

Название публикации:

Influence of Polarity and Ionic Strength on Intramolecular Spin Exchange in a Short Nitroxide Biradical, Containing Sulphur Atom in the Bridge

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Аннотация:

A short nitroxide biradical: $O=S(OR_6)_2$ (BS), where OR_6 is 1-oxyl-2,2,6,6-tetramethyl-4-oxypiperidine, has been studied by electron paramagnetic resonance spectroscopy at X-, Q-, and W-band in liquid and frozen toluene, ethanol and ionic liquid solutions. Variations of the intramolecular dynamics and conformational transitions in the biradical as a function of temperature in the range of 240–420 K, polarity and the ionic strength were characterized by changes in the isotropic ^{14}N hyperfine splitting (hfs) constant a , values of the exchange integral $|J|$, and the empirical parameter γ_3 , the ratio between conformations with slow and fast transitions. Thermodynamic parameters of the conformational rearrangements are calculated. The obtained results were compared with the X-ray structural data and quantum chemical calculations of the geometries and intramolecular transitions of biradical BS. Possible mechanisms of the polarity and the ionic strength effect on the biradical behavior in solutions of different types are discussed.

Ключевые слова:

Conformations, Electron spin resonance spectroscopy, Ion exchange, Ionic liquids, Paramagnetic resonance, Quantum chemistry, Sulfur, Conformational transitions, Electron paramagnetic resonance spectroscopy, Empirical parameters, Hyperfine splittings, Intramolecular dynamics, Possible mechanisms, Quantum chemical calculations, Thermodynamic parameter, Ionic strength