Quantum Chemical Calculations of 31P NMR Chemical Shifts: Scopes and Limitations

Journal:	*Physical Chemistry Chemical Physics*
Manuscript ID:	CP-ART-01-2015-000240.R1
Article Type:	Paper
Date Submitted by the Author:	02-Feb-2015
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Cite this: DOI: 10.1039/c0xx00000x

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Quantum Chemical Calculations of ^{31}P NMR Chemical Shifts: Scopes and Limitations†

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

The aim of this work is to convince practitioners of ^{31}P NMR method to regard simple GIAO quantum chemical calculations as a safe tool in structural analysis of organophosphorus compounds. Comparative analysis of calculated GIAO versus experimental ^{31}P NMR chemical shifts (CSs) for the wide range of phosphorus containing model compounds was carried out. The variety of combinations (at HF, DFT (B3LYP and PBE1PBE), MP2 level with 6-31G(d), 6-31+G(d), 6-31G(2d), 6-31G(d,p), 6-31+G(d,p), 6-311G(d), 6-311G(2d,2p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd) basis sets) were tested. As a whole, it is shown that, in contrast to what is claimed in the literature, high level of theory is not needed to obtain rather accurate predictions of ^{31}P CSs by GIAO method. The PBE1PBE/6-31G(d)//PBE1PBE/6-31G(d) level can be recommended for express estimation of ^{31}P CS. The PBE1PBE/6-31G(2d)//PBE1PBE/6-31G(d) combination can be recommended for routine application. The PBE1PBE/6-311G(2d,2p)//PBE1PBE/6-31+G(d) level can be proposed to obtain better results for reasonable cost. Scaling by linear regression parameters significantly improves results. The results obtained using these combinations were demonstrated on ^{31}P CS calculations for a variety of medium (large) size organic compounds of practical interest. Care has to be taken for compounds that may be involved in exchange between different structural forms (self-associates, associates with solvent, tautomers, conformers). For phosphorus located near the third group atoms ($(CH_3)_3PS$ and $P(SCH_3)_3$) the impact of relativistic effects may be notable.

Introduction

Today the GIAO method allows to calculate ^{1}H/^{13}C/^{15}N chemical shifts (CSs) with high accuracy at relatively modest level of theory and can be used for the variety of structural applications[1-15]. Moreover, its quality is also good enough to determine finer structural differences such as isomeric, conformational or tautomeric structures[16-35].

Having strong evidence that the ^{1}H/^{13}C/^{15}N GIAO calculations are reliable and very helpful in practice, it would be also desirable to extend this approach to other nuclei. From this point of view ^{31}P CSs are very attractive because, on the one hand, phosphorus is contained in many practically important compounds of organic, bioorganic and inorganic chemistry. On the other hand, the ^{31}P CS is extremely sensitive to electronic structure and range within 1000 ppm, therefore even small changes in the structure are strongly reflected in its CS[36]. Thus, if there was a reliable method to predict ^{31}P CSs, it could be useful as an additional tool for structure elucidation of novel phosphorus containing compounds.

However, despite the great need for such a tool, there is still unclear if ^{31}P CSs calculated in the framework of the GIAO method are reliable. In fact, there are relatively few reports on ^{31}P NMR CS calculations by quantum chemical methods[37-55]. In several systematic studies it was shown[48-55] that the satisfactory agreement between calculations and experiments is observed when quite "heavy" basis set or high level of theory‡ were used although deviations and exceptions were also found. It is necessary to stress that all these studies were only focused on the restricted types of small size compounds.

Summarizing literature one can conclude that obviously there is some progress in quantum chemical ^{31}P CS calculations. However some methodological questions are still left concerning the scopes and limitations of the method, in particular for practical application. Moreover, if to take into account that authors used either high levels of theory or very "heavy" basis

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/b000000x

‡ Here and further in the text "higher level of theory" means either higher level (HF-DFT-MP2) and/or more reach basis set. "Heavy combination" means level of theory used either for optimization of geometry or for chemical shift calculation steps.

sets it can hardly be applied for medium and large size compounds of practical interest.

Nevertheless in spite of limitations, it seems that with some care the method can be applied at least for phosphorus in most types of environment, although several problems have to be cleared up. First, additional shell in phosphorus may complicate the calculation of NMR parameters in frames of the GIAO method or may necessitate using "reach" basis sets and/or high level of theory, that may dramatically enlarge computational requirements, and as a result, it may become inapplicable for real size organic compounds. Therefore there should be some compromise between cost and quality, and it seems for variety of systems "cheaper" calculations may be sufficient.

Second, in most cases the shielding calculations are conducted for individual molecules, i.e. actually vacuum conditions are modeled, when there are no collisions and interactions with other molecules. This raises the question of how the data obtained for the vacuum will play solutions.

Third, in practice one operates not by shielding but with CS that for phosphorus are referred in respect with 75% H_3PO_4 in water. However, no data are available for this standard in the gas phase, which at first glance makes it difficult to use this compound as a reference in the calculations.

In this work we try to analyze the influence of the level of theory (CS//geometry) on the quality of CSs with the aim to find the compromise of being "light" enough to apply them to large compounds and still giving precision of practical value. To get this goal we will be guided by the next "road map" that comprises three goal-driven questions: 1) Is it possible to calculate ^{31}P CSs with reasonable accuracy and what is the minimum level of theory required? 2) Will the required level of theory (applied to small models) be applicable for "not small" organophosphorus compounds of practical interest? 3) What are complicated cases?

Results and Discussion

There are several factors that influence the results of calculations and thus the agreement between experimental and calculated values. In reality, it can be hardly expected that theoretical data will agree well in absolute values with experimental ones because of systematic errors and reference problem inherent to calculations. Therefore at first stage, goodness of used "combination" (CS//geometry) will be quantified by the squared correlation coefficient (R^2) between calculated and experimental sets. Thus the higher R^2 will mean that the correlation of the calculated versus experimental CSs is closer to linear although they may deviate in absolute value (i.e. linear approximation line will not cross the co-ordinate origin or its slope will not be equal to 1). The last problem may be well resolved then by referencing to the secondary reference or by empirical correction to account for the systematical error (*vide infra*).

The problem of the optimal choice for "combination" is the key point in CS calculations. These calculations consist of two steps: geometry optimization followed by the magnetic shielding calculation. Therefore, the first task is to find the optimal method for geometry optimization, which is then used in the CS calculations. Second, the influence of level of theory on resulting CSs should be analyzed. To these end, the calculations using the small model molecules (Figure 1) that cover wide range of structural types and particularities in organophosphorus chemistry were run with different "combinations". Theoretically calculated data have to be compared with gas-phase absolute shieldings. However, on the one hand, there are only very few models for which gas-phase data are available. On the other hand almost all ^{31}P NMR measurements are carried out in solution. Therefore, the solution CSs referred to H_3PO_4 were used in correlation analysis. Calculated absolute shieldings were converted into CSs by referencing to H_3PO_4 calculated in the same conditions. This combination of gas-phase and solution data poses some problems that will be discussed especially in the paper below. The test set of molecules excludes H_3PO_4 itself.

