs[12-14]. The S-Q gap of 3,5-PY (*trans-trans*; 3.08×10^{-2}, *cis-trans*; 3.03 $\times 10^{-2}$ Hartree) showed little heteroatomic perturbation effect which reflects the S-Q gap of I (3.08×10^{-2} for *trans-trans*, 2.97×10^{-2} Hartree for *cis-trans*) (1 Hartree = 627.51 kcal/mol). Ground-state singlet were not reproduced for 2,6-PY and 2,4-PY. However, the S-Q gaps of 2,6-PY and 2,4-PY exhibited larger heteroatomic perturbation than that of **I**. The S-Q gaps of 2,6-PY and 2,4-PY are 3.49×10^{-2} for *trans-trans*, 3.64×10^{-2} for *cis-trans*, and 3.62×10^{-2} for *trans-trans*, 3.61×10^{-2} for *cis-trans*, 3.37×10^{-2} Hartree for *trans-cis*. These molecular structures of 3,5-PY and 2,4-PY obtained by the geometry

optimization were depicted in Fig. 4. The results assist the MO and VB approaches mentioned above.



Dihedral angle between A and B: **-50.50°**
Dihedral angle between B and C: **-50.58°**



Dihedral angle between A and B: **-0.33°**
Dihedral angle between B and C: **-49.99°**

FIGURE 4 Molecular Structures of 3,5- and 2,4-PY Calculated by *Gaussian 94* (DFT methods).

CONCLUSION

We concluded that 3,5-PY is in the quintet ground state. The two conformers of 3,5-PY were identified. However, both 2,6-PY and 2,4-PY showed only triplet ESR spectra after the photolysis. The triplet signals are attributed to the

ground-state triplets of monocarbenes as by-products generated by side reactions. In 2,6-PY and 2,4-PY the perturbing nitrogen atoms are in active (*) positions, imposing a larger influence on their spin structures than in 3,5-PY where the nitrogen atom is in non-active position. These findings suggest that 2,6-PY and 2,4-PY are spin-singlet in the ground state in agreement with the MO and VB approaches, and with interpretation in terms of *Gaussian 94* (DFT methods). The simple extension of "π-topology rule for spin alignment in homoatomic π-systems" is invalidated for that in heteroatomic π-systems.

Acknowledgments

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