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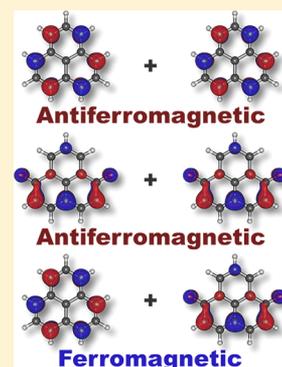
# The Role of Orbital Symmetries in Enforcing Ferromagnetic Ground State in Mixed Radical Dimers

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## Supporting Information

**ABSTRACT:** One of the first steps in designing ferromagnetic (FM) molecular materials of p-block radicals is the suppression of covalent radical–radical interactions that stabilize a diamagnetic ground state. In this contribution, we demonstrate that FM coupling between p-block radicals can be achieved by constructing mixed dimers from different radicals with differing symmetries of their singly occupied molecular orbitals. The applicability of this approach is demonstrated by studying magnetic interactions in organic radical dimers built from different derivatives of the well-known phenalenyl radical. The calculated enthalpies of dimerization for different homo- and heterodimers show that the formation of a mixed dimer with FM coupling is favored compared to the formation of homodimers with antiferromagnetic (AFM) coupling. We argue that cocrystallization of radicals with specifically tuned morphologies of their singly occupied molecular orbitals is a feasible and promising approach in designing new organic magnetic materials.



Ever since the discovery of ferromagnetic long-range ordering of spins in the  $\beta$ -phase of *para*-nitrophenyl nitronyl nitroxide,<sup>1</sup> much effort has been devoted to the design of new p-block magnetic materials.<sup>2–5</sup> The spin-carrying building blocks of these solids are neutral organic or organo main-group radicals with existing examples based on systems such as nitroxides<sup>6–9</sup> and dithiazolyls.<sup>10,11</sup> While a great number of other stable radical frameworks are also known,<sup>12–14</sup> it remains a formidable challenge to assemble them to crystalline solids in such a way that long-range magnetic ordering is achieved. Nature has a strong tendency toward spin-pairing, especially in low-symmetry p-block systems, which typically leads to bond formation and/or dimerization. The propensity of radicals to associate can be affected by synthetic design, that is, using steric protection or electron delocalization, which both prevent the favorable overlap of their frontier orbitals.<sup>12–14</sup> However, this can easily lead to complete isolation of radicals in the solid state, thus suppressing all interactions between spin-carrying building blocks and resulting in a paramagnetic material.

In systems comprising molecular radicals, ferromagnetic (FM) coupling of spins generally requires that the singly occupied molecular orbitals (SOMOs) of the interacting radicals have large amplitudes in the same spatial region to ensure sufficient exchange interaction, but at the same time the SOMOs must be orthogonal to each other to prevent covalent interaction, which stabilizes an antiferromagnetic (AFM) configuration.<sup>15,16</sup> Orthogonality is most often achieved through appropriate chemical substitution that induces a suitable supramolecular arrangement in the solid state, like the alignment of p-block radicals into slipped  $\pi$ -stacks.<sup>14</sup> Such a situation is called *accidental orthogonality*, and it is very difficult to achieve and even more difficult to fine-tune. Therefore, the

resulting magnetic properties are usually sensitive to even the smallest of perturbations. Furthermore, while ensuring orbital orthogonality, the slipped alignment of radicals keeps the neighboring SOMOs spatially separated, thereby resulting in weak magnetic interactions and low ordering temperatures.