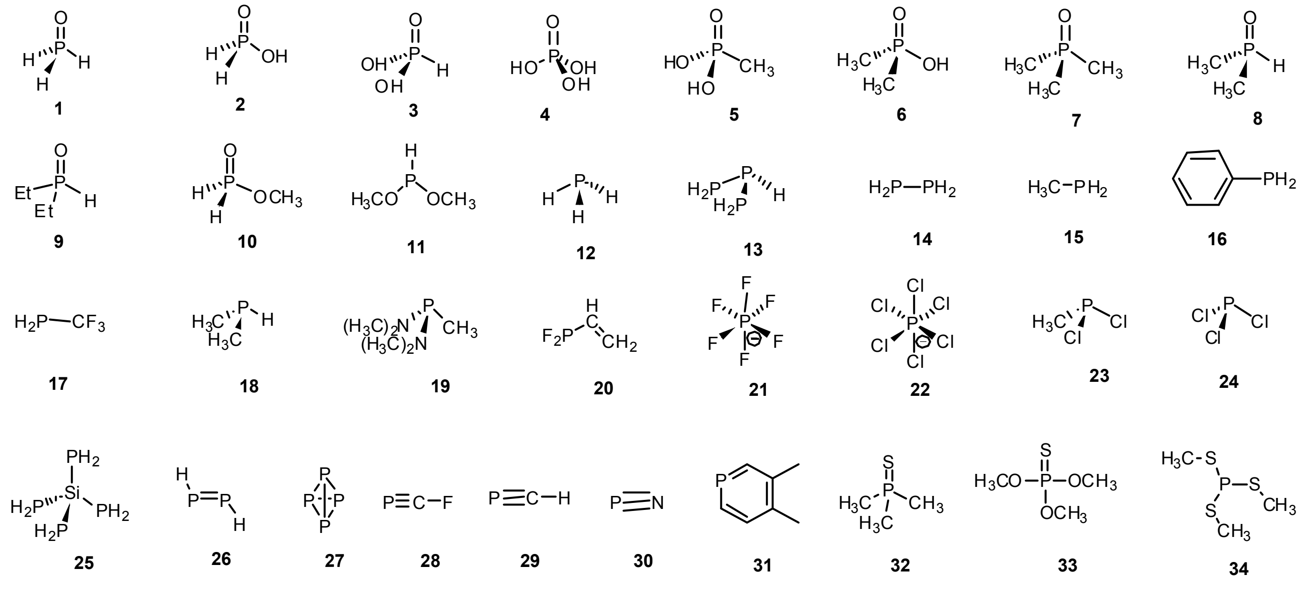

Fig. 1 Structures of model compounds.

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The influence of the combination on calculated chemical shifts

Variation of the method to optimize geometry

First, the level of theory was kept constant for CSs calculation and was varied for geometry optimization. HF, DFT and MP2 levels of theory with the variety of basis sets starting from simple 6-31-G(d) up to 6-311++G(3df,3pd) were used for optimization. In addition, the difference between two most popular functionals (PBE1PBE and B3LYP) was also checked. To ensure, two sets of data were obtained by using two levels to calculate CSs ((PBE1PBE/6-31G(d) and PBE1PBE/6-311++G(2d,2p)).

As a whole, calculated data for most of the model compounds at different levels of theory (for geometry optimization) correlate well with experimental values, e.g. in Figure 2a plot of calculated (PBE1PBE/6-31G(d)//PBE1PBE/6-31G(d)) versus experimental ^{31}P CSs is shown (results of the calculations for selected combinations are given in Table 1). Correlation coefficient (R^2) is high enough (0.93) although in several cases there is notable deviation from the line. It is worth stressing that there are two points that lie in very low/high field regions (-525.0 (P_4, **27**) and 494.0 (P_2H_2, **26**) ppm) that inevitably increase R^2 value due to the large band of correlated data (Table S1) and thus masks discrepancies in the main region. To analyze in more details this significant part of the plot, R^2 values with exception of extremely low/high field regions were recalculated (the second column Table S1). Indeed R^2 values become lower (0.874-0.927) in these cases. As one can see (Figure 2a) there are several points that deviates remarkably from linear correlation: -298.2 ($[PCl_6]^-$, **22**), -143.7 ($[PF_6]^-$, **21**), -207.0 (FCP, **28**), -13.9 (H_3PO, **1**), 191.2 (CH_3PCl_2, **23**), 275 (PN, **30**), 217 (PCl_3, **24**), 124.5 ($P(SCH_3)_3$, **34**) and 59.1 ($(CH_3)_3PS$, **32**) ppm. The variation of parameters at geometry optimization and magnetic shielding calculations do not improve correlations (Table S1, Table S2) and these points always deviate remarkably from the rest of cases. Probably in these points either additional effects interfere or the GIAO method fails to work well. Therefore these "difficult points" were excluded from the correlation analysis so far and we considered possible reasons of that disagreement in more details later. Thus, if we except these latter compounds, the correlation improves notably for the rest of 23 models (Figure 2b). These "normal" models were used for further analysis in order to reveal key factors that influence the quality of calculated ^{31}P CSs.

The close examination of theoretical versus experimental CS correlations for this set of model compounds let us get some conclusions on main factors that influence the quality of calculations. Regardless of the basis set used for CS calculations (PBE1PBE/6-31G(d) and PBE1PBE/6-311++G(2d,2p)) similar dependencies of R^2 values from the geometry optimization method were observed (e.g. the results for PBE1PBE/6-31G(d) method for CS calculations is presented in Figure 3. Data with other basis sets used to calculate CSs are given in Figure S1, S2 and Table S1, S2). First, only the inclusion of additional diffuse function slightly improves correlations and the use of better basis sets has almost no effect. Second, surprisingly, the HF level in general produces high enough correlation coefficients comparable with DFT and MP2 results (Figure 3). Third, the MP2 level improves correlation slightly but it essentially increases the time needed for calculations. Fourth, in general both popular functionals, B3LYP and PBE1PBE, give similar results although the latter seems to be slightly more preferable.

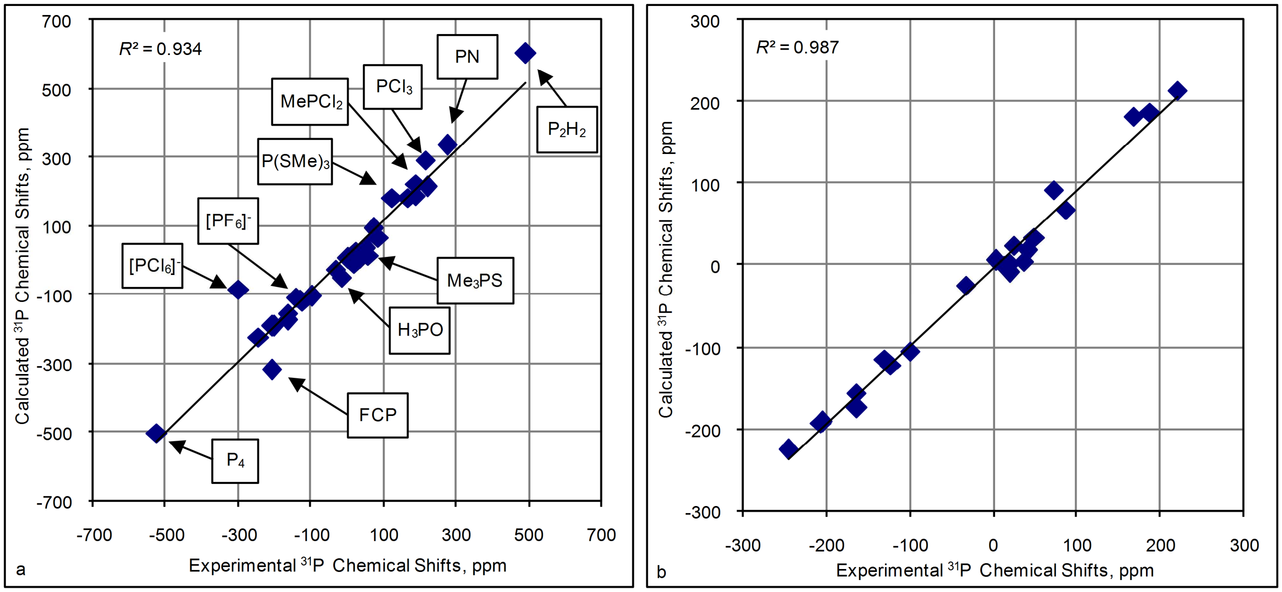

Fig. 2 Correlation of calculated (PBE1PBE/6-31G(d)//PBE1PBE/6-31G(d)) *versus* experimental ^{31}P CSs for the title compounds: a) for all model compounds and b) except "difficult cases" and data for very low/high field regions.

