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PHOSPHORUS–CARBON DIAD TAUTOMERISM IN PHOSPHONIUM COMPOUNDS. THEORETICAL STUDY

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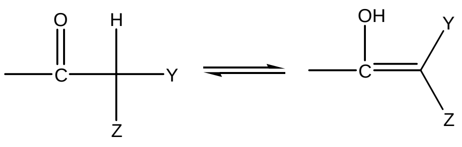
Abstract. Phosphorus–carbon diad tautomerism was studied in phosphonium compounds with such strong electron acceptor substituents as cyano-, nitro-, fluorosulphonyl-, and trifluoromethylsulphonyl groups using semiempirical, *ab initio*, and DFT methods. It was shown that in the gas phase all studied monosubstituted species are in the phosphoryl form and no enol forms should be detectable. In contrast, for doubly substituted compounds enol forms should be well detectable and in some cases even predominant. Comparison of different calculation methods indicated that *ab initio* (HF/6-31 + G*) and DFT (B3LYP/6-311 + G**) calculations give close results. Both applied semiempirical methods (PM3 and MNDO/d) seem to overestimate strongly the stability of the enol form. It was also found that the MNDO/d method gives unrealistic results for compounds containing both hypervalent phosphorus and sulphur.

Key words: enolization, phosphoryl group, calculation, PM3, MNDO/d, DFT.

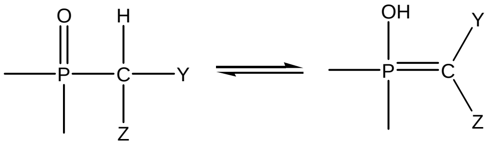
INTRODUCTION

The enolization ability of the carbonyl group is well known. This phenomenon is most pronounced in β-dicarbonyl compounds and other species with one or more strong electronegative groups Y (and Z) in the β-position relative to the carbonyl group.



It is well known that simple ketones are only marginally enolized. Strong acidifying effect of the substituents Y and Z is required for enolization. These problems were studied already seventy years ago by Arndt and co-workers [1–4].

In phosphororganic chemistry the phosphoryl group P═O is the analogue of the carbonyl group. However, very little is known about possible enol forms of the phosphoryl group.



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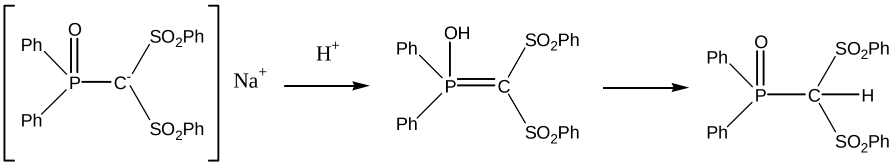
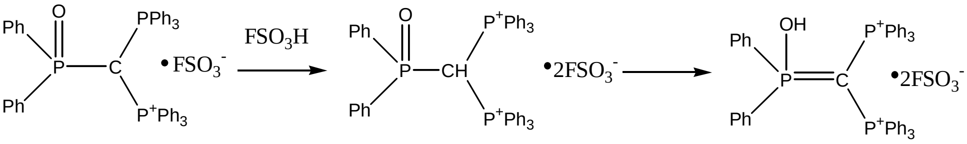
A possible enolate character of several phosphoryl anions has been proposed [5–8] and also established [9]. Kolodyazhnyj showed [10] that the sodium salt of diphenylphosphonylbis(phenylsulphonyl)methane forms unstable phosphaenol upon the acidification of its solution. The formed phosphaenol rearranges rapidly and irreversibly into phosphoryl form.



Mastryukova et al. [11] obtained a stable phosphaenol form of diphenylphosphonylbis(triphenylphosphonio)methane by the protonation of the corresponding phosphoranphosphonium salt with fluorosulphuric acid.



Mastryukova & Kabachnik [12] published a review of other experimentally established phosphoryl-phosphaenol equilibriums and concluded that the phosphoryl group can give enol forms. For this high acidity of the C—H form is required. As it is well known that the equilibrium constant of the tautomeric equilibrium K_T is given by the ratio of acidity constants (K_1 and K_2) of tautomeric forms $K_T = K_1/K_2$, it is also required that the acidity of the phosphaenol form should be close to that of the phosphoryl form. It was concluded [12] that for experimental observation of oryl–phosphoryl–phosphaenol equilibrium the substituents at the central carbon should have the sum of their Hammett constants $\Sigma\sigma^{-}_{CH}$ higher than 2.

