Available online at www.sciencedirect.com
SCIENCE DIRECT®

PERGAMON

Polyhedron 22 (2003) 2423–2426

POLYHEDRON

www.elsevier.com/locate/poly

The donor–acceptor contributions to ferromagnetic exchange coupling in heterospin biradicals

David A. Shultz

Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204, USA

Received 22 October 2002; accepted 6 January 2003

Abstract

Frontier orbital perturbation theory analysis provides insight into a donor–acceptor contribution to ferromagnetic exchange in biradicals having two, chemically distinct paramagnetic groups.

Keywords: Biradicals; Exchange coupling; Heterospin; Spin diverse

A frontier in modern chemistry is the search for molecules with novel electronic properties. Not only are such molecules inherently interesting, but they may serve as components for molecular electronics [1–4] or molecular magnetic materials [5–10]. Candidates for interesting new molecules include open-shell species comprised of multiple, chemically different paramagnetic functional groups. Such 'spin diverse' molecules are expected to be interesting because of the combined physical and electronic properties associated with the constituent paramagnetic moieties.

The simplest organic spin diverse species are certain types of biradicals. However, before examining spin diverse biradicals, it is informative to review the salient features of a more common class of biradicals: homospin biradicals, which are comprised of identical paramagnetic moieties. Examples include dinitroxides, bis(semiquinone)s, etc. as shown in Fig. 1.

The most studied electronic property associated with biradicals is the magnetic exchange coupling, which is manifest in the singlet–triplet gap [11–14]. Ferromagnetic exchange coupling produces a triplet ground state, while antiferromagnetic exchange coupling produces a singlet ground state. The classic derivation of the singlet–triplet gap in biradicals in the active-electron approximation uses the orthogonal magnetic orbital approach [5]. This analysis gives the ferromagnetic (J_F) and antiferromagnetic (J_{AF}) contribution to the exchange parameter (J) as:

$$J = J_F + J_{AF} = 2k + \frac{4\beta^2}{j - j^0} \tag{1}$$

The J_F term is the first-order correction to the energy, and equals twice the exchange integral, k, while the J_{AF} term is derived from mixing of a zwitterionic excited singlet into the ground singlet. This antiferromagnetic term is a second-order configuration interaction correction to the energy, where β is the transfer integral, j is the two-center coulomb integral, and j^0 is the one-center coulomb integral.

Molecular design principles aimed at stabilizing the triplet state over the singlet state have been developed. These design principles are embodied in π-type biradicals that are cross-conjugated [15]. Cross-conjugated π-topologies preclude annihilation of spins by π-bond formation, and provide nondisjoint SOMOs with sizeable exchange integrals [16].

Heterospin biradicals are the simplest example of a spin diverse organic species, and are those in which the paramagnetic moieties are different [17–24]. A few representative examples are shown in Fig. 2. In these cases, straightforward manifestations of donor–acceptor interactions, engrained in physical organic chemistry, can be used to shed light on exchange coupling in a new way. To our knowledge, the following analysis has

---

E-mail address: david_shultz@ncsu.edu (D.A. Shultz).

0277-5387/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0277-5387(03)00217-1

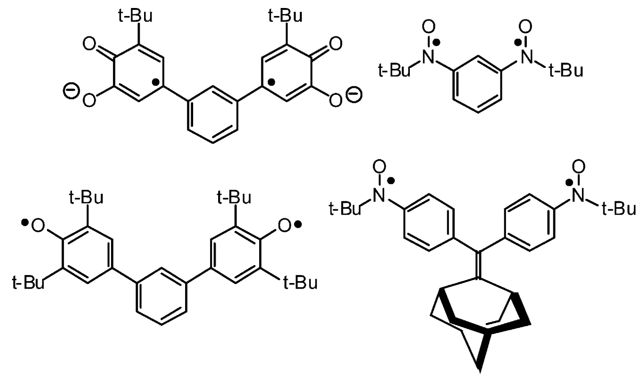

Fig. 1. Examples of homospin biradicals.

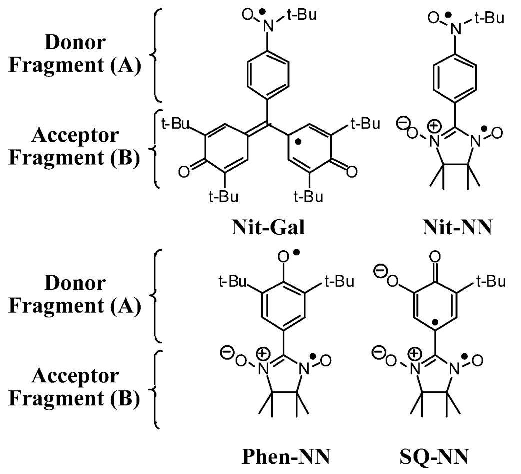

Fig. 2. Examples of heterospin biradicals.

not been presented previously to estimate a ferromagnetic contribution to J.