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Table 1 Calculated[a] (at selected levels of theory)[b] and experimental ^{31}P NMR CSs[c] for **1-34**.

№	Compound	6-31G(d)//6-31G(d)[b]		6-31G(2d)//6-31G(d)[b]		6-311G(2d,2p)//HF/6-31G(d)[a, b]		6-311G(2d,2p)//6-31+G(d)[b]		Exp.	Solvent	Ref.
		Unscaled	Scaled	Unscaled	Scaled	Unscaled	Scaled	Unscaled	Scaled			
1	H_3PO	*-49.4*	*-50.5*	*-84.5*	*-56.4*	*-62.7*	*-51.2*	*-71.2*	*-53.0*	*-13.9*	H_2O	*56*
2	H_3PO_2	-0.2	3.1	-25.8	4.1	-1.4	5.9	-9.1	4.9	12.5	H_2O	57
3	H_3PO_3	6.0	9.8	-8.5	21.9	3.5	10.6	2.5	15.7	3.0	HCl	58
4	H_3PO_4	*0.0*	*3.3*	*0.0*	*30.7*	*0.0*	*7.3*	*0.0*	*13.4*	*0.0*	H_2O	*59*
5	$CH_3P(O)(OH)_2$	24.1	29.5	17.2	48.4	28.9	34.2	29.0	40.4	24.8	H_2O	60
6	$(CH_3)_2P(O)OH$	34.0	40.3	21.7	53.0	42.1	46.5	39.4	50.1	49.4	CH_3OH	61
7	$(CH_3)_3PO$	4.9	8.6	-13.3	17.0	14.9	21.2	6.7	19.6	36.2	C_6H_6	62
8	$(CH_3)_2P(O)H$	-8.4	-5.9	-31.0	-1.3	-4.5	3.0	-11.7	2.5	20.5	CH_3OH	63
9	$(CH_3CH_2)_2P(O)H$	17.8	22.7	-5.4	25.1	18.6	24.7	13.2	25.7	41.0	$CHCl_3$	64
10	$H_2P(O)OCH_3$	2.9	6.4	-22.5	7.5	-4.6	3.0	-7.5	6.4	19.2	C_6H_6	65
11	$HP(OCH_3)_2$	166.8	185.0	146.7	181.8	194.8	189.0	172.8	174.4	171.5	na[f]	66
12	PH_3	-225.1	-241.9	-264.7	-241.9	-269.0	-243.7	-284.7	-251.9	-266.1	Gas phase	67
13	$(H_2P)_2PH$	-137.5	-146.5	-179.8	-154.5	-205.2	-184.2	-178.1	-152.6	-162.6	$(CH_3)_2CO$	68
14	$(H_2P)_2$	-191.2	-205.0	-233.6	-209.9	-229.1	-206.5	-239.1	-209.5	-203.6	$(CH_3)_2CO$	68
15	H_2PCH_3	-155.9	-166.6	-191.7	-166.8	-182.3	-162.8	-193.1	-166.6	-163.0	na	69
16	$PH_2(C_6H_5)$	-121.1	-128.6	-158.0	-132.0	-145.8	-128.7	-156.8	-132.7	-122.0	na	36
17	H_2PCF_3	-114.5	-121.5	-149.0	-122.8	-143.8	-126.8	-155.9	-131.9	-129.0	na	69
18	$HP(CH_3)_2$	-104.6	-110.7	-133.1	-106.4	-112.3	-97.5	-123.0	-101.2	-99.0	na	69
19	$CH_3P(N(CH_3)_2)_2$	67.9	77.2	51.1	83.3	79.6	81.5	70.9	79.5	86.4	$CHCl_3$	70
20	$CH_2=CHPF_2$	214.3	236.7	195.0	231.5	231.1	222.9	230.8	228.5	219.5	na	71
21	$[PF_6]^-$	*-107.5*	*-113.8*	*-116.8*	*-89.6*	*-133.6*	*-117.4*	*-133.1*	*-110.7*	*-143.7*	C_6H_6	*72*
22	$[PCl_6]^-$	*-83.1*	*-87.3*	*-140.4*	*-113.9*	*-141.6*	*-124.8*	*-143.0*	*-119.9*	*-298.2*	CH_2Cl_2	*73*
23	CH_3PCl_2	*224.1*	*247.4*	*176.6*	*212.5*	*216.7*	*209.4*	*211.9*	*210.9*	*191.2*	$CHCl_3$	*74*
24	PCl_3	*292.7*	*322.1*	*229.3*	*266.8*	*258.5*	*248.4*	*261.1*	*256.7*	*217.0*	*Gas phase*	*48*
25	$Si(PH_2)_4$	-192.4	-206.3	-230.8	-207.0	-218.6	-196.7	-233.3	-204.0	-205.0	C_6H_6	48
26	H_2P_2	*601.7*	*658.7*	*528.5*	*575.0*	*594.3*	*561.7*	*596.7*	*569.5*	*494.0*	*na*	*75*
27	P_4	*-502.4*	*-544.0*	*-569.7*	*-556.0*	*-583.0*	*-536.6*	*-582.4*	*-529.4*	*-525.0*	*Gas phase*	*49*
28	$F\text{-}C{\equiv}P$	*-319.6*	*-344.9*	*-360.1*	*-340.2*	*-350.0*	*-319.2*	*-357.9*	*-320.2*	*-207.0*	*na (193 K)*	*76*
29	$H\text{-}C{\equiv}P$	-24.7	-23.6	-75.4	-47.0	-18.9	-10.4	-26.7	-11.5	-32.0	na	77
30	PN	*336.4*	*369.7*	*286.3*	*325.5*	*323.1*	*308.6*	*351.7*	*341.2*	*275.0*	*Gas phase*	*38*
31	3,4-Dimethyl-phosphorine	187.1	207.1	152.5	187.7	206.8	200.2	197.4	197.4	187.9	$CHCl_3$	78
32	$(CH_3)_3PS$	*14.9*	*19.5*	*-8.7*	*21.7*	*25.1*	*30.7*	*10.3*	*23.0*	*59.1*	$CHCl_3$	*50*
33	$(CH_3O)_3PS$	82.0	92.6	58.2	90.6	74.8	77.0	70.9	79.5	73.0	na	50
34	$P(SCH_3)_3$	*182.0*	*201.5*	*132.8*	*167.4*	*161.6*	*158.0*	*154.9*	*169.9*	*124.5*	CCl_4	*79*
	R^2 [d]	0.987	0.987	0.989	0.989	0.991	0.991	0.993	0.993			
	RMSE[d], ppm		14.6		13.4		12.3		10.9			
	Slope[e]	0.918	1.000	0.971	1.000	1.072	1.000	1.073	1.000			
	Intercept[e]	-3.0	0.0	-29.8	0.0	-7.8	0.0	-14.4	0.0			

[a] DFT PBE1PBE was used, except third column, where HF/6-31G(d) was used for geometry optimization; [b] First row – basis set used for CS calculation, second row – basis set used for geometry optimization; [c] In ppm, referred to H_3PO_4; [d] R^2 and *RMSE* are the correlation coefficient and the root-mean-square error, respectively; calculated without low/high field region and "difficult" cases (*in italic*); [e] Linear regression parameters (data for all combination are given in the ESI); [f] not available.