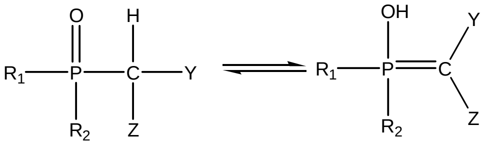
In the current work we have studied phosphoryl–phosphaenol equilibriums in the gas phase using DFT and quantum chemical calculations. Our primary goal was to establish the feasibility of such equilibriums, and to investigate the factors influencing it. As compounds with several phenyl groups attached to phosphorus were beyond our computational capabilities, we used model compounds with phenyl groups substituted by methyl groups or hydrogen atoms. We applied diverse variation of computational methods – semiempirical PM3 and MNDO/d [13, 14], *ab initio* HF/6-31 + G*, and DFT B3LYP/6-311 + G** to investigate the problem. As a result, also a comparison of the applicability of these methods for further studies of larger and experimentally accessible compounds can be made.

METHODS

Semiempirical calculations at PM3 level were performed using MOPAC 6.0 [15] program, while MNDO/d calculations were made with CS Chem3D 5.0 for Windows [16]. All *ab initio* and DFT calculations were performed using the Gaussian 98 [17] program package.

At the semiempirical PM3 and MNDO/d levels geometries of all possible conformers were optimized. *Ab initio* (HF/6-31 + G*) and DFT (B3LYP/6-311 + G**) optimizations were performed only for the most stable conformers found with both PM3 and MNDO/d methods. In all cases frequencies were calculated to ensure the completion of optimization in the minimum. Calculated frequencies were also used for the evaluation of thermodynamic parameters.

The position of the tautomeric equilibrium



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was estimated based on the tautomerization energies defined as

$$\Delta E_T = E_E - E_K$$

$$\Delta H_T = H_E - H_K$$

$$\Delta G_T = G_E - G_K$$

where E_E and E_K are total energies of forms A and B, H_E and H_K are respective enthalpies (in the case of *ab initio* and DFT calculations) or heats of formation (PM3 and MNDO/d), and G_E and G_K are respective free energies.

RESULTS AND DISCUSSION

Heats of formation for most stable conformers of all studied species calculated at semiempirical PM3 and MNDO/d levels of theory are given in Table 1. Total energies, enthalpies, and free energies calculated at HF/6-31 + G* and B3LYP/6-311 + G** levels of theory are presented in Tables 2 and 3, respectively. Table 4 lists tautomerization enthalpies for all studied species.

Table 1. Heats of formation (ΔH^f, at 298 K), calculated at PM3 and MNDO/d levels of theory. All values are in kcal/mol

R^1	R^2	R^3	PM3		MNDO/d	
			$\Delta H^f_{phosphoryl}$	ΔH^f_{enol}	$\Delta H^f_{phosphoryl}$	ΔH^f_{enol}
H	H	CH_3	–74.1	–57.1	–87.4	–42.9
H	CH_3	CH_3	–78.7	–60.4	–97.3	–52.2
CH_3	CH_3	CH_3	–82.7	–62.5	–105.4	–59.8
H	H	NH_2	–77.7	–65.3	–86.9	–63.8
H	NH_2	NH_2	–86.8	–75.1	–97.7	–72.3
NH_2	NH_2	NH_2	–94.0	–82.3	–106.8	–84.5
H	H	CH_2CN	–37.3	–34.0	–53.5	–23.8
H	CH_3	CH_2CN	–40.9	–36.4	–63.4	–34.5
CH_3	CH_3	CH_2CN	–43.8	–38.0	–71.5	–43.3
H	H	$CH(CN)_2$	–4.7	–2.6	–14.3	1.7
H	CH_3	$CH(CN)_2$	2.2	–4.6	–24.5	–10.1
CH_3	CH_3	$CH(CN)_2$	0.5	–5.5	–78.6	–43.3
H	H	CH_2NO_2	–77.3	–86.9	–60.8	–40.1
H	CH_3	CH_2NO_2	–80.4	–89.2	–71.3	–51.2
CH_3	CH_3	CH_2NO_2	–82.3	–90.9	–79.6	–60.7
H	H	$CH(NO_2)_2$	–71.6	–102.3	–28.8	–22.9
H	CH_3	$CH(NO_2)_2$	–73.8	–103.2	–38.6	–32.8
CH_3	CH_3	$CH(NO_2)_2$	–73.3	–102.9	–65.4	–42.0
H	H	CH_2SO_2F	–190.7	–201.2	–206.6	–207.5
H	CH_3	CH_2SO_2F	–193.6	–203.3	–216.0	–219.8
CH_3	CH_3	CH_2SO_2F	–194.0	–204.2	–224.8	–228.1
H	H	$CH_2SO_2CF_3$	–270.3	–283.9	–278.0	–283.1
H	CH_3	$CH_2SO_2CF_3$	–273.2	–286.0	–288.6	–295.2
CH_3	CH_3	$CH_2SO_2CF_3$	–274.8	–287.0	–279.0	–302.2
H	H	$CH(SO_2F)_2$	–292.5	–325.5	–16.4	–84.0

