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Influence of Noncovalent Cation/Anion– π Interactions on the Magnetic Exchange Phenomenon

Md. Ehesan Ali^{*,†} and Peter M. Oppeneer[‡]

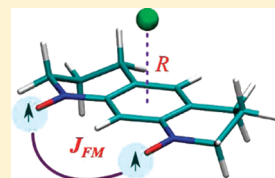
[†]Center for Theoretical Chemistry, Ruhr-Universität Bochum, D-44801, Bochum, Germany

[‡]Department of Physics and Astronomy, Uppsala University, Box 516, S-751 20 Uppsala, Sweden

 Supporting Information

ABSTRACT: The role of noncovalent ion– π interactions in controlling the intramolecular magnetic exchange interaction in 1,3-phenylene-based bis(aminoxyl) diradical has been investigated computationally through deploying an external ion in the vicinity of the π -cloud of the phenylene coupler. Using spin-polarized hybrid density functional theory-based calculations, we observe that the anions drastically enhance the magnetic exchange interaction for distances below the equilibrium distance. The phenomenon could be understood by two simultaneously occurring effects, which influence the intramolecular magnetic exchange interaction. The first one is the enhancement of the paratropic current density on the aryl couplers due to a small amount of charge transfer. The other one is the attainment of magnetization density on the anionic species due to such charge transfer, favorably altering the magnetic exchange pathway. The achieved understanding provides prospects of a completely new strategy of enhancing the intramolecular ferromagnetic coupling through the assistance of external ionic species inserted in molecular crystals.

SECTION: Molecular Structure, Quantum Chemistry, General Theory



Magnetic materials based on pure organic substances are of fundamental importance.^{1,2} The envisaged technological applications of such magnetic materials require that these exhibit strong ferromagnetic exchange interactions.³ In organic molecular magnetism, the *m*-phenylene coupler is found to be a promising spacer in conveying a substantial ferromagnetic exchange interaction between the two attached spin sources.⁴ There have already been a number of efforts devoted to increasing the strength of the ferromagnetic exchange interaction on the basis of *m*-phenylene couplers.^{5–8} Mostly these are based on substitution on the different positions of the spacer using various electron withdrawing or electron donating groups, constraining the rotation of the spin containing groups, and by cross conjugation of various spin-sources.^{9,7,10} The *m*-phenylene coupler mediates ferromagnetic exchange interactions; however, the nonmagnetic singlet state could be the ground state if the dihedral angles between the plane of the phenyl ring and the spin-containing groups become significantly large to prevent the π -conjugation.¹¹

In this work, we have adopted a different approach to enhance the ferromagnetic exchange coupling interaction mediated by *m*-phenylene couplers, namely, by deploying an additional external ion near to the coupler. The presence of such ions in the vicinity of the coupler's π -electron cloud can sustain the ion– π interactions. These interactions driven by noncovalent forces have already attracted considerable attention in recent years.^{12–15} The cation– π and anion– π interactions originate from the electrostatic and ion-induced polarization terms, which can be rationalized by means of the permanent quadrupole moment in aryl systems.¹⁶ Mecozzi et al. have demonstrated that the calculated electrostatic potential (ESP) at the vertical

single point from the center of the benzene ring can be used to predict the strength of cation– π interactions.¹⁷ Wheeler and Houk have observed that the noncovalent binding strength solely depends on the direct through-space interaction, the π -polarization effect has very little impact.^{18,19} Alternatively, the anion– π interactions have been explained by the π -acidic nature of the aryl substrates.^{20,21} Recently such interaction has experimentally been captured as the functional relevance of Cl[–] ion recognition by anion– π interactions.²²

Güell et al. have observed the influence of ion– π interactions on the local aromaticity of the aryl species upon a small amount of charge transfer between them.²³ However, the aromaticity of the aryl couplers contributes to a large extent to control the intramolecular magnetic exchange interactions. Ali and Datta have observed a proportionality relationship between the magnetic exchange coupling and difference of aromaticity index (Δ NICS) between the coupled and uncoupled aryl systems.²⁴ Using configuration interaction (CI) calculations, Barone et al.²⁵ investigated the contribution of various molecular fragments to the magnetic exchange coupling. They also noticed that the aromatic bridges play a significant role in the magnetic exchange coupling. Bhattacharya et al. and Latif et al. independently observed this connection for a series of biverdazyle radicals.^{26,27} The present work is based on seeking to exploit such fundamental understanding of the relationship between the aromaticity and the strength of the magnetic exchange coupling to tailor the desired magnetic properties.