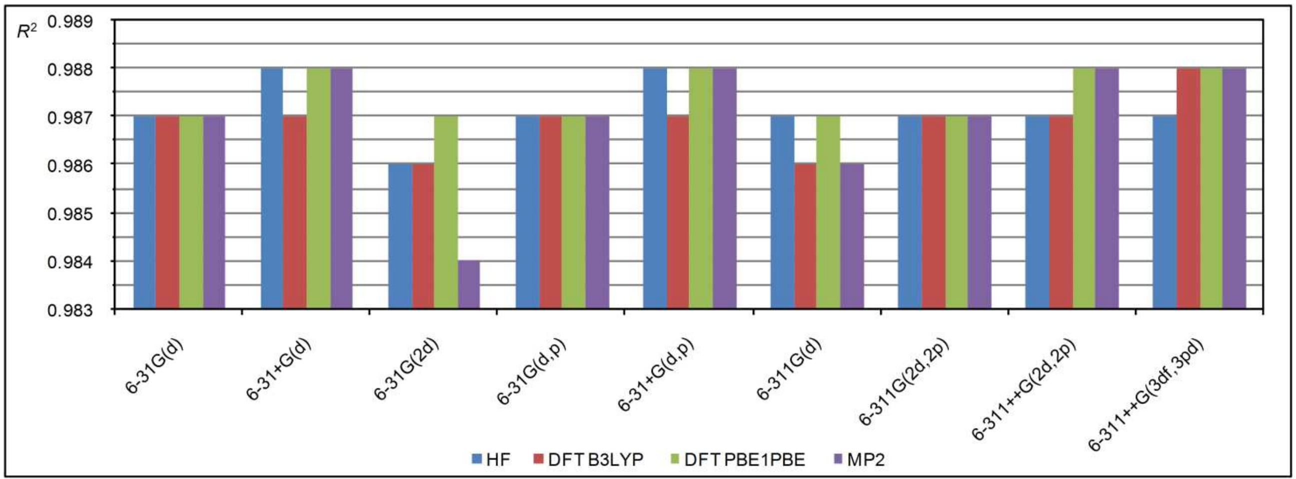

Fig. 3 R^2 values (PBE1PBE/6-31G(d) level for CS calculations) against the indicated functional/basis set approach used at geometry optimization for 23 representative molecules.

Variation of the method to calculate shielding constants

Next step involved the attempt to see how the method used to calculate CSs influences their quality. Similar as above, three fixed sets of geometries for 23 model compounds (optimized at PBE1PBE/6-31G(d), PBE1PBE/6-31+G(d,p) and PBE1PBE/6-311++G(2d,2p) levels) were used. In frames of each set, the CSs were calculated at HF, DFT and MP2 levels. Basis sets were varied in a wide range (Table S3, S4, S5). In addition, the influence of functional type was also probed. For example, in Figure 4 the R^2 data for PBE1PBE/6-31G(d) optimized geometries are shown (data for models optimized in frames of more heavier basis sets are given in ESI).

As one can see, in this case the R^2 depends more strongly on the level of theory, on the quality of the basis sets and even on the functional. All three sets (for all basis sets used for geometry optimization) demonstrate similar dependencies. Analysis of these data allows us to reveal key factors that influence the correlation coefficients. First, the inclusion of additional diffuse functions makes the correlation worse. Second, the inclusion of additional polarization functions on heavy atoms (2d) or on protons (p) augments correlation. Third, MP2 calculations in some cases (6-31G(d,p) and 6-311G(d)) improve correlations (the MP2 calculations were possible to run only up 6-311G(d) basis set. Heavier basis sets become impractical even for small compounds, vide infra). Fourth, the use of triple split valence basis sets in conjunction with additional polarization functions (6-311G (2d,2p) or 6-311++G(3df,3pd)) improve correlation coefficient, thus R^2 becomes similar to the value obtained from MP2 calculations with moderately heavy basis sets (6-31G(d,p) and 6-311G(d)).

From these data it looks like the PBE1PBE functional is superior than B3LYP for CS calculations. But perhaps this might be due to the fact that B3LYP CS calculations were carried out on geometry optimized by the PBE1PBE functional and not by B3LYP, i.e. due to use of not "parent" functional (different for optimization and CS calculations). To prove or discharge this hypothesis we carried out correlation analysis for the data obtained using B3LYP functional for both the CS calculations and geometry optimization as well (with 6-31G(d) basis set). In this case the R^2 (B3LYP/6-31G(d)//B3LYP/6-31G(d)) = 0.982 that is clearly lower than the correlation for the PBE1PBE/6-31G(d)//PBE1PBE/6-31G(d) ($R^2 = 0.987$) and even for the B3LYP/6-31G(d)//PBE1PBE/6-31G(d) combinations ($R^2 = 0.985$). Thus, the PBE1PBE functional indeed is preferable to use particularly at the CS calculation step.

It is important also that DFT (PBE1PBE) calculations, particularly with heavy basis sets result in good R^2 values which are close to MP2 results. HF level gives correlation similar to DFT results when small basis sets are used. However with triple split

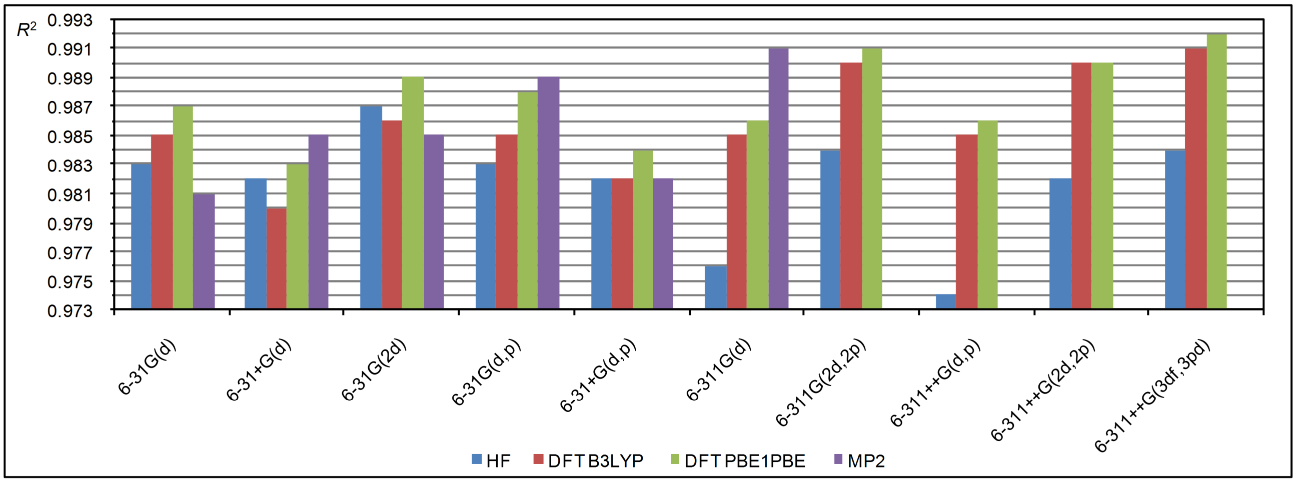

Fig. 4 R^2 values (the geometry optimized at the PBE1PBE/6-31G(d) level) against the indicated functional/basis set approach used at CSs calculations for 23 representative molecules.

valence basis sets HF calculation of CS are notably worse.

