Название публикации:

The Structure and Internal Dynamics of R6 -p-C6 H4 -R6 Biradical: EPR, X-ray Crystallography and DFT Calculations

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Аннотация:

A purposefully synthesized nitroxide biradical R6-p-C6H4-R6 (B1), where R6 is the 1-oxyl-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine group with a relatively short distance between the two radical sites, has been studied by X-band electron paramagnetic resonance (EPR) spectroscopy. Hyperfine splitting (hfs) constants on the 14N atoms, electron spin exchange integral |J|, and the distance between the two N–O fragments rNO–NO were experimentally measured. Density functional theory, DFT, calculations were performed using the ORCA 4.0.1.2 program package. The optimized geometry was compared with X-ray crystallographic data and theoretical hfs constants were compared with the respective experimental EPR values. It is concluded that the current quantum chemical approaches provide good results in calculating hfs constants as well as some other EPR parameters. It is confirmed that the intramolecular electron spin exchange in biradicals analogous to B1 is realized by the indirect mechanism rather than direct collision of the N–O· groups. It is also shown that one can calculate and predict values of |J| in other similar biradicals based on the principle of “attenuation coefficients. © 2018, Springer-Verlag GmbH Austria, part of Springer Nature.

Ключевые слова:

Density functional theory, Electron spin resonance spectroscopy, Electrospinning, Magnetic moments, Paramagnetic resonance