Toward an understanding of the ambiguous electron paramagnetic resonance spectra of the iminoxy radical from *o*-fluorobenzaldehyde oxime: density functional theory and *ab initio* studies.

Autorzy

Maciej Witwicki

Julia Jezierska

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Streszczenie

Iminoxy radicals ($R_1R_2C{=}N{-}O^{\bullet}$) possess an inherent ability to exist as *E* and *Z* isomers. Although isotropic hyperfine couplings for the species with R_1 = H allow one to distinguish between *E* and *Z*, unequivocal assignment of the parameters observed in the EPR spectra of the radicals without the hydrogen atom at the azomethine carbon to the right isomer is not a simple task. The iminoxyl derived from *o*-fluoroacetophenone oxime (R_1 = CH_3 and R_2 = *o*-FC_6H_5) appears to be a case in point. Moreover, for its two isomers the rotation of the *o*-FC_6H_5 group brings into existence the *syn* and *anti* conformers, depending on the mutual orientation of the F atom and $C{=}N{-}O^{\bullet}$ group, making a description of hyperfine couplings to structure even more challenging. To accomplish this, a vast array of theoretical methods (DFT, OO-SCS-MP2, QCISD) was used to calculate the isotropic hyperfine couplings. The comparison between experimental and theoretical values revealed that the *E* isomer is the dominant radical form, for which a fast interconversion between *anti* and *syn* conformers is expected. In addition, the origin of the significant A_F increase with solvent polarity was analyzed.

Adres publiczny

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https://www.acs.org/content/acs/en.html