OL | Organic Letters

pubs.acs.org/OrgLett Letter

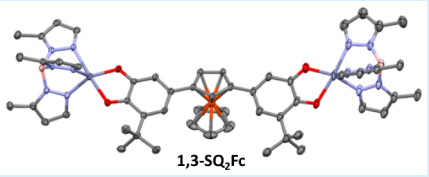
Magnetic Exchange Coupling through the Nonalternant Cyclopentadienyl π-System of Ferrocene

Patrick Hewitt, David A. Shultz,* and Martin L. Kirk*

Cite This: *Org. Lett.* 2021, 23, 8235–8239 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Electronic and magnetic coupling through nonalternant π-systems is an area of intense interest in photonics and molecular electronics research, yet relatively little is known regarding coupling through nonalternant π-systems. Herein we present magnetic exchange coupling in two semiquinone-based biradicals: **1,3-SQ$_2$Fc** has two semiquinone radicals attached to the one- and three-positions of the same cyclopentadienyl ligand (a nonalternant π-system) of ferrocene, whereas **1,1′-SQ$_2$Fc** has one semiquinone radical attached to each of the two cyclopentadienyl ligands of ferrocene.



Electronic and magnetic exchange coupling through alternant[1] organic π-systems (e.g., benzene) have been studied extensively, are well understood, and can be illustrated by topographical models.[2−11] Conversely, magnetic exchange mediated by nonalternant π-systems is not well understood.[12] As an example, we recently reported triplet ground states for biradicals composed of two S = 1/2 semiquinone (SQ) units bridged by azulene (**1,3-SQ$_2$Az**, Figure 1) and one semiquinone and one S = 1/2 nitronylnitroxide (NN) radical covalently attached to the same five-membered ring of azulene (**1,3-SQ-Az-NN**, Figure 1).[12] Ground-state ferromagnetic (high-spin) exchange coupling in **1,3-SQ$_2$Az** and **1,3-SQ-Az-NN** is not predicted by theoretical models for biradicals bridged by alternant π-systems.

Disjoint[2] biradicals have zero overlap density between singly occupied molecular orbitals (SOMOs) and negligible exchange integrals and are therefore predicted to exhibit either antiferromagnetic exchange or very weak magnetic exchange coupling and singlet ground states. In contrast, nondisjoint[2] biradicals are predicted to exhibit ferromagnetic exchange with triplet ground states. Whereas a multitude of high-spin organic molecules, dendrimers, and polymers have been prepared based on this design principle,[13−21] little is known about multispin organics that incorporate nonalternant π-systems because very few examples exist. Although two recent reports[22,12] serve as exceptions, additional examples are required to develop predictive models for the nature of magnetic exchange coupling mediated by nonalternant π-systems. To further explore magnetic exchange coupling through nonalternant π-system bridges, we describe herein the synthesis and magnetic exchange interactions in a *nondisjoint* biradical, **1,3-SQ$_2$Fc**, for direct comparison with **1,1′-SQ$_2$Fc**.

The synthesis of each semiquinone−ferrocene compound was accomplished by the general procedures in Scheme 1 (synthetic details in the SI). Neither **1,1′-SQ$_2$Fc** nor **1,3-SQ$_2$Fc** exhibits electron paramagnetic resonance (EPR) spectra, suggesting a complex electronic structure that may contain Fc → SQ charge-transfer character admixed into the ground-state configuration. (See the SI for details.)

Structures for **1,1′-SQ$_2$Fc** and **1,3-SQ$_2$Fc** were determined by X-ray diffraction, and their thermal ellipsoid plots (50%) are shown in Figure 2. The dioxolene C−O and C−C bond lengths are consistent with the S = 1/2 anionic spin and charge distribution of the semiquinone oxidation state[23−25] (Table S7). The torsion angles (ϕ) between SQ and the covalently attached cyclopentadienyl (Cp) rings vary between these structures with ϕ = ∼17 and 22° for **1,3-SQ$_2$Fc** and ϕ = ∼35° for **1,1′-SQ$_2$Fc**.