We begin by reminding the reader that to form nondisjoint SOMOs [16,11–14], an atom of positive spin density in one radical group (fragment A) is attached to an atom with negative spin density in the second radical group (fragment B) [25]. In heterospin biradicals however, it is the interaction of the SOMO of fragment A (the donor) with the LUMO of fragment B (the acceptor) that provides nondisjoint SOMOs. An example of the pertinent orbital interaction is shown in Fig. 3.

The magnitude of frontier orbital [26] interaction was first derived by Klopman and Salem for orbitally-controlled chemical reactions [27–29], and is given by:

$$\sum_{A}^{\mathrm{SOMO}}\sum_{B}^{\mathrm{LUMO}}\frac{2(c_{iA}c_{jB}\beta_{AB})^2}{E_A - E_B} \qquad (2)$$

Note that Eq. (2) has the same form as the antiferromagnetic term of Eq. (1), but Eq. (2) contributes to the *ferro*magnetic coupling. There are additional terms contributing to the exchange that arise from excited electronic states, but these will be discussed elsewhere [30]. The ferromagnetic portion of the exchange parameter is proportional to:

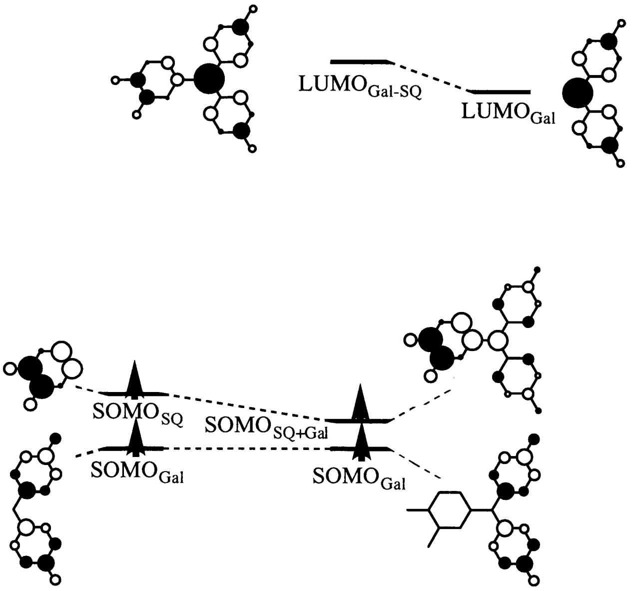

Fig. 3. Example of a $\mathrm{SOMO_{donor}}$–$\mathrm{LUMO_{acceptor}}$ interaction that generates nondisjoint heterospin biradical SOMOs.

$$J_F \propto \frac{2(c_{iA}c_{jB}\beta_{AB})^2}{|E_A - E_B|} \qquad (3)$$

The exchange integral has now been recast in terms of a donor–acceptor interaction. To maximize the ferromagnetic contribution in heterospin biradicals, one needs to

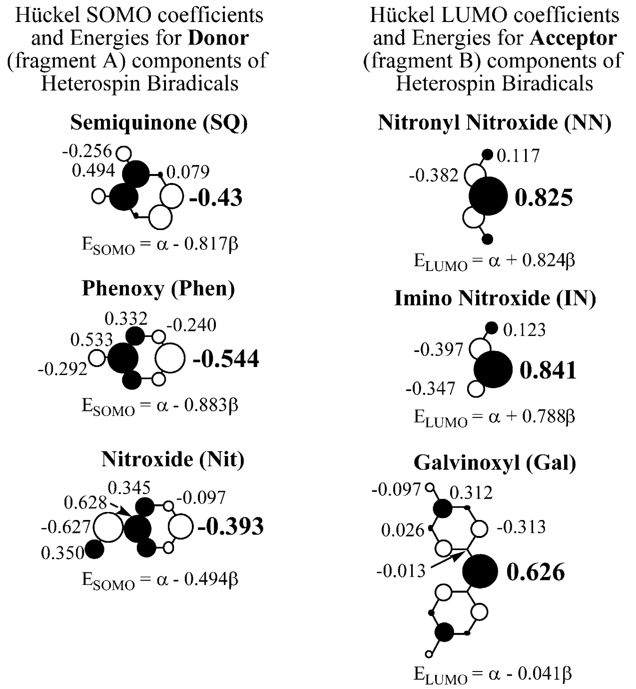

Fig. 4. Hückel parameters used to calculate the donor–acceptor contribution to ferromagnetic exchange in heterospin biradicals. The bold-faced coefficients are used in the calculations.

