A theoretical study of the tautomeric forms of hydrophosphorilic compounds

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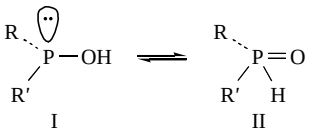
The tautomeric equilibria between hydrophosphorylic compounds in the series $Me_2POH \rightarrow (CF_3)_2POH$ on the successive substitution of hydrogen with fluorine were examined using both HFR + MP2 and DF calculations.

The diad prototropic rearrangement of hydrophosphorylic compounds is a well-known phenomenon, which has attracted considerable attention.[1,2] The following tautomeric equilibria, in which hydrophosphorylic compounds simultaneously exist as three-coordinated (I) and four-coordinated (II) species, are of prime interest:



Previously,[3] tautomerization reactions in the presence of symmetrical substituents R = R′ at the phosphorus atom were examined. The energies of tautomerization calculated for the reactions $(C_6F_5)_2POH \rightarrow (C_6F_5)_2P(O)H$ and $(MeO)_2POH \rightarrow (MeO)_2P(O)H$ in the framework of the density functional formalism (DF) were quantitatively consistent with the experimental data. The energy of tautomerization was calculated as the difference between the energies of tautomers II and I taking into account the zero-point vibration energy $E_0 = E_{0II} - E_{0I}$.

In the current work, we theoretically examined the tautomeric equilibria for hydrophosphorylic compounds with unsymmetrical substituents R, R′:

$(CH_2F)(Me)POH \rightleftharpoons (CH_2F)(Me)P(O)H$ (1)

$(CHF_2)(Me)POH \rightleftharpoons (CHF_2)(Me)P(O)H$ (2)

$(CF_3)(Me)POH \rightleftharpoons (CF_3)(Me)P(O)H$ (3)

$(CF_3)(CH_2F)POH \rightleftharpoons (CF_3)(CH_2F)P(O)H$ (4)

$(CF_3)(CHF_2)POH \rightleftharpoons (CF_3)(CHF_2)P(O)H$ (5)

It was found experimentally that at R = R′ = Me the tautomeric equilibrium is completely shifted toward species II, whereas at R = R′ = CF_3 species I is predominant.[2] There is no experimental evidence concerning hydrophosphorylic structures (1)–(5).

The calculations were performed by the spin restricted Hartree-Fock Roothaan (HFR) method on the 6-31G** basis taking into account the correlation effects at the MP2 level using the GAMESS program,[3] as well as by the DF method with the use of the PBE formula for the correlation-exchange functional[4] and the program due to D. Laikov.[5]

Both methods adequately represent the bond lengths of the compounds as compared to the experimental values in similar species (Table 1). The HFR + MP2 method systematically gave overestimated values for the Gibbs energies of tautomerization as compared to DF (Figure 1). With symmetrical and unsymmetrical substituents at the phosphorus atom, the difference between G calculated by the two methods is 4–6 or 3–10 kcal mol^{-1}, respectively. At the same time, changes in G upon the successive replacement of hydrogen in methyl groups by fluorine atoms are similar, as found by both of the methods.

Previously,[6] the data on E_0 calculated by the DF method were found to be more reliable than the HFR + MP2 data. According to our calculations, none of the test compounds is in a true equilibrium between two tautomers. The DF calculations demonstrate that in the gas phase the compound $(CH_2F)(Me)POH$ most closely approaches an equilibrium; in this case, the tautomerization Gibbs energy calculated using the DF method is equal to –1.1 kcal mol^{-1}.

Table 1 Bond lengths (Å) in the test compounds (the corresponding experimental data are taken from ref. 8).

Bond (reaction)	Experimental value	HFR + MP2	DF
P–C (1)	1.844[a]	1.831	1.855
P–C (4)	1.904[b]	1.866	1.922
P–O (5)	1.620[c]	1.639	1.656
P=O (1)	1.476[d]	1.482	1.511
P–C (1)	1.809[d]	1.855	1.832
P=O (4)	1.517[e]	1.475	1.495
P–O (4)	1.573[e]	1.610	1.620
P=O (5)	1.477[f]	1.475	1.495
P–O (5)	1.581[f]	1.639	1.656
O–C (5)	1.433[f]	1.443	1.450

[a]In PMe_3. [b]In $P(CF_3)_3$. [c]In $P(OMe)_3$. [d]In $O=PMe_3$. [e]In $O=P(OH)_3$. [f]In $O=P(OMe)_3$.

We attempted to take into account solvation effects in terms of the polarizable continuum model of a solvent, because the test reactions are known to proceed in nonpolar aprotic solvents at about 300 K. In our calculations, we decided on tetrahydrofuran as such a solvent.

At the same time, the E_0 calculated by the DF technique[6] for the reaction in which R = R′ = MeO were consistent with the results of a gas-phase experiment[7] and an experiment on the liquid-phase rearrangement of bis(pentafluorophenyl)phosphinic acid. As can be seen in Figure 1, the introduction of the compounds into a solvent makes structures I more stable than structures II, as compared to the behaviour of reactants in the gas phase. According to our study, at 300 K the species $(CF_3)(CHF_2)POH$ is closer to the eqiulibrium than other test compounds in solu-

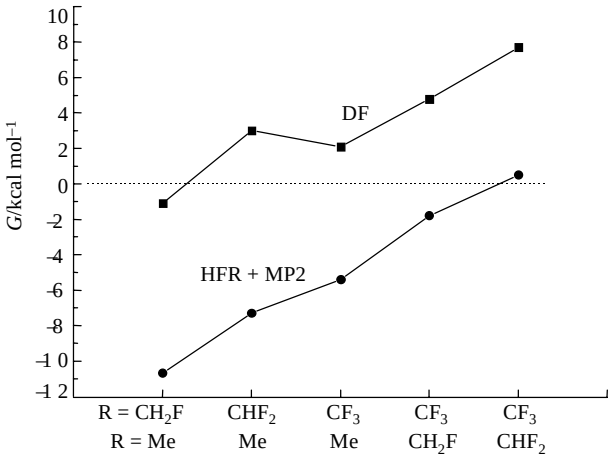


Figure 1 Comparative Gibbs energies (G) of tautomerization for reactions (1)–(5) in the gas phase, at 300 K, according to HFR + MP2 and DF data.

tion. Thus, the calculated solvation effects on ΔG (Figure 1) of the reaction for different compounds should be verified in an experiment.

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