



Theoretical study of tautomerization and isomerization of methylamino- and phenylamino-substituted cyclic azaphospholines, oxaphospholines and thiaphospholines in gas and aqueous phases

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ABSTRACT

Results of B3LYP/6-31+G(d,p) calculations are reported. Special emphasis is put on the effect of the environment on relative stability and structures of different isomers and tautomers of methylamino- and phenylamino-substituted cyclic azaphospholine, oxaphospholine and thiaphospholine in gas and aqueous phases. In the gas phase, the imino forms are found to be the most stable species for the cyclic azaphospholines and thiaphospholines, whereas for oxaphospholines, the amino species are predicted to be more stable. The calculations in the aqueous media were done by considering two different models, i.e., the PCM-SCRF and the Microsolvated/SCRF model. It is found that solvation shifts the stability towards the amino forms, except for the phenyl-substituted cyclic azaphospholine and thiaphospholine, for which the imino forms are more stable in solution. The molecular geometries change only little when going from the gas phase to the aqueous phase. The stability in gas phase and in PCM-SCRF is attributed to the presence of intramolecular hydrogen bonding. In the Microsolvated/SCRF model, the presence of intermolecular hydrogen bonds affects the relative stability of tautomers and isomers.

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1. Introduction

Tautomeric equilibrium in heterocyclic systems has for a long time been of significant interest and importance [1], and it has accordingly been studied also theoretically using very many different theoretical methods ranging from semiempirical molecular orbital methods [2,3] to more sophisticated calculations that may include electron correlation [4,5]. As one important class of compounds, the effect of solvation on the tautomeric equilibrium of five-membered ring heterocyclic systems has been subject of many studies [2,6–8]. Through studies of the tautomerism in different environment it has been found that the environment is important for the relative stability of various tautomers.

During the last two decades, results of several studies on compounds containing the amidine group, $-\text{NH}-\text{C}(\text{R})=\text{N}-$, have been reported [9–16]. As a natural extension of those we have recently started a theoretical study of the isoelectronic systems containing the $-\text{PH}-\text{C}(\text{R})=\text{N}-$ group obtained by replacing a single nitrogen atom by a phosphorous atom [17]. The present study is a continuation of this work.

Organophosphorus compounds have been found to be important in many different fields. This includes, for examples, as lubri-

cants, oil additives, water treatment cleaners, flame retarding agents, fertilizers, plasticizers and pesticides [18,19]. Phosphorus and organophosphorus compounds have also been recognized to have important biological functions. For instance, they are essential constituents of the protoplasm [20].

The possibility of placing a proton either at the nitrogen or at the phosphorus atom, an issue that has direct relevance to this work, has earlier been investigated by Kolodiaznyy et al. [21] for some other, related compounds. They concluded that the tautomeric equilibrium depends on the nature of the solvent and on the substituents at the nitrogen and phosphorous atoms. The tautomerization process in gas phase depends on the proton affinities of the proton donor and acceptor as well as the distances between those. In aqueous solution the process may be influenced by the presence of water molecules, which may provide additional proton acceptors and donors. In the present study we shall, however, not study proton transfer mechanisms, but instead the relative stability between tautomers in gas phase and in solution.

We shall report results of a theoretical investigation of the methylamino- and phenylamino-substituted cyclic azaphospholine, oxaphospholine, and thiaphospholine and their imino tautomers, both in gas phase and in aqueous solution. In particular we shall focus on how the relative stability and the molecular geometries change upon solvation. Earlier, the cyclic moieties, azaphospholine, oxaphospholine, and thiaphospholine, have been studied by Cyrański et al. [22] who focused on their aromatic properties.

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Over the years many different approaches have been suggested for the study of solvation effects [23,24]. These methods include the self consistent reaction field (SCRf) continuum models. These so called implicit methods treat the effects of the solvent as those of a polarizable continuum with a given dielectric constant and with a cavity that is occupied by the solute. Alternatively, the inclusion of explicit solvent molecules can be important and necessary, in particular when hydrogen bonding between solvent and solute takes place. In that case a quantum-mechanical treatment of some few solvent molecules is useful and, in fact, such combined Microsolvated/SCRf approaches have been used over many years [25–31]. It has been found that they provide accurate estimates of solvation energy even with a modest number of solvent molecules [31].

In the present work we will consider both approaches, i.e., the SCRf approach and the Microsolvated/SCRf approach. Our aim is to explore the changes in the relative total energies and in the structures when the compounds are solvated.