Table 1
Contributions to the ferromagnetic exchange coupling due to donor–acceptor interactions

Biradical: D/A combination	$c_{i\mathrm{A}}c_{j\mathrm{B}}$ [a]	$\lvert\Delta E\rvert(\beta)$	Ferromagnetic contribution (β) [b]
SQ–NN	−0.3548	−1.641	0.1534
SQ–IN	−0.3616	−1.605	0.1630
SQ–Gal	−0.2692	−0.758	0.1912
Phen–NN	−0.4488	−1.707	0.2360
Phen–IN	−0.4575	−1.671	0.2506
Phen–Gal	*−0.3405*	*−0.924*	*0.2510*
Nit–NN	−0.3242	−1.318	0.1594
Nit–IN	−0.3305	−1.282	0.1704
Nit–Gal	−0.2460	−0.535	0.2262

[a] Product of the Hückel π-coefficients for the atoms providing the bonding between the donor and acceptor fragments of the heterospin biradical.
[b] Ferromagnetic contribution to the exchange coupling calculated using the ferromagnetic term given by Eq. (3).

minimize the donor (fragment A SOMO)–acceptor (fragment B LUMO) energy gap, and maximize the coefficients on the connected atoms in the corresponding fragment MOs. Using Hückel theory, one can calculate the donor–acceptor contribution to the ferromagnetic exchange parameter (J_F) for different heterospin biradicals using common paramagnetic functional groups. Values for frontier orbital energies and coefficients calculated using Hückel theory [31] are found in Fig. 4, while calculations of ferromagnetic exchange contributions are listed in Table 1. The ferromagnetic contributions listed in Table 1 use only the SOMO of the donor and the LUMO of the acceptor. The additional contribution (acceptor-SOMO and donor-LUMO) is zero because the acceptor-SOMO has a node at the atom to which it joins the donor fragment.

As can be seen from both the Table 1 and Fig. 4, Galvinoxyl is the best acceptor and phenyl-nitroxide is the best donor based on frontier orbital energies. However, the maximum donor–acceptor contribution to ferromagnetic exchange is for the biradical Phen–Gal, but this is *not* a heterospin biradical, it is Yang's biradical for which $J \approx 240\ \mathrm{cm}^{-1}$ [32,33]. Several other biradicals in Table 1 are known. The biradical SQ–NN has ferromagnetic exchange coupling with $310\ \mathrm{cm}^{-1} < J < 550\ \mathrm{cm}^{-1}$ [34,35]. Iwamura prepared Nit–NN, and found $J \geq 300\ \mathrm{cm}^{-1}$ [18], while Lahti's group prepared Phen–NN, and we reported Nit–Gal, although the J-values were not measured [23,36]. We note that heterospin biradicals can have exchange parameters that exceed the value for Yang's biradical: a *homo*spin molecule. This enhanced ferromagnetic exchange coupling might be evidence of the presence of additional ferromagnetic terms arising from electronic excited states, and will be discussed in a future manuscript [30]. Therefore, we feel that heterospin species might have inherently stronger ferromagnetic coupling than homospin biradicals, and that considering ferromagnetic exchange coupling from a donor–acceptor perspective embodies an important structure-property relationship for designing high-spin molecules.

In summary, we have shown that an important portion of the ferromagnetic exchange coupling in heterospin biradicals can be understood in terms of donor–acceptor interactions that give rise to nondisjoint SOMOs. The stronger the interaction between the SOMO of the donor fragment and the LUMO of the acceptor fragment, the stronger the ferromagnetic contribution. This analysis is related to Whangbo's spin-dimer analysis of antiferromagnetic exchange in metal dimers [37–40]. Our frontier orbital interaction is easily calculated using Eq. (3). Since controlling magnetic exchange couplings is a goal in organic magnetic materials chemistry, our analysis facilitates molecular design of strongly-coupled systems. Clearly, additional compounds and experiments are required to test the utility of the heterospin approach to controlling exchange coupling in high-spin molecules, and we hope that this note will stimulate such activity.

Acknowledgements

We acknowledge the National Science Foundation (CHE-9910076) for financial support, and thank the Camille and Henry Dreyfus Foundation for a Camille Dreyfus Teacher-Scholar Award. We also thank Prof. Myung-Hwan Whangbo and Professor Martin Kirk for stimulating discussions.

References

[1] C. Joachim, J.K. Gimzewski, A. Aviram, Nature 408 (2000) 541.
[2] A.P. Alivisatos, P.F. Barbara, A.W. Castleman, J. Chang, D.A. Dixon, M.L. Klein, G.L. McLendon, J.S. Miller, M.A. Ratner, P.J. Rossky, S.I. Stupp, M.E. Thompson, Adv. Mater. 10 (1998) 1297.
[3] K. Sienick, Molecular Electronics and Molecular Electronic Devices, CRC Press, Boca Raton, FL, 1994.

