PAPER

Theoretical studies of ^{31}P NMR spectral properties of phosphanes and related compounds in solution†

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Selected theoretical methods, basis sets and solvation models have been tested in their ability to predict ^{31}P NMR chemical shifts of large phosphorous-containing molecular systems in solution. The most efficient strategy was found to involve NMR shift calculations at the GIAO-MPW1K/6-311++G(2d,2p)//MPW1K/6-31G(d) level in combination with a dual solvation model including the explicit consideration of single solvent molecules and a continuum (PCM) solvation model. For larger systems it has also been established that reliable ^{31}P shift predictions require Boltzmann averaging over all accessible conformations in solution.

Introduction

Phosphanes are of outstanding relevance as ligands in transition metal mediated catalytic processes, but also as reagents in a series of named reactions such as the Wittig, the Appel, and the Staudinger reaction. The Lewis base properties relevant in these reactions have recently led to the highly successful development of phosphanes as catalysts in organocatalytic processes. This includes applications in C–C bond forming reactions such as the Morita–Baylis–Hillman[1] and the Rauhut–Currier reaction,[2] in the addition of weak nucleophiles to Michael acceptors,[3] in the acylation of weak nucleophiles with carboxylic acid derivatives,[4] just to name a few. The Lewis basicity of catalytically active phosphanes can be characterized by their respective affinities towards cationic or neutral carbon electrophiles such as methyl cation or methyl vinyl ketone (MVK).[5] These thermodynamic properties can be complemented with kinetic data towards model electrophiles[6] in a way to allow for quantitative predictions of new phosphane-based organocatalysts. Experimental studies of organocatalytic reactions highly profit from ^{31}P NMR measurements as these allow for a direct detection of catalyst-derived species under catalytic conditions. The phosphonium intermediates expected after nucleophilic attack of phosphanes on C-electrophiles have, for example, been detected in a number of studies.[3b,7–10]

The assignment of experimentally observed signals can greatly be supported by comparison to theoretically calculated ^{31}P chemical shifts. Highly accurate shift calculations have recently been executed at correlated levels for a series of smaller systems.[11] For intermediates in organocatalytic

processes, however, these methods are usually not applicable and calculations at either the Hartree–Fock (HF) or the density functional theory (DFT) level appear as the only practical option. Despite the fact that the application of DFT methods in NMR shift calculations meets with some fundamental concerns, there have nevertheless been numerous successful studies in this area in recent years.[12–37] One additional technical point concerns the treatment of solvation effects, which are known to be quite significant for some phosphane-derived species such as triarylphosphane oxides.[38–40] In order to identify computational schemes suitable for the reliable calculation of ^{31}P shifts for phosphorous-containing molecular systems we compare here the performance of a series of DFT methods such as MPW1K, B98 and B3LYP with the *ab initio* methods HF and MP2 using the GIAO scheme. These studies will be combined with various approaches to account for solvent effects.

Results and discussions

Triphenylphosphane (PPh$_3$, **1**) is a frequently used organocatalyst and will therefore be used as a first model system for ^{31}P shift calculations on large systems. Under catalytic reaction conditions this catalyst is often degraded to the respective oxide (OPPh$_3$, **2**), either through reaction with residual atmospheric oxygen or through side reactions along a Wittig-type pathway. The ^{31}P NMR chemical shift measured for **1** (relative to the ^{31}P NMR standard of 85% aqueous phosphoric acid) is quite insensitive to solvent polarity with $\delta(^{31}P,\mathbf{1}) = -4.7$ ppm in benzene-d$_6$[41] and $\delta(^{31}P,\mathbf{1}) = -4.7$ ppm in chloroform-d$_1$.[42] As the use of aqueous phosphoric acid as the reference compound in NMR shift calculations is clearly impractical, we will in the following use the experimentally determined value of **1** as the reference for gas phase calculations. ^{31}P NMR shifts determined for phosphaneoxide **2** are

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significantly more solvent dependent with measured values of $\delta(^{31}P,2) = +24.7$ ppm in benzene-d_6[43] and $\delta(^{31}P,2) = +29.7$ ppm in chloroform-d_1.[42] Assuming the values determined in benzene to be representative also for the gas phase, NMR calculations must reproduce a shift difference of $\Delta\delta(2-1) = +29.4$ ppm. In more general terms the direct result of NMR shift calculations is the absolute magnetic shielding σ, which reflects the NMR chemical shift relative to the free nucleus. Relative ^{31}P chemical shifts between phosphorous-containing compounds X and phosphane 1 as the reference can then be derived from differences in shieldings as expressed in eqn (1).

