

Magnetic and Structural Properties of Monoradicals and Diradicals Based on Thienyl-Substituted Nitronyl Nitroxide

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We have been investigating magneto-structural correlations in organic radicals based on nitronyl nitroxide. Of these radicals, thienyl-substituted nitronyl nitroxide is interesting because the thienyl group includes a sulfur atom, which shows larger spin-orbit coupling compared with that of the atoms included in the nitronyl nitroxide moiety, and yields larger magnetic anisotropy. To acquire insight into the magnetic properties of the thienyl-substituted nitronyl nitroxide radicals, we have prepared 2- and 3-thienyl nitronyl nitroxide (2-THNN and 3-THNN) and 3-benzo[*b*]thienyl nitronyl nitroxide (3-BTHNN) as monoradicals and 2,3- and 2,5-thiophenebis(nitronyl nitroxide) (2,3-THBNN and 2,5-THBNN) as diradicals.

The magnetic behavior of the monoradicals is interpreted with the one-dimensional (1-d) Heisenberg model. Ferromagnetic (FM) intermolecular interactions with the coupling constant $J/k = +0.37$ K are observed in 3-BTHNN, while alternating antiferromagnetic (AFM) intermolecular interactions are obtained in 2-THNN with $J/k = -6.6$ K and $\alpha = 0.5$ and 3-THNN with -5.3 K and $\alpha = 0.6$. In contrast, the magnetic behavior of diradicals is explained in terms of the quite strong intramolecular AFM interactions between two spin centers each located on the two nitronyl nitroxide moieties. The coupling constants are estimated as $J/k = -290$ K for 2,3-THBNN and -112 K for 2,5-THBNN.

We discuss here the origin of the intermolecular interactions observed in the monoradicals by considering their crystal structures. The crystals of 2-THNN and 3-THNN have an isomorphic structure, in which stacked face-to-face molecular dimers arrangements are observed. Such molecular arrangements are consistent with the 1-d alternating AFM intermolecular interactions. We also discuss the origin of the strong intramolecular interactions observed in the diradicals by considering their molecular structures in the crystals. The molecular structures of thienyl moieties in these diradicals are modified from those in the unsubstituted thiophene molecule to yield strong AFM intramolecular interactions.