To determine the sign and magnitude of intramolecular magnetic exchange coupling between the two SQ spins in **1,3-SQ$_2$Fc** and **1,1′-SQ$_2$Fc**, we performed variable-temperature paramagnetic susceptibility (χ_{para}) measurements (Figure 3; see the SI for details). Fitting a dimer model to the $\chi_{para}\cdot T$ versus T data yields exchange coupling constants J = −2 cm^{-1} for **1,1′-SQ$_2$Fc** and J = −15 cm^{-1} for **1,3-SQ$_2$Fc** ($H = -2J\hat{S}_{SQ1}\cdot\hat{S}_{SQ2}$). These negative J values indicate singlet ground states and further reveal the magnitude of the antiferromagnetic exchange interaction mediated by the Fc (**1,1′-SQ$_2$Fc**) and nonalternant Cp (**1,3-SQ$_2$Fc**) bridge units.

The molecular structures (specifically, the SQ−Fc torsion angles) of **1,1′-SQ$_2$Fc** and **1,3-SQ$_2$Fc** allow for the conjugation of SQ and Fc to delocalize SQ spin density onto the Cp ring. (See the SI for additional details.) Given the

Received: September 4, 2021
Published: September 29, 2021

https://doi.org/10.1021/acs.orglett.1c02982
Org. Lett. 2021, 23, 8235−8239

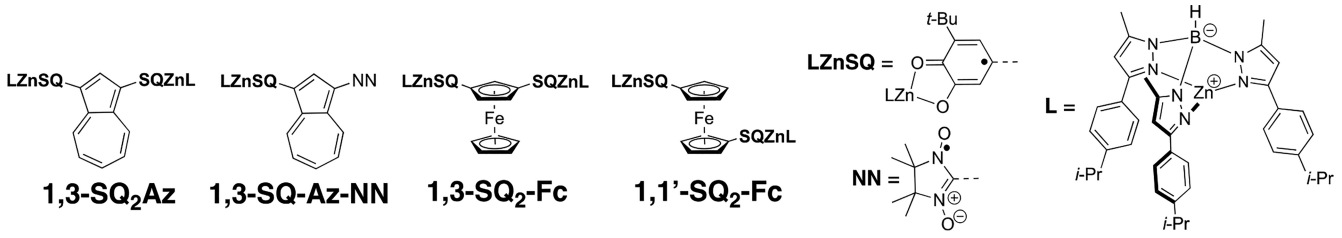
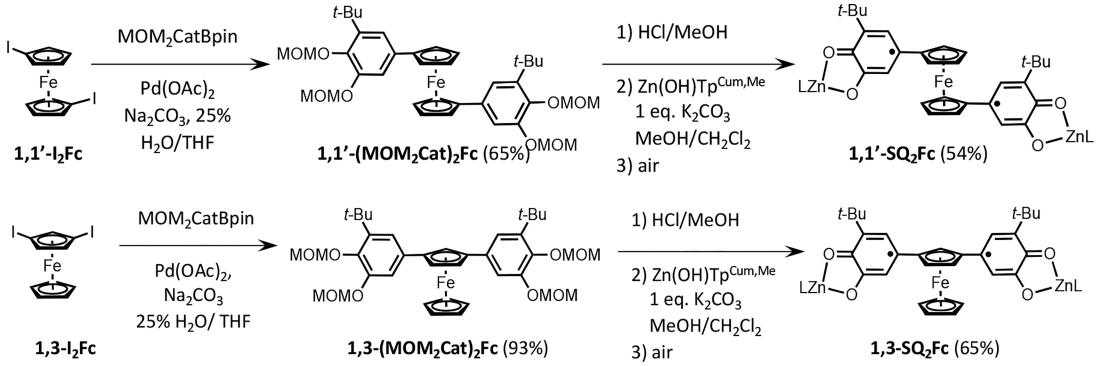


Figure 1. Azulene-bridged biradicals **1,3-SQ$_2$Az** and **1,3-SQ-Az-NN** and ferrocene-bridged biradicals **1,1′-SQ$_2$Fc** and **1,3-SQ$_2$Fc**.