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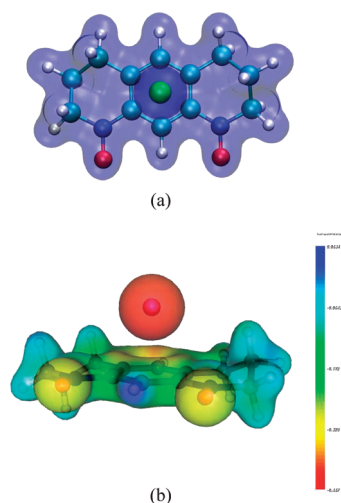


Figure 1. The ESP surface at 0.05 isodensity calculated for the optimized molecular geometry of an 1,3-aminoxyl diradical by placing a Br^- at 2.25 Å distance from the center of the *m*-phenylene coupler. (a) The ESP of the atoms is shown by the blueish surface in the top view. Color code: cyan - C; blue - N; red - O; white - H; and green - Br. (b) Side view of the ESP, with the sign of the isovalues indicated in the scale bar. The two unpaired spins of the diradical are mainly localized on the $-\text{NO}$ groups.

To investigate the effect of noncovalent interactions on the intramolecular magnetic exchange phenomenon, we have chosen a prototypical *m*-phenylene-based bis(aminoxyl) diradical. The special feature of this diradical is that the spin-containing $-\text{NO}\cdot$ are restricted for the rotational conformation due to the cyclic closed ring structure. This excludes any other interaction with an external ion except the ion- π interactions in our studies.

The diradical is similar to the 1,3-phenylene-based bis(aminoxyl) diradical that was synthesized by Rassat et al.,²⁸ and its magnetic properties were investigated by Rajca et al.¹⁰ Our molecular geometry optimization of this prototype diradical, performed with the Gaussian09 code²⁹ at the UB3LYP/6-311+G(d,p) level, reveals that the spin containing groups ($-\text{NO}\cdot$) are in one plane with the phenylene ring (see Figure 1). Three cations (Li^+ , Na^+ , and K^+) as well as three anions (F^- , Cl^- , and Br^-) are placed once at a time above the center of the optimized phenylene ring. The potential energy surface for the ion- π interactions are subsequently scanned by varying the ionic distance from the center of the aryl ring from 1.0 Å to 5.0 Å with an interval of 0.1 Å. The equilibrium distances for the anions F^- , Cl^- , and Br^- are 2.80, 3.55, and 3.75 Å, respectively, whereas for the cations Li^+ , Na^+ , and K^+ these are 1.80, 2.40, and 2.90 Å, respectively.

The counterpoise correction for the basis set superposition errors (BSSEs) is calculated for each ionic species and for all 10 points on the potential energy surface that are chosen for the calculation of the magnetic exchange coupling. The BSSEs are calculated for both spin states as well. The BSSEs are found to be a spin-dependent quantity; therefore, they have an impact on the magnetic exchange coupling calculations, with a maximum effect of up to 60 cm^{-1} for the shortest ion- π distances. The BSSE correction becomes less important for the larger ion- π distances. The magnetic coupling constants are defined by the Heisenberg spin-Hamiltonian as $\hat{H} = -J\hat{S}_A \cdot \hat{S}_B$, where $2J$ is the singlet-triplet energy splitting. A positive sign of J indicates a