$$\delta(X) = \sigma(1) - \sigma(X) + \delta(1) \qquad (1)$$

As a first step in identifying a computational protocol for reliable shift calculations we have calculated ^{31}P absolute shieldings for compounds 1 and 2 using selected density functional theory (DFT) methods, the restricted Hartree–Fock theory (RHF), and the 2nd order Møller–Plesset (MP2) perturbation theory in combination with the GIAO model. All of these calculations employ the same $6\text{-}311+G(d,p)$ basis set and use the same geometries obtained at the MPW1K/6-31G(d) level of theory. The MPW1K functional[45] is used here due to its good performance in calculations of zwitterionic structures, whose occurrence in organocatalytic reactions is quite frequent.[46,5c] At this level of theory two different minima are identified for phosphane oxide 2 (C_3 vs. C_1 symmetry; the latter structure is also found in solid-state X-ray studies).[47] Only a single minimum with C_3 symmetry can be found for phosphane 1. This is in agreement with results from solid state X-ray studies, gas phase electron diffraction measurements and earlier ab initio calculations.[48,49] Fig. 1 shows the structures obtained at the MPW1K/6-31G(d) level and Fig. 2 collects all results obtained for these systems. Predictions made at MP2, RHF and MPW1K levels are in close to quantitative agreement with experiment, while the hybrid functionals B98 and B3LYP predict the ^{31}P shift in phosphane oxide 2 to be too low. Given the slightly better predictive value of DFT methods over RHF in previous studies[25] and taking into account the high price of MP2 calculations we will continue with MPW1K as the preferred choice for further studies. We also note that predicted shifts
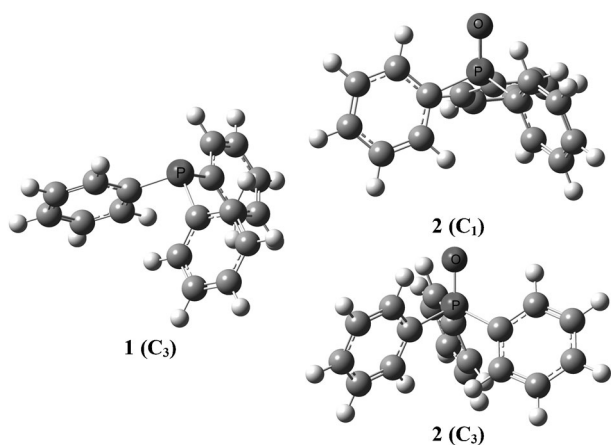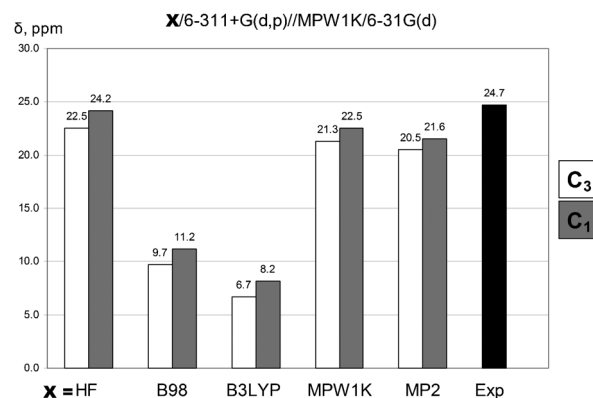

Fig. 2 Theoretically calculated and experimentally measured values for the ^{31}P resonance in OPPh$_3$ (2) using selected theoretical methods in combination with the $6\text{-}311+G(d,p)$ basis set.

for the C_3 conformer are systematically lower (and thus inferior) than those predicted for the C_1 conformer.

The triple zeta $6\text{-}311+G(d,p)$ basis set used in the shift calculations in Fig. 2 is known to provide good results for structural and energetic data of molecular systems,[50–52] but may not be the ideal choice for the prediction of NMR chemical shifts. The dependence of the ^{31}P chemical shifts calculated for phosphane oxide 2 with the MPW1K hybrid functional has therefore been analyzed using additional basis set variations. This includes on the smaller side the 3-21G and 6-31G(d) split valence basis sets often used for calculations on very large molecular systems, and on the larger side the $6\text{-}311++G(2d,2p)$ and IGLO-III basis sets. The members of the IGLO basis set family have been optimized for application in NMR and EPR calculations.[19] The results obtained for all basis sets are shown in Fig. 3. The predictive value of the small basis set 3-21G is quite low. The basis set 6-31G(d), which has been used for geometry optimization, yields a surprisingly good prediction of the ^{31}P shift in OPPh$_3$, most likely due to adventitious error cancellation. Predictions made with the $6\text{-}311+G(d,p)$ basis set can indeed be improved somewhat through inclusion of additional polarization functions (as in $6\text{-}311++G(2d,2p)$) or the use of a specifically designed basis set such as IGLO-III. It can clearly be seen that the IGLO-III and $6\text{-}311++G(2d,2p)$ basis sets provide almost the same