Table 2. Total energies (*E*), zero-point vibrational energy corrections (ZPVE), enthalpies (*H*, at 298 K), and free energies (*G*, at 298 K), calculated at HF/6-31 + G* level of theory. All values are in atomic units

R^1	R^2	R^3	$E_{phosphoryl}$	$ZPVE_{phosphoryl}$	$H_{phosphoryl}$	$G_{phosphoryl}$	E_{enol}	$ZPVE_{enol}$	H_{enol}	G_{enol}
H	H	CH_3	–456.36631	0.06510	–456.29613	–456.32740	–456.30312	0.06280	–456.23478	–456.26669
H	CH_3	CH_3	–495.41882	0.09539	–495.31689	–495.35180	–495.35391	0.09327	–495.25373	–495.28915
CH_3	CH_3	CH_3	–534.46971	0.12548	–534.33614	–534.37446	–534.40345	0.12313	–534.27168	–534.31120
H	H	NH_2	–472.37688	0.05427	–472.31765	–472.34858	–472.33880	0.05254	–472.28127	–472.31215
H	NH_2	NH_2	–527.44368	0.07348	–527.36415	–527.39784	–527.40282	0.07096	–527.32524	–527.36004
NH_2	NH_2	NH_2	–582.50813	0.09243	–582.40843	–582.44476	–582.46729	0.09095	–582.36904	–582.40541
H	H	CH_2CN	–548.09485	0.06499	–548.02339	–548.05929	–548.05307	0.06325	–547.98295	–548.01958
H	CH_3	CH_2CN	–587.14911	0.09527	–587.04591	–587.08526	–587.10684	0.09360	–587.00485	–587.04502
CH_3	CH_3	CH_2CN	–626.20159	0.12534	–626.06674	–626.10937	–626.15940	0.12348	–626.02581	–626.06992
H	H	$CH(CN)_2$	–639.80656	0.06394	–639.73459	–639.77489	–639.78950	0.06283	–639.71824	–639.75943
H	CH_3	$CH(CN)_2$	–678.85861	0.09411	–678.75492	–678.79869	–678.84672	0.09324	–678.74353	–678.78816
CH_3	CH_3	$CH(CN)_2$	–717.91217	0.12416	–717.77681	–717.82381	–717.90132	0.12307	–717.76652	–717.81526
H	H	CH_2NO_2	–659.83213	0.07028	–659.75465	–659.79409	–659.80355	0.06900	–659.72757	–659.76474
H	CH_3	CH_2NO_2	–698.88721	0.10067	–698.77788	–698.82008	–698.85871	0.09916	–698.75094	–698.79177
CH_3	CH_3	CH_2NO_2	–737.93581	0.13077	–737.79481	–737.84000	–737.91088	0.12921	–737.77150	–737.81554
H	H	$CH(NO_2)_2$	–863.27638	0.07405	–863.19289	–863.23825	–863.27229	0.07331	–863.18986	–863.23299
H	CH_3	$CH(NO_2)_2$	–902.33396	0.10443	–902.21862	–902.26639	–902.32790	0.10330	–902.21382	–902.26094
CH_3	CH_3	$CH(NO_2)_2$	–941.38651	0.13445	–941.23952	–941.29061	–941.37133	0.13169	–941.22848	–941.27482
H	H	CH_2SO_2F	–1102.38477	0.07029	–1102.30607	–1102.34925	–1102.35714	0.06908	–1102.27966	–1102.32084
H	CH_3	CH_2SO_2F	–1141.43990	0.10063	–1141.32943	–1141.37471	–1141.41290	0.09928	–1141.30361	–1141.34839
CH_3	CH_3	CH_2SO_2F	–1180.48942	0.13074	–1180.34730	–1180.39528	–1180.46275	0.12894	–1180.32191	–1180.37090
H	H	$CH_2SO_2CF_3$	–1339.12268	0.08373	–1339.02779	–1339.07712	–1339.10026	0.08278	–1339.00643	–1339.05424
H	CH_3	$CH_2SO_2CF_3$	–1378.17782	0.11402	–1378.05117	–1378.10347	–1378.15589	0.11298	–1378.03023	–1378.08163
CH_3	CH_3	$CH_2SO_2CF_3$	–1417.23074	0.14416	–1417.07240	–1417.12764	–1417.20544	0.14258	–1417.04829	–1417.10363
H	H	$CH(SO_2F)_2$	–1748.37516	0.07452	–1748.28876	–1748.33924	–1748.38202	0.07442	–1748.29589	–1748.34572