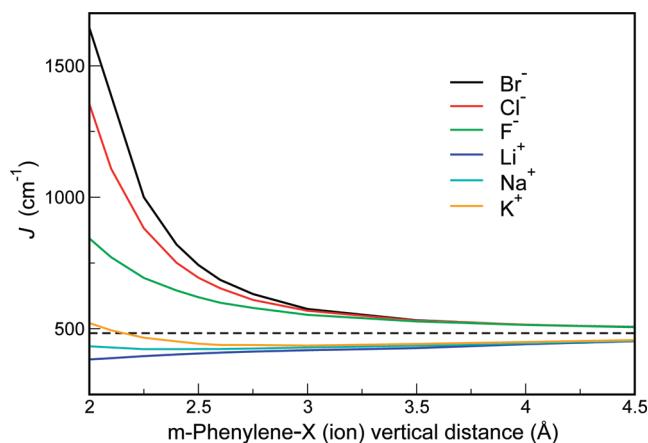


Figure 2. The calculated exchange coupling constant J (in cm^{-1}) versus the *m*-phenylene-ion distance, for the ions listed in the legend. The dotted line is for the calculated J in the absence of an external ion. The equilibrium distances for the anions F^- , Cl^- , and Br^- are 2.80, 3.55, and 3.75 Å, respectively, whereas for the cations Li^+ , Na^+ , and K^+ these are 1.80, 2.40, and 2.90 Å, respectively.

ferromagnetic interaction. In this work, the exchange interactions are obtained using spin-polarized density functional theory (DFT) calculations in combination with Noodleman's spin-projected broken-symmetry expression, $J = (E_{\text{BS}} - E_{\text{HS}})/S_{\text{max}}^2$, where E_{BS} and E_{HS} are the broken-symmetry total energy and high spin total energy, respectively.³⁰ Extensive discussions on theoretical concepts, success and challenges in the broken-symmetry methodologies can be found in several popular articles and reviews on the field.^{30–35} All the magnetic exchange constants presented here have been calculated using the M06-2X functional,^{36,37} as we find a better performance of this functional for exchange constant J calculations as compared to B3LYP by 82 cm^{-1} and PBE0 by 215 cm^{-1} .

The calculated magnetic exchange coupling between the two radical centers coupled by the *m*-phenylene spacer is ferromagnetic, which agrees with the experimental observations.¹⁰ Pure DFT-based methods overestimate the J value; nevertheless, they reproduce the nature of the magnetic coupling. The overestimation might well be attributed to an artifact of DFT-based functionals that fail to correct the inherent self-interactions errors and thereby lead to an artificial stronger delocalization of the magnetic orbitals. The nonlocal exact Hartree-Fock (HF) exchange in the hybrid-functionals acts as a remedy to the self-interaction problem. However, the introduced hybrid mixing parameter can in some cases become system dependent, and an inappropriate large mixing of HF exchange might lead to a loss of some information about the correlated behaviors of unpaired electrons. The on-site Hubbard- U approach is of the alternative solution, but the choice of the Hubbard- U value for the nonmetallic atoms or its linear response evaluation is another issue.³⁸ After having performed a series of test calculations, we have found that the M06-2X functional is a good choice for the present study. A reasonable J value (+485 cm^{-1}) is obtained, whereas the experimental values for the similar diradicals were found in solution as well as in solid state in the range of +139 to +278 cm^{-1} .^{10,39}

The calculated J for the prototype molecule and its variation in the presence of additional ionic species with their distance to the molecule are plotted in Figure 2. The presence of an external

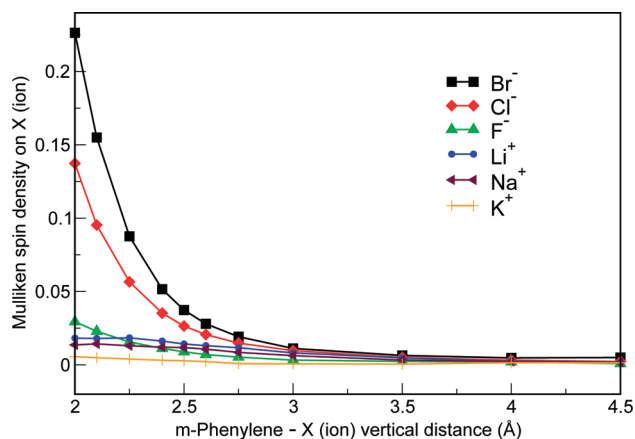


Figure 3. The accumulated Mulliken spin density on the ion versus the *m*-phenylene to ion distance.

ionic species on the coupled diradicals considerably influences the calculated J values. The source of such influence depends on the type of the external ions. A larger influence is observed for the Br^- ion, whereas the least influence is found for the Li^+ ion. The pattern of the deviation of the computed J for the ion–diradical system from the free diradical J value is different for the anions and cations. Below the equilibrium distances R_e , the calculated J increases with the decrease of the coupler–ion distances except for the Li^+ ion. The anions, especially Br^- and Cl^- , drastically enhance the magnetic exchange interactions in this distance range. This observation clearly indicates that the presence of doped anions in a molecular crystal or trapped anions in molecular cage-type structures can drastically enhance the magnetic exchange interaction through the nonconventional ion– π interactions.

