Theoretical characterisation of phosphinyl radicals and their magnetic properties: *g* matrix.

Autorzy

Maciej Witwicki

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Streszczenie

The g matrices (g tensors) of various phosphinyl radicals (R2 P(.)) were calculated using the DFT and multireference configuration interaction (MRCI) methods. The g matrices were distinctly dependent on the molecular structure of the radical. To thoroughly examine this dependence, the contributions from individual atoms and excited states were calculated. The former revealed the gain from the phosphorus atom to be preeminent unless P□O or P□S bonds are present in the radical molecule. The contributions owing to excited states arising from electronic transitions between doubly occupied molecular orbitals and the SOMO were clearly positive, as in the case of semiquinone and niroxide radicals. The transitions from the phosphorus lone pair were of paramount importance. Surprisingly, unlike for semiquinones and nitroxides, a significant negative contribution was observed from excitations from the SOMO to unoccupied molecular orbitals. For radicals with P□O bonds, this contribution to the g2 component was dominant. © 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Słowa kluczowe

ab initio calculations, density functional calculations, EPR spectroscopy, g tensor, radicals

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