Scheme 1. Syntheses of 1,1′-SQ$_2$Fc and 1,3-SQ$_2$Fc



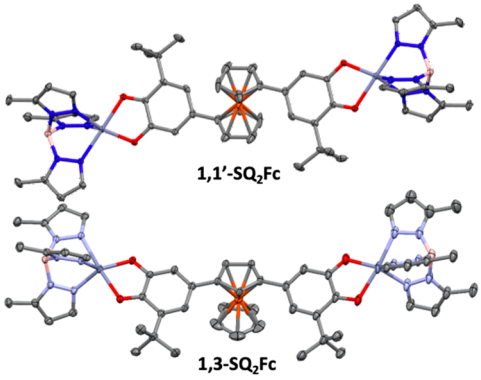


Figure 2. Thermal ellipsoid plots (50% probability) for **1,3-SQ$_2$Fc** and **1,1′-SQ$_2$Fc**. Cumenyl groups and hydrogen atoms have been omitted for clarity.

connectivity of the SQ groups in **1,3-SQ$_2$Fc**, one might expect the exchange coupling to be similar in magnitude to that of two SQ groups attached meta through a benzene bridge. However, not only is the ***J*** value for **1,3-SQ$_2$Fc** ~50% weaker than those for **1,3-SQ$_2$Ph-5-X** (X = H, *t*-Bu, OMe, NMe$_2$, NO$_2$, Ph); ***J*** = +46 with +35 cm^{-1}),[26,27] but also ***J*** for **1,3-SQ$_2$Fc** has the opposite sign compared with ***J*** for **1,3-SQ$_2$Ph-5-X**.

Compared with the ***J*** value in **1,3-SQ$_2$Az**, which possesses a nonalternant bridge, ***J*(1,3-SQ$_2$Fc)** is weaker and has the opposite sign. This is particularly surprising given that (1) the pathway from SQ to SQ in **1,3-SQ$_2$Az** is the same as that in **1,3-SQ$_2$Fc** and (2) the five-membered azulene ring carbon atoms possess partial negative charges and the Fc Cp ring carbon atoms carry 1/5 of a negative charge. Clearly, exchange coupling mediated by nonalternant π-systems is not fully understood, and it seems likely that a model based on superexchange[28−33] will require at least two dominant orbital exchange pathways.

The exchange coupling in **1,1′-SQ$_2$Fc** is about an order of magnitude weaker than that of **1,3-SQ$_2$Fc**. In fact, the weak **1,1′-SQ$_2$Fc** antiferromagnetic exchange may not reflect any properties of nonalternant π-systems,[34−38] and the coupling may indicate weak through-space Cp···Cp interactions[34,39,40] similar to those in carbene-substituted *para*-cyclophanes.[41]

Unlike magnetic exchange coupling through alternant π-systems (e.g., benzene), there is no model for predicting the nature of magnetic exchange coupling in nonalternant π-systems (e.g., azulene and Cp). Whereas the charge-separated Kekulé resonance structure in Figure 4A incorrectly predicts