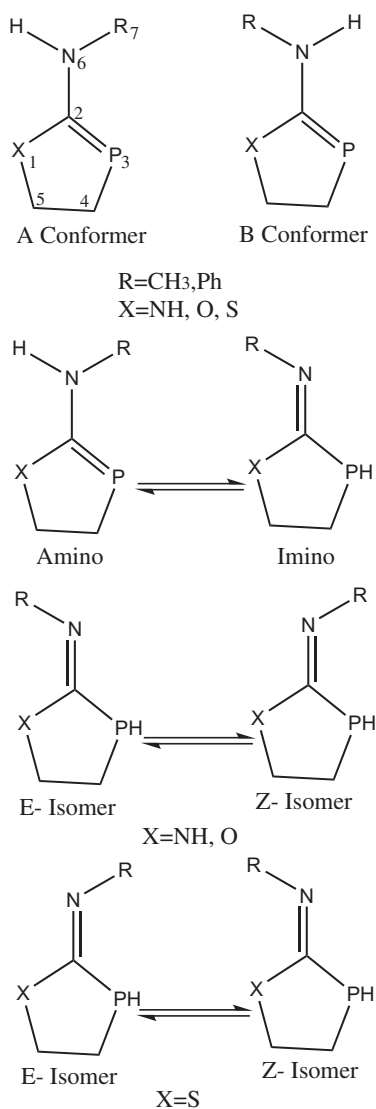


Fig. 1. Structure and atom numbering of the tautomers and isomers of methylamino-substituted cyclic azaphospholine, oxaphospholine, and thiaphospholine (Me-NH, Me-O, and Me-S) and phenylamino-substituted cyclic azaphospholine, oxaphospholine, and thiaphospholine (Ph-NH, Ph-O, and Ph-S).

The paper is organized as follows. Section 2 outlines the computational details. In Section 3, we present our results. Finally, the conclusions of the work are presented in Section 4.

2. Computational details

We carried gas phase, SCRf-PCM, and Microsolvated/SCRf calculations for different isomers and tautomers shown in Fig. 1. For the sake of simplicity we shall label the systems as Me-NH, Me-O, Me-S, Ph-NH, Ph-O, and Ph-S, respectively, where Me and Ph gives whether R in the figure is a methyl or a phenyl group, and where NH, O, and S represent X in the figure. In the calculations we used the Becke three parameter Lee–Yang–Parr (B3LYP) functional [32–34] together with the 6-31+G(d,p) basis set. All calculations were performed with the Gaussian 03 program package [35].

For the study of the influence of the solvent we considered two different models, i.e., the PCM-SCRf model whereby the solute is embedded inside a cavity surrounded by a continuum representing the water solvent, and the Microsolvated/SCRf method with which some (i.e., 3) explicit solvent molecules are treated quantum-mechanically. In the latter case, the three water molecules were placed around the hydrophilic regions of the solute as a first solvation shell, whereas the other solvent molecules were treated through the continuum model. The Integral Equation Formalism (IEF) [24,36–39] of the polarized continuum model (PCM) [36,40,41] of the self consistent reaction field (SCRf) was used to treat the continuum in both solvation models. For water we used a dielectric constant of 78.39.

For the construction of the cavity we used the United Atom Topological model (UAO) whereby the cavity is constructed through interlocking spheres centered on the heavy (that is, non-hydrogen) atoms. The radii were obtained by scaling the corre-

Table 1

Energy differences (ΔE , in kJ/mol) as found in the gas phase (marked gas), in the PCM calculations (marked PCM), and in the PCM calculations with the inclusion of three explicit water molecules (marked PCM + 3H₂O) as well as the two solvation energies (at $T = 0$ K). All quantities, except for the solvation energies, are given relative to those of the B isomer and include zero-point energies. Finally, the different isomers are shown in Fig. 1.

System	Isomer	ΔE			$\Delta E_{\text{sol},1}$	$\Delta E_{\text{sol},2}$
		Gas	PCM	PCM + 3H ₂ O		
Me-NH	B	0.00	0.00	0.00	-26.12	-9.69
	A	-6.60	-8.07	-16.86	-26.44	-18.51
	E	-9.82	-1.59	-0.18	-18.43	2.96
	Z	-17.10	-5.19	-19.72	-14.10	-9.98
Me-O	B	0.00	0.00	0.00	-16.99	-8.59
	A	-8.47	-7.09	2.09	-15.86	4.12
	E	-3.96	0.48	23.14	-13.62	15.14
	Z	2.63	2.35	20.13	-18.11	6.89
Me-S	B	0.00	0.00	0.00	-15.54	-4.89
	A	-9.31	-8.81	-0.03	-20.09	6.91
	E	-3.77	-1.00	24.05	-13.46	20.27
	Z	-11.42	-7.12	12.87	-12.18	23.29
Ph-NH	B	0.00	0.00	0.00	-24.04	-23.43
	A	0.33	-5.57	-0.29	-30.29	-22.54
	E	-17.55	-8.15	14.47	-15.06	7.13
	Z	-22.27	-19.12	-14.50	-21.15	-16.60
Ph-O	B	0.00	0.00	0.00	-18.59	-12.38
	A	-8.55	-7.44	0.34	-17.63	-5.14
	E	-7.89	0.39	22.52	-10.89	-16.72
	Z	-5.42	-3.12	3.86	-16.83	-3.74
Ph-S	B	0.00	0.00	0.00	-16.67	-1.29
	A	-6.60	-6.99	-7.98	-17.31	-3.14
	E	-9.91	-5.16	15.13	-12.49	22.03
	Z	-13.95	-7.16	-5.53	-10.58	9.53

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