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Effect of core substituents on the intramolecular exchange interaction in N,N′-dioxy-2,6-diazaadamantane biradical: DFT studies

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Abstract

© 2017 Wiley Periodicals, Inc. Density-functional theory calculations of a series of organic biradicals on the basis of the N,N′-dioxy-2,6-diazaadamantane core with different substituents at carbon atoms adjacent to the nitroxyl groups have been performed by the UB3LYP/6-311++G(2d,2p) method. Using the breaking symmetry approach, the values of the exchange interaction parameter, J, between the radical centers are calculated. It is shown that the intramolecular exchange interaction for the most part is ferromagnetic in nature, but the J parameter gradually decreases, changing its sign to antiferromagnetic interaction for the last substituent in the following sequence: CF3(CH3)COH > CH2F(H)COH > CH2OH > H > CBr3 > CH2F > CCl3 > CF3 > CH2Br > CH2Cl > CH3 > C2H5 > C3H7 > i-C4H9 > F > Br > OCH3 > Cl > CH2C6H5. The calculations at the UHSEH1PBE/6-311++G(2d,2p) level with the most of substituents show nearly the same variation sequence for the J parameter. It is concluded that spin polarization effects in the diazaadamantane cage and a direct through-space antiferromagnetic exchange interaction between the nitroxyl groups are the main mechanisms contributing to the exchange interaction parameter value in the studied series of compounds. The exchange coupling constant, J, depends on the electronic effects and geometry of the substituents, as well as on their specific interactions with the nitroxyl radical groups.

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Keywords

2,6-diazaadamantane, broken symmetry approach, DFT, exchange interaction, open-shell systems, organic biradicals

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