Thus, CS calculations at the PBE1PBE/6-31G(d) level are good enough. Inclusion of additional polarization functions should improve correlation. Notable improvement is observed for heavy basis sets, like 6-311G(2d,2p) or 6-311++G(3df,3pd).

At the same time it is necessary to stress that for most of the "combinations" slopes of linear approximation lines are not equal to 1, and these lines do not cross the co-ordinate origin (e.g. for selected combinations see Table 1), i.e. calculations suffer from disadvantage due to systematical errors. The sort of disagreement is easily eliminated via linear scaling. But before the phase-state problem and the question of correct reference have to be considered which may be also concerned with above limitations.

Calculation costs and optimal combination

In order to make a final conclusion about optimal combination that can be used in practice for middle-large size compounds it is necessary to estimate time expenditures. Thus, herewith we analyze the computational costs for the geometry optimization and for CS calculations for middle-size compound from our test list (*vide infra*), e.g. 1,2-Bis(2,4,5-tri-tert-butyl-diphospholyl) ethane (**35**) (Figure 5 and Table S6). In general, geometry optimization step is the most time consuming (Table S6), therefore the MP2 approach can hardly be recommended for geometry optimization because its use dramatically increases the computational time (e.g. data for small compound **5** are given in Table S7). It becomes practically unaffordable for middle-size compounds, and that is more, it does not improve the correlation in respect with other methods. DFT calculations with relatively simple basis sets (6-31G(d) or 6-31+G(d)) are expected to give good results. Further augmentation of the basis set leads to only insignificant improvement, while time costs increase dramatically (Figure 5a). HF level is least time consuming (Table S7) and gives reasonably good geometry, and therefore can be recommended for geometry optimization of large compounds for which DFT method is inapplicable.

The CS calculations step being less time consuming, heavier basis sets can be easily applied. The PBE1PBE/6-31G(2d) level for CS calculations is a good compromise between costs and quality. If one needs more accurate data, the 6-311G(2d,2p) basis set can be recommended since such calculations are still affordable. Further augmentation of the basis set leads only to unreasonable increase of computational costs (Figure 5b).

To sum it up the PBE1PBE/6-31G(d)//PBE1PBE/6-31G(d) level can be recommended for express estimation of ^{31}P CS. The PBE1PBE/6-31G(2d)//PBE1PBE/6-31G(d) combination can be recommended for routine application. The PBE1PBE/6-311G(2d,2p)//PBE1PBE/6-31+G(d) level should be used to obtain better results for reasonable cost (Table 1). If one deals with very large molecule, the PBE1PBE/6-311G(2d,2p)//HF/6-31G(d) can be recommended as a compromise.

Phase state problem

Theoretically calculated NMR shieldings must be compared with experimental values determined in the gas phase. However, a number of such data is very limited. On the other hand, what is more interesting for NMR spectroscopists, is the possibility of carrying out the calculations of CSs determined in solution. Therefore, the question arises: is it correct to compare CS calculated in the gas phase with experimental CS NMR data obtained for solution?

In order to answer this question, let us consider in detail the possible contributions to shielding in media. In general, the shielding of a particular atom in the environment can be written in the following form:

$$\sigma = \sigma_{\text{vacuum}} + \sigma_{\text{dia}} + \sigma_{\text{polar}} + \sigma_{\text{rovibrat.}} + \sigma_{\text{specific. solvent. effect}} \qquad (1)$$

where σ_{vacuum} – the magnetic shielding for isolated molecule in vacuum, σ_{dia} – the contribution of the bulk diamagnetic susceptibility of the sample, σ_{polar} – the impact of the medium polarity, σ_{rovibrat} – is rovibronic correlation term, $\sigma_{\text{specific. solvent. effect}}$ – the impact of specific solvent effects.

And CS is determined according to the equation (2):

$$\delta\,(X) = \sigma\,(\text{stand}) - \sigma\,(X) + \delta\,(\text{stand}) \qquad (2)$$

where the shielding of the molecule of interest (X) and the standard

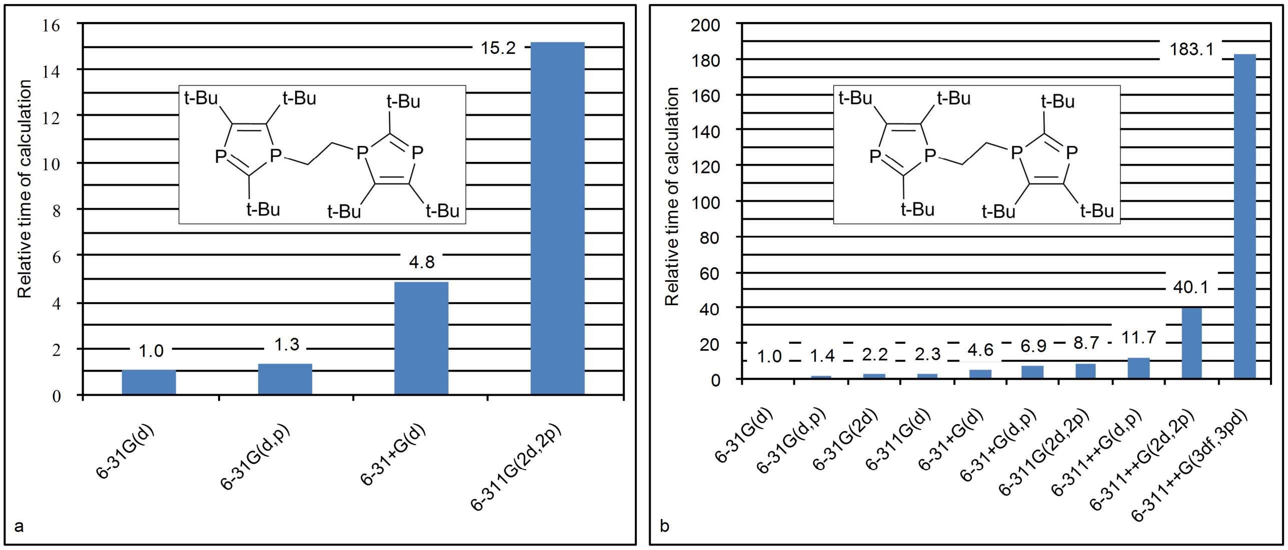

Fig. 5. Relative computational costs against the indicated basis set approach (at DFT PBE1PBE level of theory) used at geometry optimization (a) and CSs calculations (b) for **35**.

should be measured in identical conditions.

The second term in equation (1) arises because the magnetic field in solution is different form one in vacuum. However, this term for the most common solvents is small (0.3-0.8 ppm). Moreover, it is nearly the same both for the molecule X and for the standard and, therefore, its contribution to the CS can be neglected.

The third term in equation (1) accounts for the influence of the solvent's polarity on the electron density distribution. From this point of view it can be expected that more polar molecules can be more sensitive to these effects than less polar. In order to estimate the magnitude of the possible contribution due to the polarity of the solvent, one can try to calculate this contribution theoretically and measure experimentally[49].