Fig. 1 Structures of PPh$_3$ (1) and OPPh$_3$ (2) as optimized at the MPW1K/6-31G(d) level of theory.
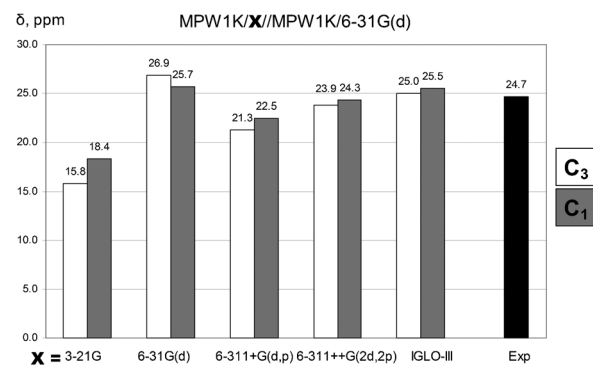

Fig. 3 Theoretically calculated and experimentally measured values for the ^{31}P resonance in OPPh$_3$ (2) using selected basis sets in combination with the MPW1K density functional method.

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results for the systems under study. The wall-clock time for calculations with the IGLO-III basis set is twice as long as with the 6-311++G(2d,2p) basis and the 6-311++G(2d,2p) basis set will therefore be used as the preferred choice in all further calculations reported here (as has also been done in other recent studies).[31,33] The basis set quality as probed through relative shift calculations for the exceedingly similar systems **1** and **2** may not necessarily be the same if two structurally rather different compounds of different sizes are compared. In order to analyze this point more clearly we have recalculated the shift of phosphane oxide **2** (C_1 conformation) using the reference compounds **3** and **6**. Trimethylphosphane (PMe$_3$, **6**) is significantly smaller than phosphane **1**, but preserves the structural feature of three P–C bonds. Moreover, ^{31}P NMR shifts measured for **6** give rather similar values of δ(^{31}P,**6**) = −61.0 ppm in benzene-d$_6$[54] and δ(^{31}P,**6**) = −61.6 ppm in chloroform-d$_1$.[55] The second reference compound phosphane (PH$_3$, **3**) is even smaller than **6** and structurally even more dissimilar to **1**. In contrast to these other reference compounds

the ^{31}P NMR chemical shifts measured for **3** in solution depend on a number of experimental factors (temperature and concentration) as well as on the solvent. The value reported for **3** in benzene at 29 °C of δ(^{31}P,**3**) = −242 ppm most closely approaches the conditions chosen for all other compounds used here, but we note that this value is distinctly different from the two values reported from gas phase measurements of δ(^{31}P,**3**) = −254.2 ppm[56] and −266.1 ppm.[53] The ^{31}P chemical shift for phosphane oxide **2** calculated with reference to compounds **1**, **3**, and **6** is graphically shown in Fig. 4 for the three larger basis sets used before in combination with the MPW1K functional. Using PMe$_3$ (**6**) as the reference compound essentially identical ^{31}P NMR shifts are calculated for **2** when using the 6-311+G(d,p), 6-311++G(2d,2p) and IGLO-III basis sets. In contrast, when using PH$_3$ (**3**) as the reference compound, significantly different ^{31}P NMR shifts are calculated for **2** when using the smaller 6-311+G(d,p) basis set as compared to the results obtained with the 6-311++G(2d,2p) and IGLO-III basis sets. This implies that relative shift calculations of compounds of exceedingly different sizes and structures may require more sophisticated theoretical methods as the comparison of two compounds as similar as **1** and **2**.