Table 3. Total energies (E), zero-point vibrational energy corrections (ZPVE), enthalpies (H, at 298 K), and free energies (G, at 298 K), calculated at B3LYP/6-311 + G** level of theory. All values are in atomic units

R^1	R^2	R^3	$E_{phosphoryl}$	$ZPVE_{phosphoryl}$	$H_{phosphoryl}$	$G_{phosphoryl}$	E_{enol}	$ZPVE_{enol}$	H_{enol}	G_{enol}
H	H	CH_3	–457.76271	0.05983	–457.69762	–457.72919	–457.71108	0.05732	–457.64851	–457.67990
H	CH_3	CH_3	–497.10474	0.08839	–497.00952	–497.04497	–497.05153	0.08653	–496.95775	–496.99375
CH_3	CH_3	CH_3	–536.44500	0.11671	–536.31976	–536.35895	–536.39010	0.11455	–536.26639	–536.30705
H	H	NH_2	–473.82487	0.04966	–473.77012	–473.80124	–473.79356	0.04816	–473.74026	–473.77140
H	NH_2	NH_2	–529.23054	0.06773	–529.15647	–529.19067	–529.19707	0.06558	–529.12458	–529.15992
NH_2	NH_2	NH_2	–584.63168	0.08479	–584.53859	–584.57785	–584.59958	0.08430	–584.50750	–584.54471
H	H	CH_2CN	–550.01956	0.05925	–549.95354	–549.99010	–549.98819	0.05803	–549.92304	–549.96001
H	CH_3	CH_2CN	–589.36350	0.08785	–589.26730	–589.30749	–589.33088	0.08658	–589.23553	–589.27637
CH_3	CH_3	CH_2CN	–628.70550	0.11624	–628.57923	–628.62291	–628.67277	0.11487	–628.54737	–628.59202
H	H	$CH(CN)_2$	–642.26204	0.05782	–642.19574	–642.23703	–642.25201	0.05740	–642.18586	–642.22754
H	CH_3	$CH(CN)_2$	–681.60391	0.08621	–681.50753	–681.55255	–681.59843	0.08591	–681.50206	–681.54761
CH_3	CH_3	$CH(CN)_2$	–720.94704	0.11467	–720.82052	–720.86891	–720.94246	0.11396	–720.81609	–720.86626
H	H	CH_2NO_2	–662.31265	0.06341	–662.24167	–662.28168	–662.29237	0.06277	–662.22226	–662.26005
H	CH_3	CH_2NO_2	–701.65735	0.09210	–701.55611	–701.59941	–701.63619	0.09103	–701.53605	–701.57789
CH_3	CH_3	CH_2NO_2	–740.99621	0.12035	–740.86501	–740.91158	–740.97773	0.11940	–740.84758	–740.89282
H	H	$CH(NO_2)_2$	–866.84937	0.06556	–866.77378	–866.82011	–866.85038	0.06517	–866.77557	–866.81969
H	CH_3	$CH(NO_2)_2$	–906.19487	0.09419	–906.08899	–906.13874	–906.19566	0.09350	–906.09078	–906.13894
CH_3	CH_3	$CH(NO_2)_2$	–945.53719	0.12259	–945.40122	–945.45447	–945.53899	0.12161	–945.40419	–945.45659
H	H	CH_2SO_2F	–1105.66805	0.06319	–1105.59672	–1105.63761	–1105.64425	0.06240	–1105.57276	–1105.61533
H	CH_3	CH_2SO_2F	–1145.01313	0.09184	–1144.91070	–1144.95768	–1144.98941	0.09081	–1144.88781	–1144.93423
CH_3	CH_3	CH_2SO_2F	–1184.35138	0.12021	–1184.21894	–1184.26865	–1184.33194	0.11922	–1184.20028	–1184.24987
H	H	$CH_2SO_2CF_3$	–1343.51897	0.07505	–1343.43189	–1343.48330	–1343.49895	0.07447	–1343.41254	–1343.46231
H	CH_3	$CH_2SO_2CF_3$	–1382.86408	0.10356	–1382.74688	–1382.80265	–1382.84365	0.10286	–1382.72711	–1382.78086
CH_3	CH_3	$CH_2SO_2CF_3$	–1422.20693	0.13200	–1422.05965	–1422.11745	–1422.18391	0.13109	–1422.03737	–1422.09432
H	H	$CH(SO_2F)_2$	–1753.55028	0.06551	–1753.47170	–1753.52464	–1753.55260	0.06573	–1753.47415	–1753.52600