According to calculations in frames of polarizable continuum model (PCM)[80] for several model compounds (H_3PO_4 (**4**, 0.02 D), $P(OEt)_3$ (**36**, 1.50 D), $(CH_3)_3PO$ (**7**, 4.32 D)), the magnetic shielding difference in vacuum and in benzene ($\varepsilon = 2.3$) should be negligible (less than 0.7 ppm) for non-polar molecules (Table S8). Only for relatively polar molecule (($(CH_3)_3PO$ (4.32 D)), this contribution may be notable (up to 7 ppm). According to the calculations, the increase of solvent's polarity (e.g. ε ($CHCl_3$) = 4.7) should not change the shielding significantly (Table S8).

On the other hand, at a fixed magnetic field, the changes in CSs for compounds $P(OEt)_3$ (**36**), $HP(O)(OEt)_2$ (**37**) and $ClP(O)(OEt)_2$ (**38**) do not exceed 0.8 ppm upon the transition from non-polar (C_6H_6, $\varepsilon = 2.3$) to moderately polar ($CHCl_3$, $\varepsilon = 4.7$) solvents (Table S8). Thus, the contribution of the polarity of the medium to phosphorus shielding is also insignificant and should not exceed 7 ppm. Therefore, the CS dependence on the polarity should be even less and may be neglected in quantum-chemical calculations.

The next is rovibrational term in eq. (1), which is not taken into account in quantum chemical calculations. According to estimations, this term is also small (less than 10 ppm)[81] and if to take into account that there is similar contribution into the shielding of the standard, the impact of this term in CS should be also small.

The most ambiguous is the situation with the last term in eq. (1) which reflects the contributions of specific intermolecular interactions. The experimentally measured CSs correspond to the thermodynamic ensemble of molecules interacting with each other and/or with the solvent molecules. In most cases, the interactions are weak dispersion ones of the title and solvent molecules, and the gas phase approximation is correct. A different situation may occur in the presence of specific intermolecular interactions. In these cases, the changes in geometry (due to association, self-association, tautomeric or conformational transformations) can be significant and may influence CSs notably, so that the calculated and experiment data can dramatically disagree. In such cases, in order to verify the absence of significant effects of intermolecular interactions and self-association on CSs, it is necessary to examine the concentration dependence of the CSs or solvent dependence (polar/nonpolar). In each such case, it should be considered individually.

Thus, if there are no specific interactions, the calculated CSs for vacuum should well reproduce experimental values.

Problem of the right choice of reference

Today, the accepted reference standard for ^{31}P NMR spectroscopy is 85% water solution of H_3PO_4. However, there is no value for it in the gas phase that makes difficult to use this compound as a reference in the calculations. The situation seems to be even more problematic, if to take into account that the real standard is high concentrated compound with functional groups prone to strong specific hydrogen bonding. In addition, water is a very polar solvent that also may be involved in association with H_3PO_4 molecules[59]. Therefore, strong medium effects can be expected for this standard. As a result, the isolated molecule approximation may be not valid in calculations for this compound.

Alternatively, the secondary reference like PH_3 is often used because its value in the gas phase is documented. But in fact, its ^{31}P CS strongly depends on the phase state as well (-266.1 and -238 ppm in gas and neat liquid, respectively)[48] implicating notable association effects in solution. In other words, the PH_3 is also not good reference. Thus, in fact, both references widely used in calculations, are not perfect.

However, to our opinion, in fact there is no need to refer exclusively to the gas phase data. After all, if one tries to be fully correct and refer to the standard in the gas phase, the results of calculations for compound of interest should be also compared only with its gas phase data that is impossible in most of the cases.

On the other hand, for most "normal" systems referencing relative to the generally accepted standard H_3PO_4 give CSs, which can be compared with experimental data in solution. That is, the calculated data correlate well the experiment for solution with some under- or over-estimation (depending on "combination' used). As a last resort, the empirical correction can be applied to overcome this problem.

Linear Scaling

Linear scaling allows the improvement of the calculated CSs via a linear regression of the calculated CSs versus experimental data[82-85]. The linear regression method is capable of correcting systematic errors across the whole ^{31}P NMR spectra. As a result, the slope and the intercept from the best-fit line allow for the calculation of the empirically scaled CSs according to eq 3

$$\delta_{scaled} = (\delta_{unscaled} - \text{intercept})/\text{slope} \qquad (3)$$

where $\delta_{unscaled}$ is the calculated CS for a particular nucleus. Thus, in eq 3, the intercept helps to correct the error for a reference compound while the slope provides information about the size of the systematic error[‡]. This operation has been carried out for each of the four "combinations", and the root-mean-square errors (*RMSE*s) relating the scaled CS predictions with experiment appear in the bottom row of Table 1. While not small enough as one might like, the *RMSE* = 10.9 ppm for the best "combination" nonetheless indicates that DFT calculations of ^{31}P CSs, followed by linear scaling, do provide a chemically useful degree of accuracy. The procedure that we recommend as the "express method" (PBE1PBE/6-31G(d)//PBE1PBE/6-31G(d)), yields a slightly greater *RMSE* = 14.6 ppm than the PBE1PBE/6-311G(2d,2p)//PBE1PBE/6-31+G(d) combination which gives the best compromise between accuracy and economy.

[‡] Parameters of the linear scaling equation for different calculation levels are given in the ESI.

It is interesting to note that the scaled CSs for frequently used secondary reference, PH_3 agree better with its experimental value in liquid than in the gas phase implying that referencing to its gas phase would produce worse CSs for the whole the set of model compounds.

The “difficult” cases

At the beginning of the analysis we found that there are some “exceptions” for which the difference between experimental and calculated data was essential regardless of the level of theory used. These are PN (**30**), P_2H_2 (**26**), $[PCl_6]^-$ (**22**), $[PF_6]^-$ (**21**), FCP (**28**), $(CH_3)_3PS$ (**32**), $(CH_3O)_3PS$ (**33**), $P(SCH_3)_3$ (**34**), PCl_3 (**24**) and H_3PO (**1**). Some of these “exceptions” (PN, P_2H_2, PCl_3, $[PCl_6]^-$, $[PF_6]^-$) were already discussed in literature[38, 48, 86].

In general, the reasons for such discrepancies may be divided into two types: the drawback of theoretical models and the interference of additional medium effects in real experiment that is not accounted for. For example, it was supposed that the disagreement between experimental and calculated ^{31}P CSs for PCl_3 and PN might be due to the inadequate description of their structures at the DFT level. Therefore if to take into account that the paramagnetic contribution to the magnetic shielding in these molecules is large, CS will strongly depend on the bond lengths[47].

On the other hand, relativistic effects arising on magnetic shielding of nucleus located in the vicinity of the atoms from the third period may be also strong[5, 51, 54]. The relativistic spin–orbital interaction is not accounted for in our calculations and therefore the problems for $(CH_3)_3PS$ and $P(SCH_3)_3$ might be well due to the contribution of relativistic effects from vicinal sulfur atoms. The same reason may account for the discrepancy for PCl_3.

Some of the above “exceptions” may be due to “incorrect” description of molecular system in calculations. Namely, if molecules in solution are prone to association or self-association, the isolated molecule model will not be correct[53, 55]. Intra- or intermolecular coordination involving phosphorus results in a dramatic ^{31}P nuclear shielding amounting to approximately 150 ppm on changing the phosphorus coordination number by one[55]. Thus, the impact of associated forms in solution may dramatically change the observed ^{31}P CSs.

