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Electron spin exchange interaction revealed the variations of nitroxide-substituted resorcin[4]arene cavity size in different model systems.

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Paramagnetic calix- and resorcinarene derivatives, besides the classical ability to formate host-guest complexes, can be important for creating molecular magnets and chemical sensors, as well as scaffold for spin-labelled biomolecules. The resorcinarene-based nitroxide tetraradicals [1] were shown to exhibit an outstanding antiradical and antioxidant properties.

In the present work, properties of resorcin[4]arene-based nitroxide tetraradical, bearing heptyl groups at the macrocycle's lower rim were studied using EPR spectroscopy. Integral spectra of the compound investigated consist of classical triplet, corresponding to the contribution of four individual nitroxide moieties and a singlet, which is the result of spin-spin interaction between them. For better qualitative visualization and division of the spectral components, measurements were performed using high microwave power values (up to 100 mW). Such approach is based on the effect of different saturation dependencies for the spectral components.

It was shown that electron spin exchange intensity, determined by the distance between nitroxide groups in solution and therefore the resorcin[4]arene cavity size depends on solvent, and is strongly sensitive to the presence of some transition metal cations. Lower-rim functionalization with methyl substituents instead of heptyl groups leads to decrease of exchange interactions, and such result correlates with previous investigations of resorcinarene conformational stability. Adding α-phosphatydylcholine liposomes and human serum albumin to the buffer solution of spin-labelled resorcinarene provide bidirectional effects of cavity volume changes. The cavity size was increased by binding with the bilayer structure and lowered in the case of interaction with the protein.

1. *A.I. Vovk, A.M. Shivanyuk, R.V. Bugas, O.V. Muzychka, A.K. Melnyk.* Antioxidant and antiradical activities of resorcinarene tetranitroxides // Bioorg. Med. Chem. Lett. - 2009. - **19** - P. 1314-1317.