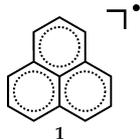
In the context of transition-metal complexes, Kahn and co-workers enforced strong FM coupling by taking advantage of symmetry-imposed orthogonality of the SOMOs of two transition-metal ions within a common ligand framework.<sup>17–19</sup> In this Letter we demonstrate how Kahn's *strict orthogonality* approach can be extended to p-block radical chemistry by using two different radicals with complementary SOMO morphologies, resulting in complete cancellation of SOMO–SOMO overlap and FM coupling. While radical cocrystallization has been previously applied in the design of main-group ferromagnets,<sup>20–26</sup> all currently published examples use building blocks with qualitative identical SOMOs and which cannot, therefore, display anything more than accidental orthogonality. We will demonstrate the applicability of the approach by quantum chemical calculations on radical dimers constructed from derivatives of the real-life odd-alternate hydrocarbon phenalenyl (**1**).<sup>27–31</sup> Compound **1** was chosen as a testing ground for the proposed approach because of its structural tunability<sup>32</sup> and the wealth of available data (both experimental and computational). However, the results herein can also be applied to other p-block radical frameworks. To the best of our knowledge, quantitative theoretical studies on real-world radical pairs with mixed orbital symmetries have not been published before, although the importance of the nodal

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properties of SOMOs has been noted,<sup>16</sup> and various systems composed of neutral organic radicals and diamagnetic spacers have been thoroughly investigated.<sup>33–37</sup>



The magnetic properties of a radical dimer consisting of radicals  $a$  and  $b$  can be described by the Heisenberg–Dirac–van Vleck (HDvV) Hamiltonian

$$\hat{H}_{\text{HDvV}} = -J\hat{S}_a \cdot \hat{S}_b \quad (1)$$

where  $\hat{S}_a$  and  $\hat{S}_b$  are effective spin operators acting on the radicals  $a$  and  $b$ , respectively, and  $J$  is the exchange coupling constant, which determines the type (FM or AFM) and magnitude of the interaction. A negative value favors AFM alignment of the spins, whereas a positive value stabilizes a FM configuration. The nature of the interaction can be qualitatively rationalized by considering the two radical SOMOs  $\chi_a$  and  $\chi_b$ . The orbitals are not, in general, orthogonal but have a finite overlap  $\langle \chi_a | \chi_b \rangle = S_{ab}$ . In practice, it is more useful to formulate expressions in terms of orthogonal magnetic orbitals  $\phi_a$  and  $\phi_b$  ( $\langle \phi_a | \phi_b \rangle = 0$ ), which maximally resemble  $\chi_a$  and  $\chi_b$ . At the orthogonal limit of the SOMOs ( $S_{ab} = 0$ ),  $\phi_a = \chi_a$  and  $\phi_b = \chi_b$ . Following Anderson,<sup>38</sup> the exchange coupling constant can then be approximated in terms of  $\phi_a$  and  $\phi_b$  as

$$J = 2K_{ab} - \left( \frac{2}{U_{aa} - U_{ab}} + \frac{2}{U_{bb} - U_{ba}} \right) t_{ab}^2 \quad (2)$$

where  $K_{ab} = \langle \phi_a \phi_b | r_{12}^{-1} | \phi_b \phi_a \rangle$  is an exchange integral and  $t_{ab} = \langle \phi_a | \hat{F} | \phi_b \rangle$  is the transfer integral between  $\phi_a$  and  $\phi_b$  given by the matrix element of the Fock operator  $\hat{F}$ ;  $U_{ij} = \langle \phi_i \phi_j | r_{12}^{-1} | \phi_i \phi_j \rangle$  are Coulomb repulsion energies.  $K_{ab}$ ,  $t_{ab}^2$ ,  $U_{aa} - U_{ab}$ , and  $U_{bb} - U_{ba}$  are all positive numbers.

The first term on the right-hand side of eq 2 is the direct exchange interaction, which always favors a FM configuration, while the second term is the kinetic exchange, which favors AFM exchange. The direct exchange is large when the two magnetic orbitals have large amplitudes in the same spatial region, that is, the overlap of the densities of the two SOMOs is large. This, however, also leads to strong transfer interaction (i.e., covalency), which usually dominates over the direct exchange and leads to overall AFM coupling and a diamagnetic ground state. In order for the coupling to be FM, the transfer interaction must be zero or very nearly so. In the strict orthogonality approach, the transfer interaction is made to vanish by symmetry considerations. The Fock operator must transform as a representation of the dimer point group and can be written in a basis of symmetry-adapted orbitals where all matrix elements between orbitals transforming according to different representations of the molecular point group vanish, and the respective transfer parameters are then exactly zero, leading to FM coupling.