Table 4. Tautomerization enthalpies (ΔH) calculated at different levels of theory. All values are in kcal/mol

R^1	R^2	R^3	ΔH(PM3)	ΔH(MNDO/d)	ΔH(HF)	ΔH(B3LYP)
H	H	CH_3	–17.0	–44.5	–38.5	–30.8
H	CH_3	CH_3	–18.3	–45.1	–39.6	–32.5
CH_3	CH_3	CH_3	–20.2	–45.6	–40.5	–33.5
H	H	NH_2	–12.4	–23.1	–22.8	–18.7
H	NH_2	NH_2	–11.7	–25.4	–24.4	–20.0
NH_2	NH_2	NH_2	–11.7	–22.3	–24.7	–19.5
H	H	CH_2CN	–3.3	–29.7	–25.4	–19.1
H	CH_3	CH_2CN	–4.5	–28.9	–25.8	–19.9
CH_3	CH_3	CH_2CN	–5.8	–28.2	–25.7	–20.0
H	H	$CH(CN)_2$	–2.1	–16.0	–10.3	–6.2
H	CH_3	$CH(CN)_2$	6.8	–14.4	–7.1	–3.4
CH_3	CH_3	$CH(CN)_2$	6.0	–35.3	–6.5	–2.8
H	H	CH_2NO_2	9.6	–20.7	–17.0	–12.2
H	CH_3	CH_2NO_2	8.8	–20.1	–16.9	–12.6
CH_3	CH_3	CH_2NO_2	8.6	–18.9	–14.6	–10.9
H	H	$CH(NO_2)_2$	30.7	–5.9	–1.9	1.1
H	CH_3	$CH(NO_2)_2$	29.4	–5.8	–3.0	1.1
CH_3	CH_3	$CH(NO_2)_2$	29.6	–23.4	–6.9	1.9
H	H	CH_2SO_2F	10.5	0.9	–16.6	–15.0
H	CH_3	CH_2SO_2F	9.7	3.8	–16.2	–14.4
CH_3	CH_3	CH_2SO_2F	10.2	3.3	–15.9	–11.7
H	H	$CH_2SO_2CF_3$	13.6	5.1	–13.4	–12.1
H	CH_3	$CH_2SO_2CF_3$	12.8	6.6	–13.1	–12.4
CH_3	CH_3	$CH_2SO_2CF_3$	12.2	23.2	–15.1	–14.0
H	H	$CH(SO_2F)_2$	33.0	67.6	4.5	1.5

PHOSPHORYL–PHOSPHAENOL TAUTOMERISM EQUILIBRIUM

Enolization energies (see Table 4), calculated at the highest applied level of theory – B3LYP/6-311 + G** – indicate that no monosubstituted phosphoryl compound with very strong electron acceptor substituents studied should undergo experimentally detectable enolization. In all these cases the phosphoryl forms are at least by 10 kcal/mol more stable than the corresponding enols. The most enolizing substituents appear to be the nitro and trifluoromethylsulphonyl groups, with very close enolizing power. The last fact is somewhat surprising as the substituent parameters for the nitro group ($\sigma_\alpha = -0.26$, $\sigma_F = 0.65$, and $\sigma_R = 0.18$, see for example [18]) are smaller than the corresponding ones for the CF_3SO_2 group (–0.58, 0.84, and 0.21, respectively).

In contrast, for doubly substituted compounds we predict that in some cases (dinitro- and difluorosulphonyl compounds) the enol form should be predominant and in other cases (dicyano compounds) at least detectable.

Fair correlation was found between our calculated enolization reaction energies and experimental acidities [19] of corresponding substituted methanes (see Fig. 1). This correlation could be useful for prediction of enolization extent in compounds not studied in the present work.