The Mulliken atomic spin population of the external ion and its plot against the ion– π distances for all ionic species, shown in Figure 3, reveal that the cations remain nonmagnetic throughout the whole range of varying distances (2–5 Å). However, the anions have a definite trend to acquire a considerable amount of spin density, particularly below their equilibrium distances. The amount of spin-density on the anion inversely increases with the distance, and a maximum value is found for the Br^- ion at 2 Å (0.23). The spin-density on the Br^- ion at 2.25 Å and at 4.5 Å are shown in Figure 4. The accumulated spin density on the Br^- is of the same spin type as the spin-density on the unpaired spin centers. This unusual spin-density facilitates the enhanced spin–exchange interaction.

Below R_e , the charge distribution on the external ion also starts to perturb from the usual ionic distribution. The ESP plot in Figure 1b rules out any direct overlap of the charge densities of the two subsystems, although a repulsive potential develops below the R_e . This perturbation becomes larger as the distances decrease. However, the nature of the perturbation is completely different for anions and for cations. Cations pull equal amounts of α and β π -electron density from the phenylene-ring toward them when placed at distances below the R_e . As a consequence, the cations remain silent with regard to the magnetization distribution when varying the distance. On the other hand, some amount of anionic charge (β -electron density) spills into the π -ring systems from electron charge rich anions. Again, as the distance between the anion and the π -ring system decreases the spilling increases. These extra charges on the π -ring systems have a larger

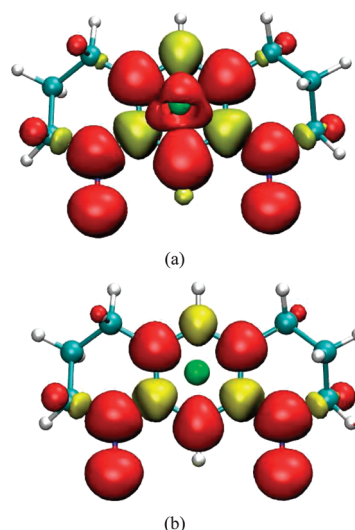


Figure 4. Plot of the spin-density induced by bromide– π interactions, for a Br^- –coupler vertical distance of (a) 2.25 Å, and (b) 4.5 Å.

impact on the aromaticity of the coupler. The NICS calculations indicate that, as the spilling to the π -ring systems increases, the paratropic current inside the π -ring systems increases, too. This increase of paratropic current density on the coupler directly has an impact on the magnetic exchange interaction of the connected spin sources. The enhancement of paratropic current density is not possible in a similar fashion for the cations, and for these it remains almost constant throughout all distances. The accumulated spin-density on the anionic species has the same spin-type (α -density) as the unpaired spins (see Figure 4). Hence the larger the (β -spin density) charge transfer to the π -systems, the more the overall α spin density on the anion increases and a better facilitation of the intramolecular magnetic exchange interaction occurs.

In summary, the presence of an external ion near the aromatic coupler distinctly influences the magnetic exchange interaction. Especially, the anions Br^- and Cl^- drastically influence the magnetic exchange interaction when these occur at distances below their respective equilibrium distances. The reason for such drastic enhancement is found to be twofold. First, there is the increase of the paratropic current density due to the small amount of charge transfer to the aromatic ring system from the anion. The other reason is the accumulation of magnetization density on the external anion upon the occurring charge transfer. The accumulated spin-density on the external ions alters the microscopic intramolecular exchange coupling to a more favorable spin distribution that greatly stimulates an enhanced exchange constant J .

■ ASSOCIATED CONTENT

S Supporting Information. The atomic charges on the external ions and the calculated NICS values with varying phenylene–ion distances. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ehesan.ali@theochem.rub.de.

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