We conclude at this point that from the methods surveyed here the GIAO-MPW1K/6-311++G(2d,2p)//MPW1K/6-31G(d) is the most appropriate for ^{31}P shift predictions in large molecular systems. This approach was subsequently tested for a larger set of systems included in a previous methodological survey by van Wüllen[25] (Table 1). To be consistent with this study PH$_3$ (**3**) was selected as the reference compound. From this latter study we include in Table 1 only those methods with the best error statistics as quantified by the squared correlation coefficient (R^2) and the mean absolute deviation (MAD = $1/n\sum|\delta_{exp} - \delta_{calc}|$) with respect to experimental values. In terms of these two error metrics the
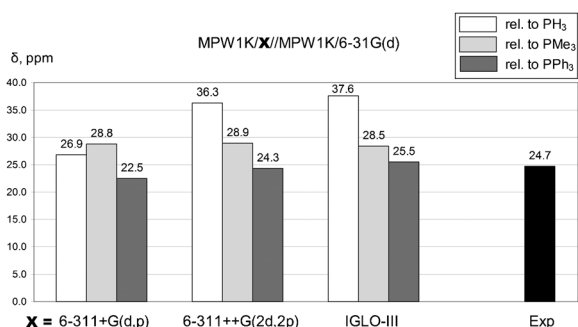

Fig. 4 Theoretically calculated and experimentally measured values for the ^{31}P resonance in OPPh$_3$ (**2**, C_1) using selected basis sets and three different reference compounds in combination with the MPW1K density functional method.

Table 1 ^{31}P NMR chemical shifts calculated at selected levels of theory in the gas phase using PH$_3$ (**3**) as the reference system

		Method							
		GIAO MPW1K[a]	IGLO BP[b]	IGLO B3LYP[b]	GIAO BP[b]	GIAO B3LYP[b]	GIAO MP2[b]	Exp.	Experimental conditions
3	PH$_3$	−266.1	−266.1	−266.1	−266.1	−266.1	−266.1	−266.1	Gas-phase[53]
4	PF$_3$	+126.1	+113.8	+100.8	+132.5	+115.7	+109.7	+106	Gas-phase[53]
5	PCl$_3$	+246.4	+244.3	+236.9	+269.9	+259.6	+224.9	+217	Gas-phase[53]
6	P(CH$_3$)$_3$	−77.8	−69.1	−73.9	−53.8	−58.4	−75	−63	Gas-phase[53]
7	P(^{i}C$_3$H$_7$)$_3$	+2.8	+15.5	+11.4	+31.8	+27.3	+10.6	+19.3	Benzene-d$_6$[57]
8	P(OCH$_3$)$_3$	+154.4	+115	+109	+137.9	+128.4	+129.3	+140	Toluene-d$_8$[58]
9	OP(CH$_3$)$_3$	+13.1	−5.7	−6.7	+19.1	+14	+18.7	+32	Benzene[59,60]
10	OP(OCH$_3$)$_3$	+4.5	−34.4	−37	−9.1	−16.7	−5	+3.7	Benzene[61]
11	Si(PH$_2$)$_4$	−236.5	−223.5	−228.9	−219.5	−226	−243.1	−205	Benzene-d$_6$[62]
12	Cr(CO)$_5$(PH$_3$)	−127.5	−150.5	−143.3	−128.6	−123	−176.7	−130	Benzene-d$_6$[63]
13	PH$_4^+$	−128.0	−151.4	−156	−122.8	−128.9	−127.6	−105	Methanol[64]
14	P(CH$_3$)$_4^+$	+13.2	+2.5	−2.9	+30.4	+22.1	+12.5	+25.1	DMSO[65]
15	PF$_6^-$	−138.7	−119.9	−140.8	−95.1	−120.2	−119.5	−146	Benzene-d$_6$[66]
16	P$_4$	−584.2	−512.9	−524.1	−516.7	−532.5	−549.1	−552	Gas-phase[67]
17	PN	+366.4	+307.8	+325.5	+326.1	+342.7	+202.2	+275	Gas-phase[68]
R^{2c}		0.9953	0.9805	0.9856	0.9842	0.9890	0.9907		
MAD[c]/ppm		17.2	24.5	23.4	19.5	16.5	16.5		