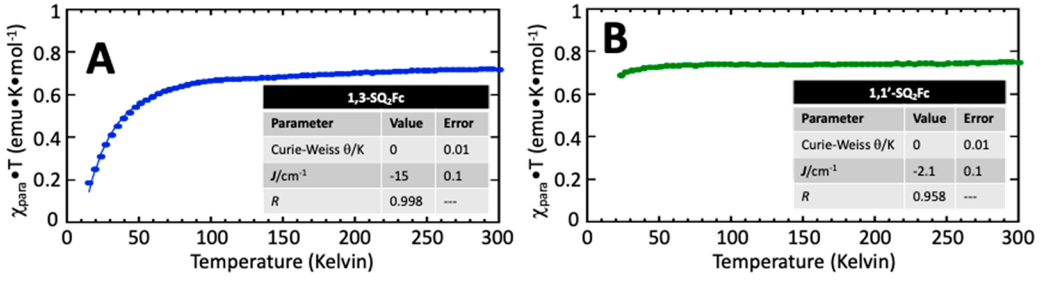


Figure 3. Plots of paramagnetic susceptibility−temperature product (χ_{para}·T) versus temperature for crystalline samples of (A) **1,3-SQ$_2$Fc** and (B) **1,1′-SQ$_2$Fc**. See the SI for fit details.

https://doi.org/10.1021/acs.orglett.1c02982
Org. Lett. 2021, 23, 8235−8239

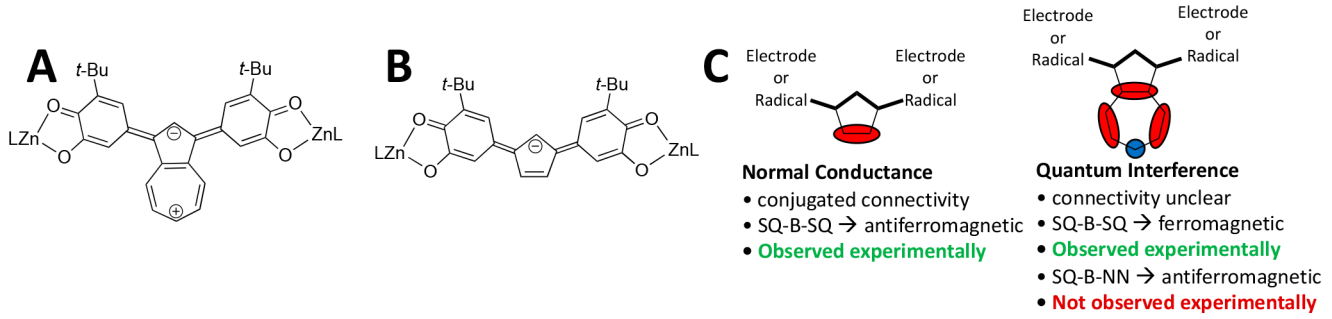


Figure 4. (A,B) Resonance and (C) conductance graphical methods for evaluating magnetic exchange.

antiferromagnetic coupling in **1,3-SQ$_2$Az**, the corresponding structure (Figure 4B) correctly predicts antiferromagnetic coupling in **1,3-SQ$_2$Fc**. The correlation of bridge-mediated magnetic exchange parameters, J, and molecular conductance, G,[6,42,43] suggests that the graphical method of Markussen[44] might be used to predict exchange coupling[6] through an Fc Cp ring. Figure 4C illustrates this method for Cp and Az bridges. The shortest pathway is highlighted with bold bond lines, and if the remaining atoms can be grouped together in pairs, then normal conductance is predicted. This is typical for a conjugative pathway (e.g., the prediction for Cp), and one may correctly conclude that two SQ radicals will be antiferromagnetically coupled. This method also correctly predicts a cross-conjugated connectivity,[45] leading to ferromagnetic SQ−SQ exchange in **1,3-SQ$_2$Az**.[12] Unfortunately, this approach does not work for **1,3-SQ-Az-NN**. We suspect that there are multiple coupling pathways present in these biradicals for which the graphical method may not be utilized. Further studies are planned to explore these pathways.

The synthesis and characterization of biradicals possessing nonalternant bridges represent the first steps in understanding the nature of electronic and magnetic coupling in nonalternant π-systems, which are currently elusive and contested.[46,47] Biradicals **1,1′-SQ$_2$Fc** and **1,3-SQ$_2$Fc** exhibit weak antiferromagnetic exchange with $J = -2$ and -15 cm^{-1}, respectively. The coupling in **1,3-SQ$_2$Fc** differs in both magnitude and sign from those of **1,3-SQ$_2$Az** (nonalternant bridge) and **1,3-SQ$_2$Ph** (alternant bridge). A graphical model can be used to predict the signs of the exchange coupling in **1,3-SQ$_2$Fc** and **1,3-SQ$_2$Az**, but it fails to predict the sign of the exchange coupling in **1,3-SQ-Az-NN**. Our results highlight the need for new molecules and models to predict the sign of the exchange coupling and, by extension, the electronic coupling mediated by nonalternant π-systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c02982.

