Effect of Spin-Orbit Coupling on the Sign of Magnetic Anisotropy of Quintet Dinitrenes

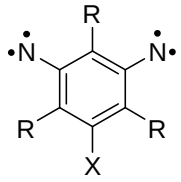
Akimov Alexander V.,[1*] Korchagin Denis V.,[1] Savitsky Anton,[2] Chapyshev Sergei V.,[1] Misochko Eugenii Ya.[1]

[1] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432, Chernogolovka, Moscow Region, Russian Federation*

[2] *Faculty of Physics, Technical University Dortmund, Otto-Hahn-Str. 4a, D-44227, Dortmund, Germany*

** E-mail: shura@icp.ac.ru*

In comparison with conventional EPR spectroscopy (X-band, 9 GHz), W-band 94 GHz EPR spectroscopy allows to determine the sign of the ZFS parameters of high spin nitrenes [1, 2]. We report on W-band EPR spectroscopic studies of dinitrene belong to class of quintet 1,3,5-tribromophenylene-2,4-dinitrenes **1c** obtained as in the photolysis of diazide in frozen solution. The main aim of the research was to understand the factors affecting the sign and magnitude of *D* in aromatic tetraradicals with large SOC and quintet spin multiplicity. For this purpose, a number of models phenylenedinitrenes **1b** and **1d**–**f** (Scheme 1) has been additionally studied by quantum chemical methods.



1a R = X = H
1b R = Br, X = N_3
1c R = Br, X = F
1d R = Br, X = CN
1e R = Br, X = Cl
1f R = Br, X = Br

Scheme 1. Structures of quintet phenylenedinitrenes **1a-f**.

In overall, our experimental (W-band EPR spectroscopy) and theoretical (quantum chemical calculations and tensor analysis) studies show in which cases high-spin nitrenes may have negative ZFS owing to the presence of the heavy atoms at appropriate sites nearby the nitrene centers and exhibit the bistability property as organic single-molecule magnets.

We acknowledge funding from the Ministry of Science and Higher Education of the Russian Federation (Grant No. 075-15-2020-779)

[1] A.V. Akimov, A.A. Masitov, D.V. Korchagin, S.V. Chapyshev, E.Ya. Misochko, A. Savitsky, W-Band EPR Studies of High-Spin Nitrenes with Large Spin-Orbit Contribution to Zero-Field Splitting, *J. Chem. Phys*. **2015**, *143*, p. 084313.

[2] D.V. Korchagin, A.V. Akimov, A. Savitsky, S.V. Chapyshev, S.M. Aldoshin, E.Ya. Misochko, Steric Heavy Atom Effect on Magnetic Anisotropy of Triplet Tribromophenyl Nitrenes, *J. Phys. Chem. A*. **2018**, *122*, pp. 8931–8937.