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INTRAMOLECULAR EXCHANGE INTERACTION IN XYLYLENE TYPE BIRADICALS.

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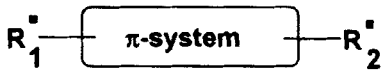
Abstract The singlet-triplet splitting $\Delta E = E_T - E_S$ is calculated for the *ortho*-, *meta*-, and *para*- xylylenes and their heteroatomic analogous. It is shown that when the radical centers $R^{\bullet}$ ($R^{\bullet} = H_2C^{\bullet}$ - , H_2N^{+}- or $H\underline{N}$-) are twisted sufficiently far out of conjugation with the benzene ring, the ΔE tends to zero or is negative, i.e. in some cases the *para*-isomers have a triplet ground state, while the *meta*-isomers have a singlet ground state. The concept of indirect exchange is proposed for explanation of the nature of the magnetic interaction between the radicals $R^{\bullet}$ through benzene ring.

INTRODUCTION

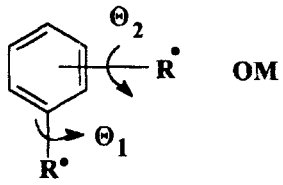
In order to make organic ferromagnets or molecular based magnets, one of the most important requirements are the combined molecular units which mainly consist of organic high spin molecules.[1-3]

For obtaining extended organic high spin compounds usually the radical centers are coupled by (through) *meta*-phenylene.[1-3] The *meta* high-spin coupling strategy is connnected with the theorem of Coulson-Rushbrooke-Longuet-Higgins.[4] The *meta*-xylylene has two degenerate non bonding MO's (NBMO) which justify (Hund's rule) the triplet character of the ground state.[5] More accurate studies [6,7] confirm the prediction of the simple HMO theory. Recently it was reported that two sterically hindered *meta*-phenylene bis(tert-butyl nitroxides)[8] had each been found to have a singlet, rather than a triplet ground state. For the *para*-phenylenediphenthiazinyl dication even a triplet ground state is obtained while the *meta*-isomer possesses a singlet ground state as proven experimentally.[9] Ab initio calculations[10] confirmed the later experimental results, which showed that when radical centers at C-1 and C-3 are twisted sufficiently far out of conjugation with the benzene ring, *meta*-phenylene can also lead to antiferromagnetic coupling between the two radical centers.

The present theoretical study is meant as a prelimenary communication and treats a particular case of the problem of the character of intermolecular magnetic interaction between two radicals connected by means of a π-electron system ($R^{\bullet}_1$ and $R^{\bullet}_2$ are



radical subunits with singly occuppied frontier orbitals). Here the interaction of the radicals: $R^{\bullet} = H_2C^{\bullet}$-(**1a-3a**) , $H_2N^{\bullet+}$-, (**1b-3b**), and $H\underline{N}^{\bullet}$- (**1c-3c**) via the benzene ring is treated:



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In the case of systems, such as **OMPs** (by a given substituent $R^{\bullet}$) the energy and the character of the spin exchange interaction are determined by two main factors: the topology and the value of the dihedral angles Θ_1 and Θ_2. At the limit $\Theta_1 = \Theta_2 = 0$ the π-electrons are delocalized. The ground state spin multiplicity: singlet-or triplet-, is determined by the topology of the isomers. Kekulé structures can be attributed to the *ortho-* and *para-* isomers, but no Kekulé formula can be described for the *meta*-isomer.

METHOD OF INVESTIGATION

The geometry and the character of the spin exchange interaction are obtained by means of the all-valence electrons quantum chemical AM1 method.[11] We perform a complete geometry optimization for fixed values of dihedral angles Θ between 0 and 90 degrees. The AM1 SCF-CI treatment was limited to six molecular active spaces (3x3 CI).

NUMERICAL RESULTS AND DISCUSSION

The numerical results show the effect of the dihedral angle Θ on the singlet-triplet splitting $\Delta E_{S-T} = E_S - E_T$ and are summarized in Fig. 1. When the dihedral angles Θ_1 and Θ_2 are around 0^o in agreement with the experimental results, the *ortho*-and *para* isomers have robust singlet ground states, whereas the *meta*-isomers have triplet ground states. For dihedral angles $\Theta > 0^o$, the stability of the triplet-versus the singlet decrease. For dihedral angles around 90^o the the singlet-triplet splitting ΔE tends to zero or is negative as in the case of **3c**, i.e. the *para* isomer have a triplet ground state.

The nature of the spin exchange interaction between the radicals $R^{\bullet}$ through benzene ring (and through an arbitrary π-coupling unit) can be qualitatively interpreted in π-electron approximation.