Synthetic details and X-ray crystallographic information. Synthesis, structure, and fluid/frozen solution EPR spectra of **1-SQFc**. Cyclic voltammetry and electronic absorption spectra of **1,3-SQ$_2$Fc**, **1,1′-SQ$_2$Fc**, and **1-SQFc** (PDF)

Accession Codes

CCDC 2106485 and 2107484−2107485 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

David A. Shultz − *Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, United States;* orcid.org/0000-0001-8121-6812; Email: shultz@ncsu.edu

Martin L. Kirk − *Department of Chemistry and Chemical Biology, The University of New Mexico, Albuquerque, New Mexico 87131-0001, United States;* orcid.org/0000-0002-1479-3318; Email: mkirk@unm.edu

Author

Patrick Hewitt − *Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.1c02982

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

D.A.S. acknowledges financial support from the NSF (CHE-1931291 and CHE-1764181). M.L.K. acknowledges financial support from the NSF (CHE-CHE-1900237). This work was performed in part by the Molecular Education, Technology and Research Innovation Center (METRIC) at NC State University, which is supported by the State of North Carolina. Funding for D8 VENTURE acquisition was provided in part by North Carolina Biotechnology Center grant NCBC#2019-IDG-1010. We thank Dr. Lukasz Wojtas of the USF X-ray Facility for the structure determination of **1-SQFc**. (See the Supporting Inforamtion (SI)).

■ REFERENCES

(1) Salem, L. *Molecular Orbital Theory of Conjugated Systems*; W. A. Benjamin, Inc.: New York, 1966.
(2) Borden, W. T. *Diradicals*; Wiley: New York, 1982.
(3) Rajca, A.; Richard, J. P. The Physical Organic Chemistry of Very High-Spin Polyradicals. *Adv. Phys. Org. Chem.* **2005**, *40*, 153−199.
(4) Baumgarten, M. High Spin Organic Molecules. In *World Scientific Reference on Spin in Organics*; Miller, J. S., Ed.; World Scientific Publishing: Singapore, 2018; Vol. *IV*, pp 1−93.