Let us first consider the more often encountered situation: a homodimer constructed of two radicals with identical SOMOs. Let us further assume that the two SOMOs in the dimer geometry are related to one another by a symmetry operation of the dimer point group, say inversion. This is the situation most often encountered for p-block radicals in the crystalline state. A variational minimization of the total energy relative to orbital variations, under the constraint that the orbitals must

remain orthonormal and transform as representations of the molecular point group, leads to two symmetry-adapted orbital combinations: a doubly occupied orbital of *gerade* (g) symmetry and an unoccupied orbital of *ungerade* (u) symmetry:

$$\phi_g = \frac{1}{\sqrt{2}}(\phi_a + \phi_b) = \frac{1}{\sqrt{2 + 2S_{ab}}}(\chi_a + \chi_b) \quad (3)$$

$$\phi_u = \frac{1}{\sqrt{2}}(\phi_a - \phi_b) = \frac{1}{\sqrt{2 - 2S_{ab}}}(\chi_a - \chi_b) \quad (4)$$

The orthogonal magnetic orbitals can then be written as

$$\phi_a = \frac{1}{\sqrt{2}}(\phi_g + \phi_u) \text{ and } \phi_b = \frac{1}{\sqrt{2}}(\phi_g - \phi_u) \quad (5)$$

and the transfer parameter is given by

$$t_{ab} = \langle \phi_a | \hat{F} | \phi_b \rangle = \frac{1}{2} \langle \phi_g + \phi_u | \hat{F} | \phi_g - \phi_u \rangle = \frac{1}{2}(\epsilon_g - \epsilon_u) \quad (6)$$

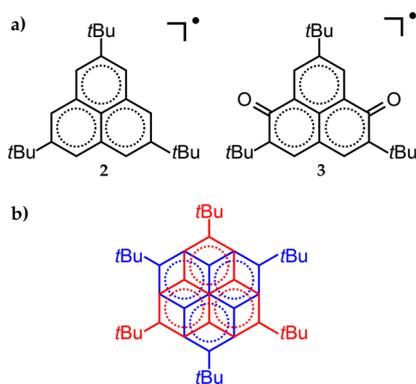
because the Fock operator is diagonal in the symmetry-adapted molecular orbitals with eigenvalues  $\epsilon_g$  and  $\epsilon_u$ . Thus, the transfer parameter is given by the negative of the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap, which is always nonzero when the two radicals are interacting. The gap vanishes only when the spatial distance between the two SOMOs grows large, but this then also leads to a vanishing  $K_{ab}$  and a paramagnetic ground state.

Let us then consider a situation where a mixed dimer is constructed from two different radicals with SOMOs of different morphology. Let us assume that the dimer has a point-group symmetry with at least two different irreducible representations and that the two radical SOMOs are *not* carried onto each other by any symmetry operation. In practice this means that the point group contains a mirror plane, which dissects the two SOMOs in the dimer geometry. Let us further assume that the two SOMOs transform according to different representations of the point group. In this situation, no linear combination mixing  $\chi_a$  and  $\chi_b$  can be taken that would still be a symmetry-adapted function. Therefore, the variational minimization of the energy with symmetry constraints imposed simply yields the two orbitals  $\phi_a = \chi_a$  and  $\phi_b = \chi_b$ , which are orthogonal to each other. Because now  $\hat{F}$  is diagonal in  $\phi_a$  and  $\phi_b$

$$t_{ab} = \langle \phi_a | \hat{F} | \phi_b \rangle = 0 \quad (7)$$

and the interaction must be FM. This result can be equivalently interpreted as a vanishing HOMO–LUMO gap, which leads to FM coupling configuration by Hund's rule. Thus, the condition of strict orthogonality in radical dimers can be summarized as follows: each magnetic orbital (which in this situation are equivalent to the radical SOMOs) must form a basis for a different representation of the molecular point group of the dimer. It is immediately obvious that these conditions can be realized only in a mixed dimer consisting of two different radicals. The rationalization presented here also holds for pseudosymmetries that are sufficiently close to exact symmetries of idealized models, as demonstrated by the calculations below.