[a] GIAO-MPW1K/6-311++G(2d,2p)//MPW1K/6-31G(d). [b] Results taken from ref. 25; basis set for NMR calculations: IGLO-II; geometries optimized at the BP/IGLO-II level. [c] PH$_3$ (the reference compound) and PN (worst case in the present work as well as in ref. 25) have been excluded from the error analysis.
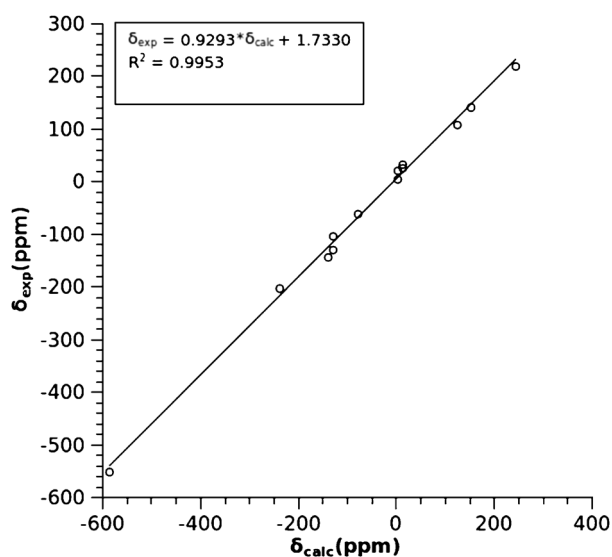
Fig. 5 Experimental ^{31}P chemical shifts *vs*. calculated at the GIAO-MPW1K/6-311++G(2d,2p)//MPW1K/6-31G(d) level of theory listed in Table 1.

Table 2 Individual conformations of P(OMe)$_3$ (**8**) used in Boltzmann-averaged ^{31}P chemical shift calculations

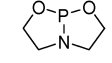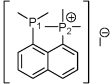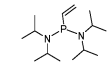|	ΔG_{298}/ kJ mol^{-1}	δ^{a}/ ppm
8_1	0.0	+155.9
8_2	2.6	+152.5
8_3	8.5	+128.9
8_4	15.4	+174.6
8_5	32.4	+121.0

^{a} Relative to PH$_3$.

GIAO-MPW1K/6-311++G(2d,2p) method employed here gives slightly better (slightly better R^2, while MAD is 0.7 ppm larger) results as compared to the GIAO-MP2/IGLO-II//BP/ IGLO-II approach considered to be the most accurate in the van Wüllen study. As in this previous study we exclude the PN system from the error analysis. The correlation between ^{31}P shifts measured experimentally and those calculated at the GIAO-MPW1K/6-311++G(2d,2p) level is shown graphically in Fig. 5. Larger molecular systems are often conformationally quite flexible and the question naturally arises how to deal with this point in ^{31}P NMR shift calculations. Assuming rapid interconversion between individual conformers (on the NMR time scale) it would seem obvious to calculate ^{31}P NMR shifts as the Boltzmann-weighted average over all conformations. The shifts reported in Table 1 at the GIAO-MPW1K level were actually obtained by Boltzmann-averaging at 298.15 K using free energies obtained at the MP2(FC)/6-31+G(2d,p)// MPW1K/6-31G(d) level of theory. This latter method has been used recently in the accurate prediction of thermo-chemical data of a large set of N- and P-based Lewis bases.[5] To illustrate the importance of conformational averaging already in gas phase calculations ^{31}P shifts calculated for individual conformers of trimethoxyphosphane P(OMe)$_3$ (**8**) have been collected in Table 2 together with the respective relative free energies ΔG_{298}. While the energetically most favorable conformers of **8** have almost the same ^{31}P chemical shift at +155.9 and +152.5 ppm, respectively, this is not so for the conformation located 8.5 kJ mol^{-1} above the global minimum with a ^{31}P chemical shift at +128.9 ppm. The Boltzmann weight of this conformer is quite low in the gas phase and the average shift predicted as +154.4 ppm is thus quite close to the individual values for the best two conformers. However, solvent effects even in apolar organic media can be large enough to change the relative energies of individual conformers and can therefore lead to major changes in ^{31}P NMR shifts.