(5) Cardamone, D. M.; Stafford, C. A.; Mazumdar, S. Controlling quantum transport through a single molecule. *Nano Lett.* **2006**, *6* (11), 2422−2426.
(6) Tsuji, Y.; Hoffmann, R.; Strange, M.; Solomon, G. C. Close relation between quantum interference in molecular conductance and diradical existence. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, E413−E419.
(7) Tsuji, Y.; Hoffmann, R. Frontier Orbital Control of Molecular Conductance and its Switching. *Angew. Chem., Int. Ed.* **2014**, *53*, 4093−4097.
(8) Koga, J.; Tsuji, Y.; Yoshizawa, K. Orbital Control of Single-Molecule Conductance Perturbed by pi-Accepting Anchor Groups: Cyanide and Isocyanide. *J. Phys. Chem. C* **2012**, *116* (38), 20607−20616.
(9) Tsuji, Y.; Staykov, A.; Yoshizawa, K. Orbital Views of Molecular Conductance Perturbed by Anchor Units. *J. Am. Chem. Soc.* **2011**, *133* (15), 5955−5965.
(10) Taniguchi, M.; Tsutsui, M.; Mogi, R.; Sugawara, T.; Tsuji, Y.; Yoshizawa, K.; Kawai, T. Dependence of Single-Molecule Conductance on Molecule Junction Symmetry. *J. Am. Chem. Soc.* **2011**, *133* (30), 11426−11429.
(11) Iwamura, H. Design of Organic Molecules and Molecular Assemblies with Electron Spin Alignment. *Pure Appl. Chem.* **1987**, *59*, 1595.
(12) Hewitt, P.; Shultz, D. A.; Kirk, M. L. Rules for Magnetic Exchange in Azulene-Bridged Biradicals: quo vadis? *J. Org. Chem.* **2021**, submitted.
(13) Rajca, A.; Utamapanya, S. Toward Organic Synthesis of a Magnetic Particle: Dendritic Polyradicals with 15 and 31 Centers for Unpaired Electrons. *J. Am. Chem. Soc.* **1993**, *115*, 10688−10694.
(14) Rajca, A. Toward Organic Synthesis of a Nanometer-Size Magnetic Particle. *Adv. Mater.* **1994**, *6* (7/8), 605−607.
(15) Rajca, A., High-Spin Polyradicals. In *Magnetic Properties of Organic Materials*, Lahti, P., Ed. Marcel Dekker, Inc.: New York, 1999; pp 345−359.
(16) Rajca, A. From High-Spin Organic Molecules to Organic Polymers with Magnetic Ordering. *Chem. - Eur. J.* **2002**, *8* (21), 4834−4841.
(17) Gallagher, N. M.; Bauer, J. J.; Pink, M.; Rajca, S.; Rajca, A. High-Spin Organic Diradical with Robust Stability. *J. Am. Chem. Soc.* **2016**, *138*, 9377−9380.
(18) Calzolari, A.; Rajca, A.; Casu, M. B. From radical to triradical thin film processes: the Blatter radical derivatives. *J. Mater. Chem. C* **2021**, *9*, 10787−10793.
(19) Murata, K.; Ushijima, H.; Ueda, H.; Kawaguchi, K. A Stable Carbon-Based Organic Magnet. *J. Chem. Soc., Chem. Commun.* **1992**, 567.
(20) Murata, H.; Takahashi, M.; Namba, K.; Takahashi, N.; Nishide, H. A High-Spin and Durable Polyradical: Poly (4-Diphenylaminium-1, 2-Phenylenevinylene). *J. Org. Chem.* **2004**, *69*, 631−638.
(21) Wang, P.; Lin, S.; Lin, Z.; Peeks, M. D.; Van Voorhis, T.; Swager, T. M. A Semiconducting Conjugated Radical Polymer: Ambipolar Redox Activity and Faraday Effect. *J. Am. Chem. Soc.* **2018**, *140* (34), 10881−10889.
(22) Haraguchi, M.; Tretyakov, E.; Gritsan, N.; Romanenko, G.; Gorbunov, D.; Bogomyakov, A.; Maryunina, K.; Suzuki, S.; Kozaki, M.; Shiomi, D.; Sato, K.; Takui, T.; Nishihara, S.; Inoue, K.; Okada, K. (Azulene-1,3-diyl)-bis(nitronyl nitroxide) and (Azulene-1,3-diyl)-bis(iminonitroxide) and Their Copper Complexes. *Chem. - Asian J.* **2017**, *12* (22), 2929−2941.
(23) Pierpont, C. G.; Lange, C. W. The chemistry of transition metal complexes containing catechol and semiquinone ligands. *Prog. Inorg. Chem.* **2007**, *41*, 331.
(24) Bhattacharya, S.; Boone, S. R.; Fox, G. A.; Pierpont, C. G. Periodic Trends in Charge-Distribution For Transition-Metal Complexes Containing Catecholate and Semiquinone Ligands - Synthetic, Physical, and Stereodynamic Properties of the Tris(3,5-Di-Tert-Butylquinone) Complexes of Ruthenium and Osmium. *J. Am. Chem. Soc.* **1990**, *112* (3), 1088−1096.
(25) Pierpont, C. G.; Buchanan, R. M. Transition Metal Complexes of o-Benzoquinone, o-Semiquinone, and Catecholate Ligands. *Coord. Chem. Rev.* **1981**, *38*, 45.
