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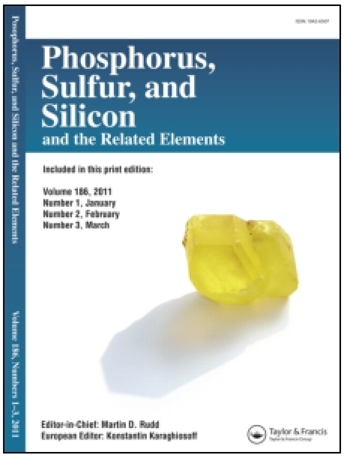

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Conformational Composition and Spin Properties of ß-Phosphone Nitroxyl Radicals in Gaseous Phase and Solutions

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As part of our studies of the extremely high sensitivity to substitutients A,B,R, temperature and solvents of phosphorus hyperfine splitting in ESR spectra of β-phosphone nitroxyl radicals ABP(O)CR$_2$N(Î$^•$)Bu^t, we have studied them theoretically. The conformational composition and spin delocalization in H$_2$P(O)CH$_2$N(Î$^•$)Í, (ÌåÎ)$_2$P(O)CÌå$_2$N(Î$^•$)Ìå and (ÍÎ)$_2$P(O)CÌå$_2$N(Î$^•$)Bu^t has been studied by UHF/6-31G* and MNDO (GAMESS). Solvent effects on conformational equilibrium, rotational and inversion barriers, charge distributions and spin properties of β-phosphone nitroxyl were calculated by SCRF UHF/6-31G* method.

The torsion angles (ψ, OPCN; φ, PCNO), relative energies (kcal/mol) ΔE (UHF/6-31G*) and ΔE* (MP2/UHF/6-31G*), spin densities at phosphorus nucleus (ρ(r$_P$)) and dipole moment (μ) of the stable conformers of H$_2$P(O)CH$_2$N(O$^•$)H.
For solution ρ^f(r$_P$) – spin densities calculated for gaseous phase geometry

	Gaseous phase, ε=1						Solution, ε=80					
	ψ	φ	ΔE	ΔE*	ρ(r$_P$) 10^4	μ	ψ	φ	ΔE	ρ^f(r$_P$) 10^4	ρ(r$_P$) 10^4	μ
G1	58	76	0.22	0.08	0.0271	3.65	47	63	0.83	0.0283	0.0311	5.25
G2	-52	-162	0.63	1.53	0.0011	3.51	-41	-170	2.24	0.0012	0.0001	4.62
G3	96	-42	2.86	3.38	0.0053	5.99	78	-65	0.00	0.0063	0.0207	7.75
T1	-168	-51	0.00	0.00	0.0085	3.82	-168	-46	1.24	0.0093	0.0068	4.68
T2	174	66	0.45	0.08	0.0273	3.50	172	-69	1.14	0.0294	0.0153	5.04

The effect of reactive electric field induced by solvent on spin density distribution is direct as well as it is the consequence of geometry alteration. Theoretical calculations give explanation of experimental results and predict some new patterns of the phosphorus hyperfine splitting dependencies upon temperature and solvents.

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