For example, the accurate prediction of ^{31}P NMR CSs of ion pair systems requires consideration of the full system[49]. Therefore, the deviations for the small ions $[PCl_6]^-$ and $[PF_6]^-$, presumably, are due to considerable solvent or contrion effects[48].

In a similar way, intermolecular coordination may be responsible for the discrepancies observed for PN, P_2H_2 and FCP. In solution these molecules may exist not only in monomolecular but in associated form, as well. The calculations for the $(PN)_3$ complex do in fact demonstrate that, on the one hand, trimer is much more stable than monomer. On the other hand, while theoretical CS (PBE1PBE/6-31G(d)//PBE1PBE/6-31G(d)) for monomer deviates to the lower field (336.4 ppm) from experimentally observed (275.0 ppm), the value for the trimer shifts in the opposite direction (262.1 ppm). Thus, experimental value lies somewhere in between these calculated values for two structural forms, i.e. calculated and experimental CSs agree if one supposes that there is a fast exchange between these forms. The similar considerations can also be applied for P_2H_2 and FCP molecules as well.

Another reason for the discrepancy may occur for the system that is involved in intramolecular exchange processes. In this case the consideration of only one form may be not enough. For example, the calculations for phosphine oxide ($H_3P{=}O$, **1a**) underestimate ^{31}P CS by ca. 36 ppm (Figure 6). However, if to suppose that this form is in exchange with acid tautomer[58, 87-95] the contradiction will be resolved.

According to the calculations, these two forms are close in energy in vacuum (Table S9). In H_2O solution, e.g. in frame of PCM, the preference is expected to invert although the energy gap is still small (Table S9), i.e. the populations of these two forms should be close or comparable. Further on, if to take into account that the calculation for phosphinous acid (**1b**) predicts ^{31}P CS at notable lower field (ca. 34 ppm), the experimental value corresponds to intermediate between these tautomeric forms which may be in fast exchange in NMR time scale (Figure 6).

This hypothesis is also strongly supported by finding that similar pentafluorophenyl derivative in solution exists in an equilibrium between the phosphinous acid ($C_6F_5(C_2F_5)POH$, **39a**) and the phosphane oxide ($C_6F_5(C_2F_5)P(O)H$, **39b**) tautomers[96]. Due to higher barrier of exchange in this case both tautomers are observed separately in ^{31}P NMR spectra (80.6 and -1.9 ppm, respectively). To this end, the calculations PBE1PBE/6-31G(d)//PBE1PBE/6-31G(d) for pentafluorophenyl derivative predicts ^{31}P CSs in good agreement with experiment (71.4 and -10.8 ppm for acid and oxide tautomers, respectively).

In the case of other acids (e.g. H_3PO_2 (**2**), H_3PO_3 (**3**)) no deviations from experiment were observed suggesting strong preference to one tautomeric form (Table S9). Energy analysis for these acids also supports this conclusion, viz. there is essential preference to one dominant form and solvent has only insignificant effect on the energy gap. Thus, in solution these acids are in one form and calculations well describe their NMR CSs.

The second question – will the required level of theory (established for small models) work well “for larger organophosphorus compounds of practical interest”? And will it be within the limits of computational resources? To answer these questions typical representatives of several classes of phosphorus compounds with molecular weight about 200-300 (Figure 7) were analyzed. Calculations were run on PBE1PBE/6-311G(2d,2p)//PBE1PBE/6-31+G(d), PBE1PBE/6-31G(2d)//PBE1PBE/6-31G(d) and PBE1PBE/6-31G(d)//PBE1PBE/6-31G(d) levels of theory. Linear scaling procedure was applied to GIAO calculated CSs (Table S10).

As a whole, calculated values agree well with experimental data for all combinations tested (e.g. for PBE1PBE/6-311G(2d,2p)//PBE1PBE/6-31+G(d) combination see Figure 7 and Table 2, for the rest see Table S10). In all cases correlations are

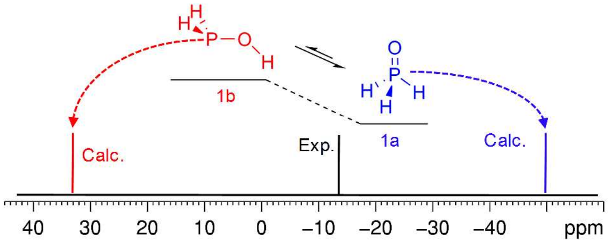

Fig. 6 Equilibrium of Phosphine Oxide (**1a**) and Phosphinous Acid (**1b**) and schematical representation of ^{31}P spectra of **1**.

close to linear (R^2= 0.989 - 0.996) and *RMSE* are small (9.0 - 11.6 ppm).

Table 2 Calculated[a] and experimental ^{31}P NMR CSs for **35**, **40-48**.

№	$\delta_{unscaled}$	δ_{scaled}	δ_{exp}[b]	Solvent	Ref.
35	32.1 309.6	43.3 302.0	54.8 322.9	C_6H_6	97
40	-172.4 63.9	-147.3 72.9	-157.7 76.7	na[c]	98
41	-129.3	-107.2	-110.0	na	99
42	-68.6	-50.5	-54.5	na	100
43	-41.9 84.1 -7.1 58.7	-25.7 91.7 6.7 68.1	-29.7 100.5 -10.6 75.7	$CHCl_3$	101
44	22.5	34.3	24	C_6H_6	102
45	74.3 -36.5	82.6 -20.6	84.1 -22.6	$CHCl_3$	103
46	15.0 5.8	27.4 18. 8	27.6 18.3	$CHCl_3$	104
47	-23.1	-8.1	-10.2	$CHCl_3$	105
48	36.8	47.7	38.7	$CHCl_3$	106
R^2	0.996	0.996			
RMSE, ppm		9.0			

[a] At PBE1PBE/6-311G(2d,2p)//PBE1PBE/6-31+G(d) level; [b] in ppm; [c] not available.

Application of ^{31}P NMR CSs for isomeric structure determination

Being very sensitive to chemical structure, the ^{13}C and ^{15}N CSs can be safely used to establish fine structural features such as isomerism and tautomerism[16-35]. The ^{31}P CS is even more sensitive to structure modifications and, perhaps, could be also used to analyze features of geometry of phosphorus containing compounds. To check this idea, we used 10-ethyl-7,8,9-triphenyl-4-oxa-1,10-diphospatricyclo[5.2.1.02,6]-deca-8-ene-3,5-dione (**45**) for which several isomeric forms can be realized and for which reliable structural data are available[103] obtained by alternative method. Thus, we run the CS calculations for four isomers of **45** (Figure 8a) and compared with experimental data for both phosphorus atoms (Table S11).

According to the calculations, the ^{31}P CSs essentially depend on isomeric structure varying within 100 ppm (Table S11). However only in the case of the A isomer, the differences between theoretical and experimental ^{31}P CSs are small (less than 3 ppm) while in other cases deviations are high (Figure 8b). Thus the analysis of ^{31}P CSs allows simple and unequivocal assignment of isomeric form of **45** to structure A that is in full agreement with X-Ray data[103].