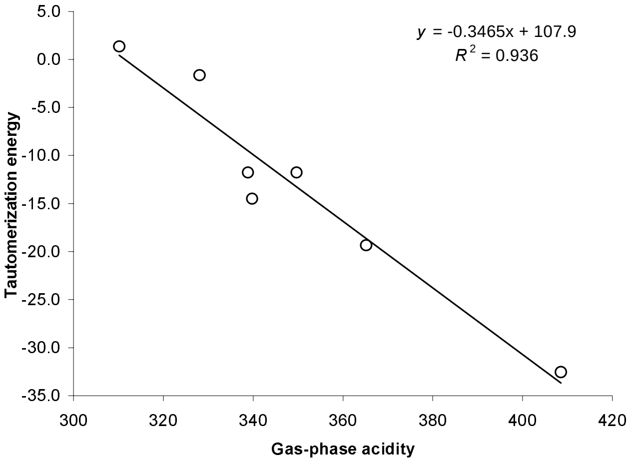

Fig. 1. Correlation between experimental gas-phase acidities [19] and calculated (B3LYP/6-311 + G**, $R^1 = R^2 = CH_3$) tautomerization energies. For $CH_2(NO_2)_2$ and CH_3SO_2F, where no experimental data were available, calculated (B3LYP/6-311 + G**) gas-phase acidities (310.2 and 338.9 kcal/mol, respectively) were used.

Experimental observations led Mastryukova & Kabachnik [12] to the conclusion that for experimental observation of phosphoryl–phosphaenol equilibrium the substituents at the central carbon should have the sum of their Hammett constants $\sum\sigma^{-}_{CH}$ higher than 2. Our gas-phase calculations (see Table 4) indicate that for the studied model compounds the required sum of substituent constants σ_F should be 1.3 (two nitro substituents) or higher for the enol form to be more stable than the phosphoryl form. However, it should be kept in mind that Mastryukova & Kabachnik [12] used in their experimental work different substituents R^1 and R^2 (phenyl groups instead of methyl groups or hydrogen atoms) than was possible in the current study. Further study of the influence of bulkier substituents R^1 and R^2 seems thus highly desirable.

COMPARISON OF THE COMPUTATIONAL METHODS USED

Tautomerization energies calculated at semiempirical PM3 and *ab initio* HF/6-31 + G* levels were compared with results obtained at the highest applied level of theory – B3LYP/6-311 + G**. Statistical linear regression analysis was performed according to the formula

$$\Delta H_T \text{ (method)} = a \cdot \Delta H_T \text{ (B3LYP/6-311 + G**)} + b,$$

where *a* is the slope of regression line and *b* is the intercept. Results of correlation analysis are presented in Table 5.

Comparison of *ab initio* HF/6-31 + G* and B3LYP/6-311 + G** results indicates reasonable correspondence between the two methods. The average unsigned error is 4.3 kcal/mol, and the correlation between the two methods is good (see Fig. 2), as also indicated by the correlation coefficient R^2 (0.960) and average deviation of points from correlation line (1.6 kcal/mol). The non-zero intercept (–2.53 ± 0.78) and non-unity slope (1.11 ± 0.05) indicate, however, the presence of some systematic deviation between the two methods. It is noteworthy that as a rule the energies of the tautomerization reaction obtained at HF/6-31 + G* level are greater (more positive, i.e. equilibrium is shifted towards the formation of the phosphoryl compound). The only exception is $H_2P(O)CH(SO_2F)_2$, where the DFT results predict less enolization than the HF method.

Table 5. Results of correlation analysis

Method	Slope *a*	Intercept *b*	Correlation coefficient R^2	Number of points *N*
HF/6-31 + G*	1.11 ± 0.05	–2.53 ± 0.78	0.960	25
HF/6-31 + G[a]	1.12 ± 0.04	–2.33 ± 0.63	0.979	23
PM3	1.31 ± 0.16	22.2 ± 2.66	0.761	25
PM3[b]	1.47 ± 0.07	28.29 ± 1.19	0.968	19
MNDO/d	1.16 ± 0.29	1.05 ± 4.97	0.417	25
MNDO/d[c]	1.11 ± 0.07	–6.90 ± 1.31	0.949	16

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[a] without $H_2P(O)CH(SO_2F)_2$ and $Me_2P(O)CH(NO_2)_2$;
[b] without amino- and dicyano compounds;
[c] without sulphuryl compounds.