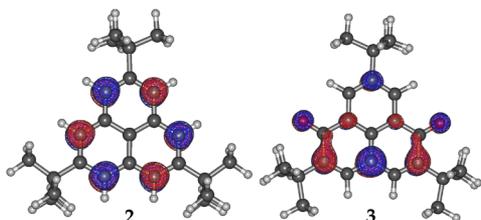
The two phenalenyl derivatives 2,5,8-tri-*tert*-butyl-phenalenyl (2, Figure 1a)<sup>39</sup> and 2,5,7-tri-*tert*-butyl-6-oxophenalenoxyl



**Figure 1.** (a) Structures of 2,5,8-tri-*tert*-butyl-phenalenyl (**2**) and 2,5,8-tri-*tert*-butyl-6-oxophenalenoxyl **3**; (b) projection graph of staggered conformation of a 2–2 dimer.

(**3**, [Figure 1a](#))<sup>40</sup> provide an ideal testing ground for the application of strict orthogonality to p-block radicals. Both **2** and **3** are stable species with highly delocalized SOMOs and crystallize in staggered dimers (see [Figure 1b](#)). The radical–radical interaction in 2–2 is very strong and AFM, bordering on a 12-center-2-electron covalent bond.<sup>41,42</sup> The nature of this interaction has been the subject of numerous experimental and theoretical studies, and it has been thoroughly discussed in the literature.<sup>41–54</sup> The exchange coupling constant for the radical–radical interaction has been estimated based on superconducting quantum interference device (SQUID) and electron paramagnetic resonance (EPR) measurements as  $-1390\text{ cm}^{-1}$  and  $-2910\text{ cm}^{-1}$ , respectively.<sup>39,40,55,56</sup> The SQUID measurements have been carried out in the presence of paramagnetic impurities, and the value can be considered tentative at best. Considering the large difference between the SQUID and EPR values, the experimental coupling constant should simply be interpreted as “large” and AFM. Less experimental data is available for 3–3. The crystal structure has been determined, but it is highly disordered. Based on the distance between the central carbons of the two radicals in 2–2 (3.201 Å) and 3–3 (3.492 Å), the radical–radical interaction in 3–3 can be considered considerably weaker.

The phenalenyl and 6-oxophenalenoxyl cores of **2** and **3** have  $D_{3h}$  and  $C_{2v}$  symmetries, respectively. Although the presence of *tert*-butyl groups lowers the actual symmetry, the SOMOs resemble those in the idealized symmetries very closely and will be discussed as such. The SOMOs of both **2** and **3** ([Figure 2](#)) have reflection symmetry relative to a mirror plane perpendicular to the radical plane, which is retained in the staggered dimer structure. The SOMO of **2** is antisymmetric relative to reflection, whereas the SOMO of **3** is symmetric. Thus, in a mixed 2–3 dimer, the two SOMOs form a basis for a different representation of the approximate



**Figure 2.** Singly occupied molecular orbitals (SOMOs) of **2** and **3**.

dimer point group and should show FM interaction and a triplet ground state.

The geometries of the 2–2, 3–3, and 2–3 dimers were optimized at the density functional theory (DFT) level. The range-separated LC- $\omega$ PBE hybrid exchange–correlation (XC) functional<sup>57–59</sup> with the empirical DFT-D3 dispersion correction<sup>60</sup> utilizing the Becke–Johnson damping function<sup>61</sup> was chosen based on a validation study. This choice of XC functional and dispersion correction was able to accurately produce the experimentally observed distance between the two monomers in the 2–2 dimer. Furthermore, the LC- $\omega$ PBE XC functional has been previously shown to produce accurate estimates of exchange coupling constants in various systems.<sup>62–65</sup> Details of the computational methods and the validation study are given in the [Supporting Information](#). The geometry optimizations were carried out in both the low-spin (LS) state where the spin projection was confined to  $M_S = 0$  and the high-spin (HS) state where  $M_S = 1$ . These geometries were taken as reasonable approximations of the singlet and triplet geometries, respectively. The exchange coupling constants were evaluated in these geometries ( $J_{LS}$  and  $J_{HS}$ ) and on the basis of an adiabatic singlet–triplet gap ( $J_{\text{adiabatic}}$ ) using the broken symmetry (BS) formalism<sup>66–68</sup> in conjunction with the Yamaguchi projection<sup>69–72</sup> (see the [Supporting Information](#)). The results are listed in [Table 1](#)