(26) Sloop, J. C.; Shultz, D. A.; Coote, T.; Shepler, B.; Sullivan, U.; Kampf, J. W.; Boyle, P. D. Synthesis of and structure-property relationships in zinc complexes of bis-metaphenylene semiquinone biradical species. *J. Phys. Org. Chem.* **2012**, *25*, 314−321.
(27) Shultz, D. A.; Bodnar, S. H.; Lee, H.; Kampf, J. W.; Incarvito, C. D.; Rheingold, A. L. The Singlet-Triplet Gap in Triplet Ground-State Biradicals Is Modulated by Substituent Effects. *J. Am. Chem. Soc.* **2002**, *124*, 10054−10061.
(28) Shultz, D. A.; Kirk, M. L.; Zhang, J.; Stasiw, D. E.; Wang, G.; Yang, J.; Habel-Rodriguez, D.; Stein, B. W.; Sommer, R. D. Spectroscopic Signatures of Resonance Inhibition Reveal Differences in Donor-Bridge and Bridge-Acceptor Couplings. *J. Am. Chem. Soc.* **2020**, *142*, 4916−4924.
(29) Stasiw, D. E.; Zhang, J.; Wang, G.; Dangi, R.; Stein, B. W.; Shultz, D. A.; Kirk, M. L.; Wojtas, L.; Sommer, R. D. Determining the Conformational Landscape of σ and π Coupling Using para-Phenylene and "Aviram−Ratner" Bridges. *J. Am. Chem. Soc.* **2015**, *137*, 9222−9225.
(30) Kirk, M. L.; Shultz, D. A.; Stasiw, D. E.; Lewis, G. F.; Wang, G.; Brannen, C. L.; Sommer, R. D.; Boyle, P. D. Superexchange Contributions to Distance Dependence of Electron Transfer/Transport: Exchange- and Electronic Coupling in Oligo(para-Phenylene)- and Oligo(2,5-Thiophene)-Bridged Donor-Bridge-Acceptor Biradical Complexes. *J. Am. Chem. Soc.* **2013**, *135*, 17144−17154.
(31) Kirk, M. L.; Shultz, D. A. Transition Metal Complexes of Donor-Acceptor Biradicals. *Coord. Chem. Rev.* **2013**, *257*, 218−233.
(32) Kirk, M. L.; Shultz, D. A.; Depperman, E. C.; Habel-Rodriguez, D.; Schmidt, R. D. Spectroscopic Studies of Bridge Contributions to Electronic Coupling in a Donor-Bridge-Acceptor Biradical System. *J. Am. Chem. Soc.* **2012**, *134*, 7812−7819.
(33) Kirk, M. L.; Shultz, D. A.; Depperman, E. C.; Brannen, C. L. Donor-acceptor biradicals as ground state analogues of photoinduced charge separated states. *J. Am. Chem. Soc.* **2007**, *129*, 1937−1943.
(34) Koivisto, B. D.; Ichimura, A. S.; McDonald, R.; Lemaire, M. T.; Thompson, L. K.; Hicks, R. G. Intramolecular pi-dimerization in a 1,1'-bis(verdazyl)ferrocene diradical. *J. Am. Chem. Soc.* **2006**, *128* (3), 690−691.
(35) Pal, A. K.; Datta, S. N. Ferrocene-based diradicals of imino nitroxide, nitronyl nitroxide and verdazyl, and their cations are possible SMM: A quantum chemical study. *Chem. Phys. Lett.* **2017**, *676*, 70−76.
(36) Sporer, C.; Heise, H.; Wurst, K.; Ruiz-Molina, D.; Kopacka, H.; Jaitner, P.; Kohler, F.; Novoa, J. J.; Veciana, J. Magneto-structural characterization of metallocene-bridged nitronyl nitroxide diradicals by X-ray, magnetic measurements, solid-state NMR spectroscopy, and ab initio calculations. *Chem. - Eur. J.* **2004**, *10* (6), 1355−1365.
(37) Jurgens, O.; Vidal-Gancedo, J.; Rovira, C.; Wurst, K.; Sporer, C.; Bildstein, B.; Schottenberger, H.; Jaitner, P.; Veciana, J. Transmission of magnetic interactions through an organometallic coupler: A novel family of metallocene-substituted alpha-nitronyl aminoxyl radicals. *Inorg. Chem.* **1998**, *37* (18), 4547−4558.
(38) Souto, M.; Lloveras, V.; Vela, S.; Fumanal, M.; Ratera, I.; Veciana, J. Three Redox States of a Diradical Acceptor-Donor-Acceptor Triad: Gating the Magnetic Coupling and the Electron Delocalization. *J. Phys. Chem. Lett.* **2016**, *7* (12), 2234−2239.
(39) McConnell, H. M. Ferromagnetism in Solid Free Radicals. *J. Chem. Phys.* **1963**, *39*, 1910.
(40) Jürgens, O.; Vidal-Gancedo, J.; Rovira, C.; Wurst, K.; Sporer, C.; Bildstein, B.; Schottenberger, H.; Jaitner, P.; Veciana, J. Transmission of Magnetic Interactions through an Organometallic Coupler: A Novel Family of Metallocene-Substituted alpha-Nitronyl Aminoxyl Radicals. *Inorg. Chem.* **1998**, *37*, 4547.
(41) Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. Molecular Design and Model Experiments of Ferromagnetic Intermolecular Interaction in the Assembly of High-Spin Organic Molecules -