[4] O. Kahn, J. Krobert, C. Jay, Adv. Mater. 4 (1992) 718.
[5] O. Kahn, Molecular Magnetism, VCH, New York, 1993.
[6] K. Itoh, M. Kinoshita, Molecular Magnetism, New Magnetic Materials, Gordon and Breach, Amsterdam, 2000, p. 347.
[7] P.M. Lahti, Magnetic Properties of Organic Materials, Marcel Dekker, New York, 1999.
[8] J.S. Miller, M. Drillon, Magnetism: Molecules to Materials: Models and Experiments, Wiley-VCH, New York, 2001, p. 430.
[9] J.S. Miller, M. Drillon, Magnetism: Molecules to Materials II: Molecule-Based Materials, Wiley-VCH, New York, 2001, p. 489.
[10] J.S. Miller, M. Drillon, Magnetism: Molecules to Materials III: Nanosized Magnetic Materials, Wiley-VCH, New York, 2001.
[11] W.T. Borden, Diradicals, Wiley, New York, 1982.
[12] D.A. Dougherty, Acc. Chem. Res. 24 (1991) 88.
[13] A. Rajca, Chem. Rev. 94 (1994) 871.
[14] W.T. Borden, in: P.M. Lahti (Ed.), Magnetic Properties of Organic Materials (chapter 5), Marcel Dekker, New York, 1999.
[15] N.F. Phelan, M. Orchin, J. Chem. Ed. 45 (1968) 633.
[16] W.T. Borden, E.R. Davidson, J. Am. Chem. Soc. 99 (1977) 4587.
[17] R. Kumai, M.M. Matsushita, A. Izuoka, T. Sugawara, J. Am. Chem. Soc. 116 (1994) 4523.
[18] K. Inoue, H. Iwamura, Angew. Chem. Int. Ed. Engl. 34 (1995) 927.
[19] H. Iwamura, K. Inoue, T. Haymizu, Pure Appl. Chem. 68 (1996) 243.
[20] D.A. Shultz, G.T. Farmer, J. Org. Chem. 63 (1998) 6254.
[21] M. Tanaka, K. Matsuda, T. Itoh, H. Iwamura, J. Am. Chem. Soc. 120 (1998) 7168.
[22] H. Kumagai, K. Inoue, Molecular Crystals and Liquid Crystals Science and Technology Section a—Molecular Crystals and Liquid Crystals 334 (1999) 487.
[23] Y. Liao, C. Xie, P.M. Lahti, R.T. Weber, J. Jiang, D.P. Barr, J. Org. Chem. 64 (1999) 5176.
[24] M. Nishizawa, D. Shiomi, K. Sato, T. Takui, K. Itoh, H. Sawa, R. Kato, H. Sakurai, A. Izuoka, T. Sugawara, J. Phys. Chem. B 104 (2000) 503.
[25] This is an equivalent but prehaps more instructive explanation for nondisjointed biradicals than simply stating that they are cross-conjugated
[26] K. Fukui, T. Yonezawa, H. Shingu, J. Chem. Phys. 20 (1952) 722.
[27] G. Klopman, J. Am. Chem. Soc. 90 (1968) 223.
[28] L Salem, J. Am. Chem. Soc. 90 (1968) 553.
[29] L. Salem, J. Am. Chem. Soc. 90 (1968) 543.
[30] E.C. Depperman, M.L. Kirk, D.A. Shultz, manuscript in preparation.
[31] Calculations were performed with the freeware program HMO version 1.3© 1989, 1991, by Allan Wissner.
[32] K. Mukai, K. Ishizu, Y. Deguchi, J. Phys. Soc. Jpn 27 (1969) 783.
[33] E.A. Chandross, R. Kreilick, J. Am. Chem. Soc. 86 (1964) 1263.
[34] D.A. Shultz, S.H. Bodnar, K.E. Vostrikova, J.W. Kampf, Inorg. Chem. 39 (2000) 6091.
[35] D.A. Shultz, E. Kira, K.E. Vostrikova, S.H. Bodnar, H.-J. Koo, M.-H. Whangbo, M.L. Kirk, E.C. Depperman, J.W. Kampf, J. Am. Chem. Soc. 125 (2003) 1607.
[36] D.A. Shultz, A.K. Boal, Mol. Cryst. Liq. Cryst. 272 (1995) 75.
[37] H.J. Koo, M.H. Whangbo, J. Solid State Chem. 153 (2000) 263.
[38] H.J. Koo, M.H. Whangbo, J. Solid State Chem. 151 (2000) 96.
[39] H.-J. Koo, M.-H. Whangbo, S. Coste, S. Jobic, J. Solid State Chem. 156 (2001) 464.
[40] H.-J. Koo, M.-H. Whangbo, Inorg. Chem. 40 (2001) 2161.