Conclusions

Comparative analysis of calculated (GIAO) versus experimental ^{31}P NMR CSs for the wide range of organophosphorus model compounds was carried out. The variety of combinations (levels of theory (HF, DFT, MP2), functionals (B3LYP and PBE1PBE) and

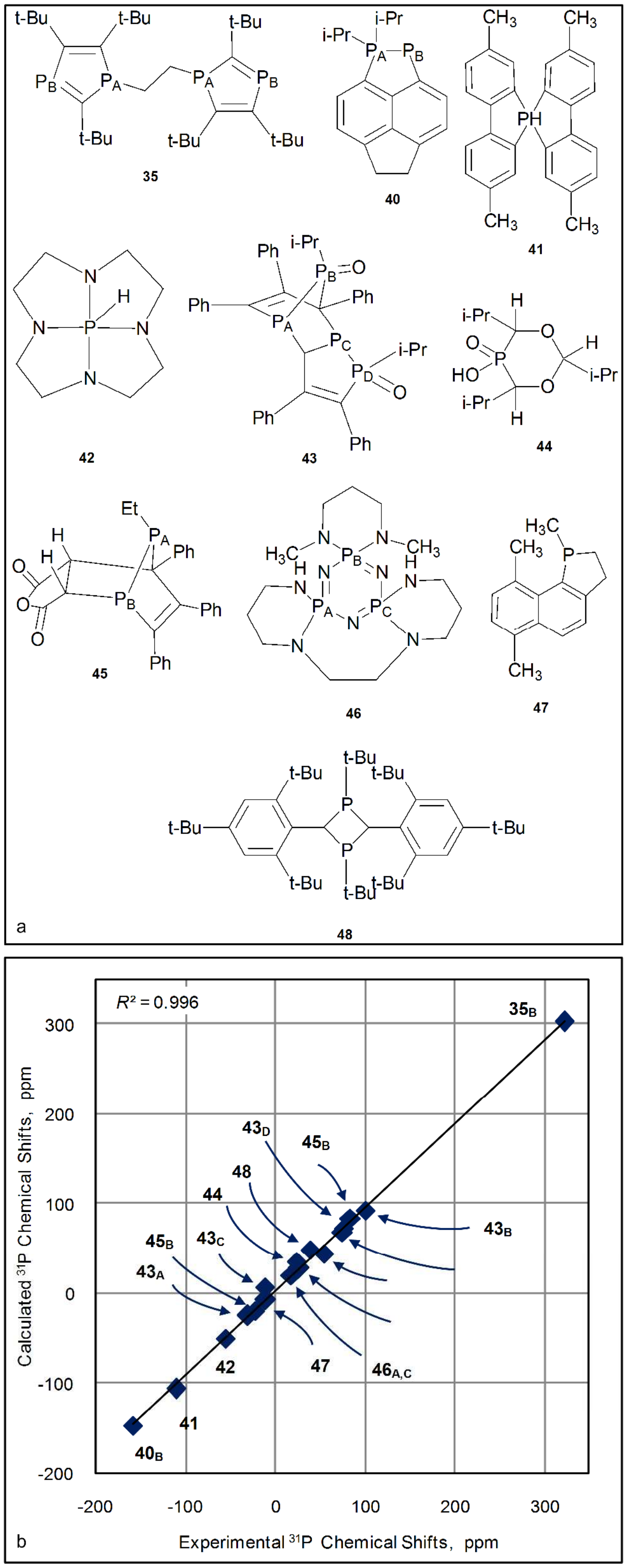

Fig. 7 Structures of “large compounds” **35**, **40-48** (a) and correlation of experimental *versus* calculated at PBE1PBE/6-311G(2d,2p)//PBE1PBE/6-31+G(d) ^{31}P NMR CS for **35**, **40-48** (b).

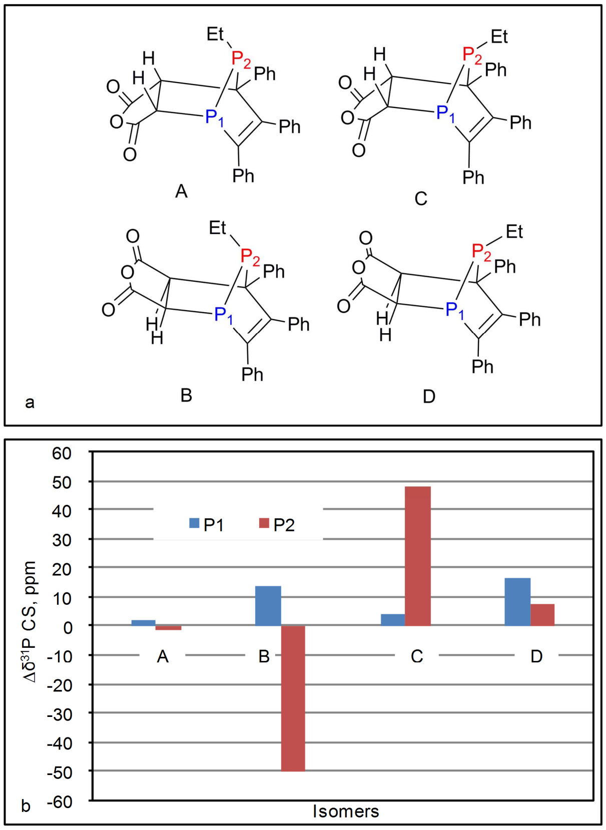

Fig. 8 Possible structural isomers of **45** (a) and $\Delta\delta = \delta_{calc} - \delta_{exp}$ for isomers of **45** (b). Calculations at PBE1PBE/6-311G(2d,2p)//PBE1PBE/6-31+G(d) level of theory.

basis sets (6-31G(d), 6-31+G(d), 6-31G(2d), 6-31G(d,p), 6-31+G(d,p), 6-311G(d), 6-311G(2d,2p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(3df,3pd))) were tested to reveal main factors that influence the quality of calculated data. As a whole, with the exception of some "difficult" cases (FCP, OPH_3, PN, P_2H_2, PCl_3, $[PCl_6]^-$, $[PF_6]^-$, $(CH_3)_3PS$, $P(SCH_3)_3$) the calculated ^{31}P CSs satisfactorily correlate with experimental data.

To sum it up, the PBE1PBE/6-31G(d)//PBE1PBE/6-31G(d) level can be recommended for express estimation of ^{31}P CS of organophosphorus compounds. The PBE1PBE/6-31G(2d)//PBE1PBE/6-31G(d) combination can be recommended for routine application. The PBE1PBE/6-311G(2d,2p)//PBE1PBE/6-31+G(d) level can be proposed to obtain better results for reasonable cost. In the case of very large molecules the PBE1PBE/6-311G(2d,2p)//HF/6-31G(d) can be recommended as a compromise. Scaling by linear regression parameters significantly improves results.

Care has to be taken for compounds that may be involved in exchange between different structural forms (self-associates, associates with solvent, tautomers, conformers) and therefore, experimental ^{31}P CS may correspond to the exchange averaged values. In such suspicious cases the disagreement between calculated and experimental data most likely "says" that the problem formulation is incorrect.

Some problems for phosphorus located near the third group atoms ($(CH_3)_3PS$ and $P(SCH_3)_3$) may be due to the impact of relativistic effects that was not accounted in our calculations.

^{31}P CSs can be safely used to establish fine structural peculiarities such as isomeric and tautomeric structures.

Experimental part

All of calculations were performed on the Gaussian 03 program[107]. PC with Core i7-3960x CPU at 16 GB RAM with 64x Windows 7 operation system were used. NMR experiments were performed with a Bruker AVANCE-500 spectrometer (11.7 T) at 303 K. ^{31}P spectra were acquired at fixed magnetic field and referred to external H_3PO_4.

Acknowledgements

This study was financially supported in part by the Russian Foundation for Basic Research (Projects 13-03-00169 and 14-03-31952). Dmitry G. Yakhvarov thanks Russian Scientific Fund (project 14-13-01122) for supporting of the research activity towards phosphane oxide H_3PO.

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