https://doi.org/10.1021/acs.orglett.1c02982
Org. Lett. 2021, 23, 8235−8239

Generation ond Characterization of the Spin States of Isomeric Bis(phenylmethylenyl) 2.2 Paracyclophanes. *J. Am. Chem. Soc.* **1987**, *109* (9), 2631−2639.
(42) Kirk, M. L.; Dangi, R.; Habel-Rodriguez, D.; Yang, J.; Shultz, D. A.; Zhang, J. Transferrable Property Relationships Between Magnetic Exchange Coupling and Molecular Conductance. *Chem. Sci.* **2020**, *11*, 11425−11434.
(43) Kirk, M. L.; Shultz, D. A.; Zhang, J.; Dangi, R.; Ingersol, L.; Yang, J.; Finney, N. S.; Sommer, R. D.; Wojtas, L. Heterospin Biradicals Provide Insight into Molecular Conductance and Rectification. *Chem. Sci.* **2017**, *8*, 5408−5415.
(44) Markussen, T.; Stadler, R.; Thygesen, K. S. The Relation between Structure and Quantum Interference in Single Molecule Junctions. *Nano Lett.* **2010**, *10* (10), 4260−4265.
(45) Valkenier, H.; Guédon, C. M.; Markussen, T.; Thygesen, K. S.; van der Molen, S. J.; Hummelen, J. C. Cross-conjugation and quantum interference: a general correlation? *Phys. Chem. Chem. Phys.* **2014**, *16*, 653−662.
(46) Schwarz, F.; Koch, M.; Kastlunger, G.; Berke, H.; Stadler, R.; Venkatesan, K.; Lörtscher, E. Charge Transport and Conductance Switching of Redox-Active Azulene Derivatives. *Angew. Chem., Int. Ed.* **2016**, *55* (39), 11781−11786.
(47) Xia, J.; Capozzi, B.; Wei, S.; Strange, M.; Batra, A.; Moreno, J. R.; Amir, R. J.; Amir, E.; Solomon, G. C.; Venkataraman, L.; Campos, L. M. Breakdown of Interference Rules in Azulene, a Nonalternant Hydrocarbon. *Nano Lett.* **2014**, *14*, 2941−2945.

https://doi.org/10.1021/acs.orglett.1c02982
Org. Lett. 2021, 23, 8235−8239