EPR and density functional studies on 3-pyridylmethaniminoxy radical :^{1}H hyperfine couplings as a structural criterion for iminoxyls derived from pyridinealdoximes.

Autorzy

Adrian Jaszewski

Julia Jezierska

Małgorzata Krowicka

Elżbieta Kalecińska

Rok wydania

2000

Czasopismo

Applied Magnetic Resonance

Numer woluminu

18

Strony

85-100

DOI

10.1007/BF03162101

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

3-pyridylmethaniminoxyl has been generated by γ-irradiation of the parent oxime in the solid state and by incorporation of 3-pyridinealdoxime into the channels of thermally activated pentasil zeolite ZSM-5. The radical formed by both methods exhibits an electron paramagnetic resonance (EPR) spectrum with a characteristic powder pattern. The assignment of the hyperfine structure of the anisotropic spectra to the couplings with^{14}N and^{1}H nuclei of Z geometrical isomer of 3-pyridylmethaniminoxy radical has been aided significantly by comparison with the coupling parameters calculated with the density functional theory (DFT). It has been found that 3- and 4-pyridylmethaniminoxyls generated in the oxime matrices, in contrast to the radicals derived from 2-pyridinealdoxime, have a possibility to isomerize. The EPR spectra of γ-irradiated 3- and 4-pyridinealdoximes show a distinct temperature dependence of particular isomer contributions which have been correlated with the relative energies of the isomers derived from DFT calculations. Hybrid density functional methods have been also used to determine the structure of transition states for isomerization (via inversion at nitrogen) and rotation (of pyridyl ring) as well as to predict the appropriate energy barriers.

Adres publiczny

https://doi.org/10.1007/BF03162101

Strona internetowa wydawcy

http://link.springer.com