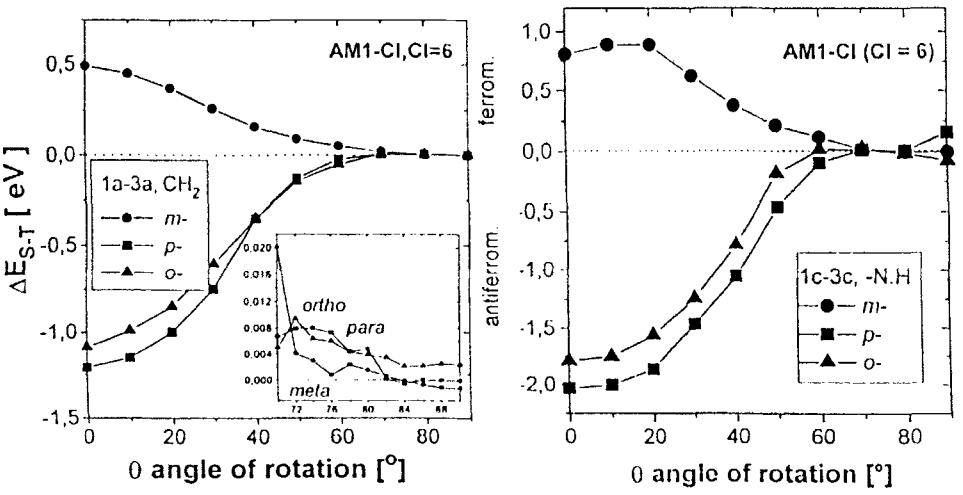
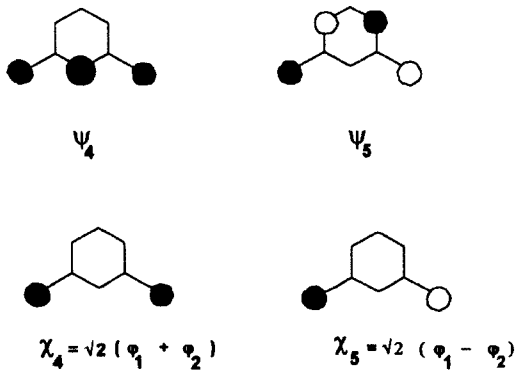


FIG. 1: The effect of θ on ΔE_{S-T} of **1a-3a**. (left) and on ΔE_{S-T} of **1c-3c** (.right)

For $\Theta << 90^{o}$ a strong mixing of the 2p AO's of the R- fragments with the benzene MO's occurs. At $\Theta = 90^{o}$ the off diagonal matrix elements of the SCF -energy matrix including the 2p AO's and the benzene AO's are equal to zero, therefore the 2p AO's are localized and degenerate. As far as we can see there is a significant difference between the degenerate partially occupied NBMO's of *meta*-xylylene by $\Theta = 0^{o}$ ($\psi_{4,5}$), which are delocalized, and the degenerate 2p AO's of *o*-, *m*-, and *p*- isomers by $\Theta = 90^{o}$ ($\chi_{4,5}$), which are localized on the methylene unit:



For $\Theta = 90^{o}$ Hund's rule cannot be used directly to predict the spin multiplicity because the electrons are localized on nonoverlapping 2p AO sets. The exchange integral between the 2p AO's is negligible and does not introduce any significant coupling between the uncompensated spins. Even in the case of *ortho-* isomer the exchange integral between the 2p - 2p AO's $J < 2.10^{-3}$ eV (STO-3G basis set). Still, indirect exchange interaction mediated by the delocalized π-electron of the benzene ring may exist. The physical aspect of the exchange interaction between the localized 2p electrons is very close to the indirect exchange mechanism of isolated transition-metal cations separated by nonmagnetic anions according to Kramers-Anderson scheme.[12,13] In order to illustrate the significance of the indirect exchange mechanism (spin polarisation) of the localized 2p-electrons via delocalized π-electrons of the benzene ring, the calculation have been carried out for *meta*-xylylene in framework of the PPP approximation.[14] The electron correlation was accounted for including all the mono-and doubly-excited singlet-, respectively triplet-, configurations.

The geometries of the singlet and triplet states, respectivelly, are obtained by means of the AM1 method.[11] The two center Coulomb integrals were calculated according to Mataga-Nishimoto formula.[15] In Table 1 are given the results of the calculated S-T spliting for the meta-xylylene. Within the π-electron approximation the spin polarization of delocalized π-electron was taken into account only, and the indirect spin exchange through the σ- electrons - through bond exchange has to be neglected.

TABLE 1.Calculated values of the singlet-triplet splitting $\Delta E_{S-T} = E_S - E_T$ (eV) for the *meta* - xylylene.

$\Delta E\ (\Theta = 0^{o})$	$\Delta E(\Theta = 90^{o})$	$\Delta E\ (\Theta = 0^{o})$	$\Delta E(\Theta = 90^{o})$
PPP-CI		AM1-CI	
0.378	-0.050	0.480	-0.001

Our result for *meta*-xylylene are in good agreement with the results of *ab initio* calculation by Borden at al.[10] This is an in-dication that the spin polarization of the π-electrons is the main contribution to the intermolecular magnetic interaction between two radicals connected by means a π-electron system , if the two planes of π-conjugation are almost orthogonal.

Preliminary ab initio calculations support the AM1 results and further indepth calculations with extended basis set are in progress.

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