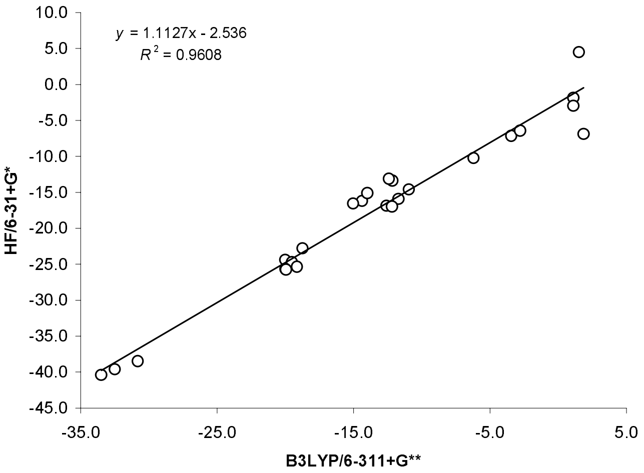

Fig. 2. Correlation between tautomerization energies calculated at HF/6-31 + G* and B3LYP/6-311 + G** levels of theory.

The two most deviating points from the correlation line are those corresponding to the two strongly enolized compounds – $H_2P(O)CH(SO_2F)_2$ and $Me_2P(O)CH(NO_2)_2$ (deviations from the correlation line are 5.3 and –6.5 kcal/mol, respectively). It should be noted that exclusion of those two points from correlation improves somewhat the overall correlation ($R^2 = 0.97$), but the slope and intercept of the correlation line remain practically the same. It is also interesting to note that the points corresponding to other strongly enolized (according to our calculations) compounds, $H_2P(O)CH(NO_2)_2$ and $Me_2P(O)CH(NO_2)_2$, are nicely placed close to the correlation line.

Energies of the tautomerization reaction obtained by the semiempirical PM3 method strongly differ from those obtained at B3LYP/6-311 + G** level of theory (average difference is 17.2 kcal/mol). The correlation between those two datasets is weak (see Fig. 3), as indicated by the square of the correlation coefficient: R^2 is only 0.761. The slope (1.31 ± 0.16) and intercept (22.2 ± 2.66) of the regression line clearly indicate systematic overestimation of the enolization of the studied phosphoryl compounds by the PM3 method. Figure 2 shows that there are two groups of points that deviate strongly from the correlation line. These points correspond to amino substituted compounds (points 4–6) and dicyano compounds (points 10–12). The elimination of those six points from regression analysis strongly enhances the overall correlation ($R^2 = 0.968$), but as indicated by the intercept (28.3 ± 1.2) and slope of the correlation line (1.47 ± 0.07) also adds to the systematic difference between the two methods. Those observations indicate that the PM3 method can be used for the prediction of phosphorus–carbon diad tautomerism only if empirical corrections are made.

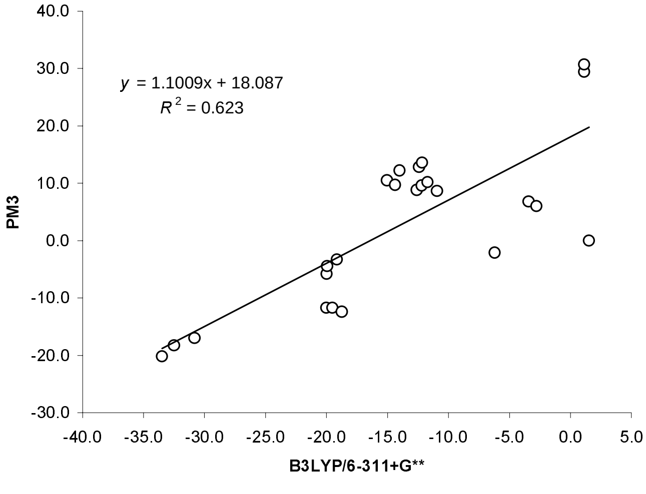

Fig. 3. Correlation between tautomerization energies calculated at PM3 and B3LYP/6-311 + G** levels of theory.

As all the compounds studied in this work have so-called hypervalent phosphorus (and in some cases also sulphur) atoms, where explicit inclusion of d-orbitals in semiempirical calculations has been considered important, we also included the MNDO/d method in the current study. Figure 4 indicates that the results of MNDO/d calculations correlate even worse with those obtained at B3LYP/6-311 + G** level of theory than the PM3 results do (correlation coefficient R^2 is only 0.44). Closer examination of data reveals that this discrepancy stems from the overestimation of the enolization energies for all compounds containing the sulphuryl group. This phenomenon is probably due to the fact that the MNDO/d method was parametrized on the compounds that did not contain both hypervalent sulphur and phosphorus atoms.

