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Dynamic phenomena in barrelenephosphinyl radicals: a complementary approach by density matrix analysis of EPR spectra and DFT calculations

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The paper shows the possibilities of the complementary use of the density matrix formalism for the simulation of the anisotropic EPR spectra and the DFT potential energy surface calculations to obtain a detailed picture of the motions of radical molecules. The combined approach is illustrated by a comparative EPR study of three phosphorus derivatives of barrelene. Three compounds were chosen as the model molecules for the observation of different temperature depend-ent dynamics of radical fragment. Each molecule based on the same barrelene skeleton has a different set of substitu-ents which by influencing the local chemical environment are likely to modify the internal dynamics. The temperature dependent EPR spectra are simulated by means of the density matrix formalism and the geometry of radicals are calcu-lated with DFT. The motion is described in terms of rotational barriers, DFT calculated energy profiles and hypotheti-cal intramolecular distortions. These two approaches lead to a similar microscopic picture of the intramolecular radical motion.