**Table 1.** Calculated Exchange Coupling Constants (in  $\text{cm}^{-1}$ ) of Dimers 2–2, 3–3, and 2–3 in LS and HS Geometries ( $J_{LS}$  and  $J_{HS}$ ) and As Evaluated from the Adiabatic Singlet–Triplet Splitting ( $J_{\text{adiabatic}}$ )

	$J_{LS}$	$J_{HS}$	$J_{\text{adiabatic}}$
2–2	–2141	–515	–1741
3–3	–75	–33	–102
2–3	370	435	468

and are fully consistent with experimental measurements in the case of 2–2 and 3–3 and with theoretical prediction in the case of 2–3. The predicted exchange interaction in 2–2, as calculated in the LS geometry, is  $-2141\text{ cm}^{-1}$ , which falls between the two experimentally determined values. The exchange interaction in 3–3 is weak and AFM, as can be expected based on the considerably longer radical–radical distance in 3–3 as compared to 2–2. In the mixed 2–3 dimer, however, the interaction is FM and relatively strong, as predicted by theory. The type of the exchange interaction does not depend on whether the coupling constant is calculated in the LS or HS geometry, or by using the adiabatic singlet–triplet splitting; thus, the results can be considered as reliable and insensitive to small structural variations.

The results listed in [Table 1](#) unambiguously confirm that constructing a dimer from radicals with SOMO symmetries that form bases for different representations of the point group corresponding to the dimer pseudosymmetry leads to FM interaction. The next question that arises is how favorable the formation of the mixed dimer is energetically. Because any cocrystallization requires mixing the two different radicals, it is always possible that the radicals will not form a mixed dimer but will instead opt to dimerize into diamagnetic homodimers. To shed light on this matter, the dimerization enthalpies of 2–2, 3–3, and 2–3 were determined computationally. The enthalpies were calculated by using the DFT optimized geometries, enthalpy corrections, and exchange coupling

constants, coupled with electronic energies evaluated using the highly accurate DLPNO-CCSD(T) method.<sup>73–77</sup> Details of the calculations are given in the [Supporting Information](#), and the calculated dimerization energies and enthalpies are listed in [Table 2](#). The energies were corrected for basis set super-

**Table 2. Calculated Dimerization Energies and Enthalpies (in kJ mol<sup>-1</sup>) of Dimers 2–2, 3–3, and 2–3 in LS and HS Geometries**

	$\Delta E_{\text{LS}}$	$\Delta E_{\text{HS}}$	$\Delta H_{\text{LS}}$	$\Delta H_{\text{HS}}$
2–2	–76.2	–67.1	–68.9	–54.9
3–3	–65.9	–65.0	–59.3	–58.0
2–3	–74.3	–74.4	–67.2	–72.5

position error (BSSE) using the counterpoise correction.<sup>78</sup> The large number of short intermolecular distances between the atoms of the two radicals leads to very significant BSSE (20–30 kJ mol<sup>-1</sup>, see [Table S3](#)), and correcting this is absolutely vital in order to obtain reliable results.

The energies and enthalpies in [Table 2](#) show essentially the same trend for which reason we will discuss only the enthalpies as they provide a closer comparison with experiment. The dimerization enthalpy of the low-spin state of 2–2 has been determined experimentally as –31.4, –36.8, or –39.9 kJ mol<sup>-1</sup> depending on the measurement<sup>41,42</sup> (see the [Supporting Information](#) for further discussion). The computed dimerization enthalpy of 2–2 is considerably larger than the experimental values, but it is still reasonable. The observed deviations might arise from nonelectrostatic solvent interactions stabilizing the free radicals in the experimental measurements. However, the calculated trends and relevant differences between the different dimerization enthalpies should still be reliable, and these are the quantities we are most interested in.