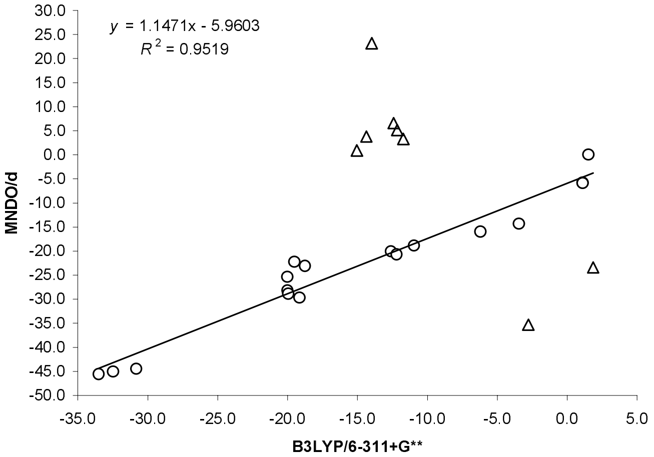

Fig. 4. Correlation between tautomerization energies calculated at MNDO/d and B3LYP/6-311 + G** levels of theory.

Exclusion of all six sulphuryl compounds from correlation enhances the correlation significantly (R^2 is now 0.957). The systematic differences between MNDO/d and B3LYP/6-311 + G** results still remain as indicated by the slope (1.11±0.07) and intercept (–6.9±1.31) of the regression line. However, these values are much smaller than those for the PM3 method (1.31 and 22.2, respectively), and close to HF/6-31 + G* ones (1.11 and –2.53, respectively). So, the MNDO/d method seems to be the preferable semiempirical method for the calculation of enolization energies for larger systems that do not contain hypervalent sulphur. For this group of compounds reparametrization of the MNDO/d method seems to be highly desirable.

CONCLUSIONS

Our results indicate that in the gas phase all monosubstituted species studied exist in the phosphoryl form and the enol forms should not be detectable. In contrast, for doubly substituted compounds enol forms should be well detectable and in some cases even predominant. The sum of substituent constants σ_F equal or higher than 1.3 is required for the predominance of the enol form over the phosphoryl form.

Comparison of different calculation methods indicated that *ab initio* (HF/6-31 + G*) and DFT (B3LYP/6-311 + G**) calculations give close results with good correlation. Both applied semiempirical methods (PM3 and MNDO/d) seem to overestimate strongly the stability of the enol form. It was also found that the MNDO/d method gives unrealistic results for compounds containing both hypervalent phosphorus and sulphur. However, when these compounds are excluded, good correlation was found between the calculated enolization energies. Thus, it is reasonable to prefer the MNDO/d method for further investigation of phosphorus–carbon diad tautomerism, provided that no hypervalent sulphur atoms are present.

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FOSFOONIUMI ÜHENDITE PROTOTROOPSE TAUTOMEERIA TEOREETILINE UURIMINE

Peeter BURK, Uldo MÖLDER ja Kaido TÄMM

Kvantkeemiliste (MNDO/d, PM3, HF/6-31 + G*) ja tihedusfunktsionaaliteooria (B3LYP/6-311 + G**) meetoditega uuriti fosforüül-fosfaenoolset tasakaalu tugevate elektronaktseptoorsete asendajatega ühendites. Saadud tulemused näitavad, et gaasifaasis eksisteerivad kõik monoasendatud ühendid fosforüülvormis ja enoolvormi ei ole peaaegu võimalik määrata. Diasendatud ühendites on enoolvorm hästi määratav ja mõningatel juhtudel isegi domineeriv. Enoolvormi domineerimiseks fosforüülvormi üle peab substituentide σ_F konstantide summa olema võrdne või suurem kui 1,3. Meetodite omavaheline võrdlus näitab, et *ab initio* HF/6-31 + G* meetod ja B3LYP/6-311 + G** meetod annavad lähedasi tulemusi ja nendevaheline korrelatsioon on hea. Mõlemad kasutatud poolempiirilised meetodid (PM3 ja MNDO/d) hindavad tugevalt üle enoolvormi stabiilsust. Leiti ka, et MNDO/d annab ebareaalseid tulemusi ühendite korral, mis sisaldavad hüpervalentse fosfori kõrval ka hüpervalentset väävlit. Nende ühendite kõrvalejätmisel saab aga hea korrelatsiooni arvutatud enolisatsioonienergiate vahel. MNDO/d näibki olevat eelistatum poolempiiriline arvutusmeetod uurimaks suuremate, *ab initio* ja DFT tasemel käsitlematute fosfooniumi ühendite tautomeerset tasakaalu eeldusel, et uuritavad ühendid ei sisalda hüpervalentset väävlit.