The interaction energy can be roughly divided into two components that arise from the SOMO–SOMO interaction (i.e., AFM exchange or covalency) and dispersion interaction (or more generally, van der Waals interactions). Because the covalent interaction is possible only in AFM configuration, the interaction in the HS states can be estimated as arising purely from van der Waals forces.<sup>50,52</sup> In the case of 3–3 and 2–3, the dimerization enthalpy is almost the same in the LS and HS states. In 3–3, the energy difference between the LS and HS states originates from weak covalency arising from the AFM interaction, and in 2–3 from the stabilization of the HS state by the exchange interaction. The presence of the *tert*-butyl groups prevents the monomers in 2–3 from sliding relative to each other and, thus, prevents the formation of covalent interaction stabilizing the LS state. Only in 2–2 is the covalency between the monomers strong enough to provide a clear energetic difference between the enthalpies of the LS and HS states. Kertesz and co-workers have shown that in case of the simple 1–1 dimer with no substituents, all bonding interaction arises from SOMO–SOMO covalency.<sup>50</sup> Thus, the energetics favoring the formation of the HS dimers 2–2, 3–3, and 2–3 can be attributed to the van der Waals interactions between the *tert*-butyl substituents, with SOMO–SOMO interaction playing only a minor role in the overall stability of these systems. This is extremely encouraging as in mixed radical dimers where FM SOMO–SOMO interaction takes place, any covalency is necessarily absent, and the interactions stabilizing the radical dimer must arise either from dispersion

or electrostatics, and in the case of neutral radicals, only the former can make a significant contribution to the dimerization enthalpy. It is also encouraging to observe that the total enthalpy change for the formation of two equivalents of 2–3 from two equivalents of 2 and 3 is –145.0 kJ mol<sup>-1</sup>, whereas the respective value for the formation of one equivalent of 2–2 and one equivalent of 3–3 is –128.2 kJ mol<sup>-1</sup>. Thus, the calculations show that the formation of the mixed dimer is favored over conventional homodimers. The more favorable dimerization enthalpy of 2–3 is most likely a result of short O–H contacts (2.565 Å to 2.806 Å) that leads to a more favorable noncovalent radical–radical interaction. It should be pointed out that the calculated enthalpies of 2–2 are not in full agreement with experiment and that the magnetic properties will ultimately be determined by the solid-state structure, which is also affected by crystal forces not accounted for in calculations. The results do nonetheless demonstrate that the formation of the mixed dimer is energetically comparable to formation of homodimers and can be made even more favorable by further structural modifications.

In summary, we have shown both by theoretical rationalization and by practical calculations on dimers of different phenalenyl derivatives that constructing mixed dimers from radicals with SOMOs that transform differently under the symmetry operations of the dimer will lead to a triplet ground state and FM interaction. We have further shown that the energetics for the formation of the mixed dimer remain favorable compared to the formation of the diamagnetic AFM coupled dimers, despite the lack of covalent SOMO–SOMO interaction in the FM case. The results were demonstrated here for phenalenyl-based systems, but they can be generalized to any p-block radical framework where the radicals have sufficient symmetry or pseudosymmetry (namely, a mirror plane) that the SOMOs can be assigned to different representations of the overall point group. If the skeleton of a  $\pi$ -conjugated p-block radical has reflection symmetry, the symmetry of the SOMO (symmetric or antisymmetric relative to the reflection) can be tuned by introduction of substituents that take part in the  $\pi$  conjugation as is done by the oxygen atoms in the case of 2 and 3. Thus, the approach presented here can be applied to existing systems of cocrystallized radicals with relatively minor structural modifications and provides valuable guidelines to the future design of p-block radical-based magnetic molecular materials.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the [ACS Publications website](#) at DOI: [10.1021/acs.jpcllett.8b01507](https://doi.org/10.1021/acs.jpcllett.8b01507).

Computational details, validation of different exchange–correlation functionals, additional computational data, and optimized Cartesian coordinates of the studied systems ([PDF](#))

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## Notes

The authors declare no competing financial interest.

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