With a protocol in hand for the calculation of gas phase ^{31}P chemical shifts of large molecular structures (GIAO-MPW1K/ 6-311++(2d,2p)//MPW1K/6-31G(d)), we can address the question of how to account for solvent effects in a systematic manner. We compare in the following two different approaches to account for solvent effects: (a) use of the Polarizable Continuum Model (PCM) in combination with NMR shift calculations (solution model 1); and (b) inclusion of one explicit solvent molecule in the geometry optimization of the substrate and subsequent NMR shift calculations on this solvent/solute complex using the PCM continuum solvation model at the stage of NMR shift calculations (solution model 2). These two models have been tested on a set of systems for which there are data measured in solvents of different polarities (chloroform-d$_1$ and benzene-d$_6$) and which cover a large range of ^{31}P NMR chemical shifts (from -50 to $+160$ ppm). In order to avoid problems associated with the solution phase properties of PH$_3$ (**3**) all calculations have been performed using Ph$_3$P (**1**) as the reference system. As one can see from the data presented in Table 3 and in Fig. 6 and 7 the best results are obtained using solution model 2, where a combination of explicit and continuum solvation is employed. Use of the PCM continuum solvation model alone is particularly unsatisfactory for phosphane oxides **2** and **9**. The large solvent effects observed for this latter class of compounds even for a low-polarity solvent such as chloroform are clearly due to specific hydrogen bonding interactions between the phosphane oxide oxygen atom and the chloroform C–H bond (Fig. 8). Our observation is in accordance with the recently demonstrated insufficiency of PCM models for systems with strong directional solvent–solute interactions.[74,75]

It was mentioned before that conformational averaging is an important step in the process of chemical shift calculations inasmuch as the shifts depend dramatically on the confor-mational state of the molecule. The effects of conformational mobility on the calculated solution phase ^{31}P shifts will here be
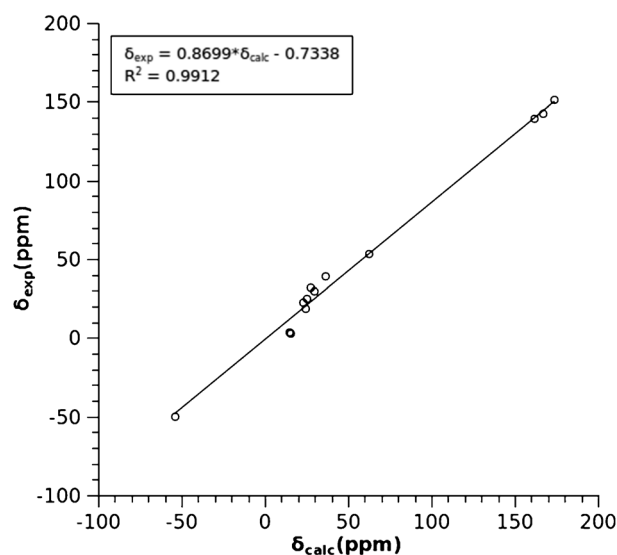
Table 3 Experimentally measured and theoretically calculated ^{31}P NMR chemical shifts in the gas phase and in solution using PPh$_3$ (**1**) as the reference system

System		^{31}P NMR chemical shift				
		Gas-phase	Solution model 1	Solution model 2	Exp.	Solvent
1	PPh$_3$	−4.7	−4.7	−4.7	−4.7	Chloroform-d[42]
		−4.7	−4.7	−4.7	−4.7	Benzene-d$_6$[41]
2	OPPh$_3$	+24.1	+26.6	+29.6	+29.7	Chloroform-d$_1$[42]
		+24.1	+26.6	+25.4	+24.7	Benzene-d$_6$[43]
8	P(OCH$_3$)$_3$	+166.6	+166.9	+167.3	+142	Chloroform[44]
9	OP(CH$_3$)$_3$	+25.3	+29.8	+36.3	+39.3	Chloroform-d$_1$[59,60]
		+25.3	+28.1	+27.3	+32.0	Benzene-d$_6$[59,60]
10	OP(OCH$_3$)$_3$	+16.7	+16.7	+15.9	+3.0	Chloroform-d$_1$[61]
		+16.7	+16.6	+14.6	+3.7	Benzene-d$_6$[61]
18	[PPh$_3$Me$^+$]I$^-$	+15.5	+17.1	+23.1	+22.2	Chloroform-d$_1$[69]
19	PBr$_2$Ph	+175.4	+176.7	+173.8	+150.7	Chloroform-d$_1$[70]
20		+160.7	+163.5	+161.8	+139.0	Chloroform-d$_1$[71]
21		−56.3P$_1$	−55.1P$_1$	−54.1P$_1$	−50.6P$_1$	Chloroform-d$_1$[72]
		+27.4P$_2$	+25.1P$_2$	+24.7P$_2$	+18.1P$_2$	Chloroform-d$_1$[72]
22		+61.5	+64.7	+62.8	+53.1	Chloroform-d$_1$[73]
	R^{2a}	0.9811	0.9858	0.9912		
	MAD^a/ppm	11.9	11.4	9.6		

^{a} PPh$_3$ (the reference system) has been excluded from the error analysis.
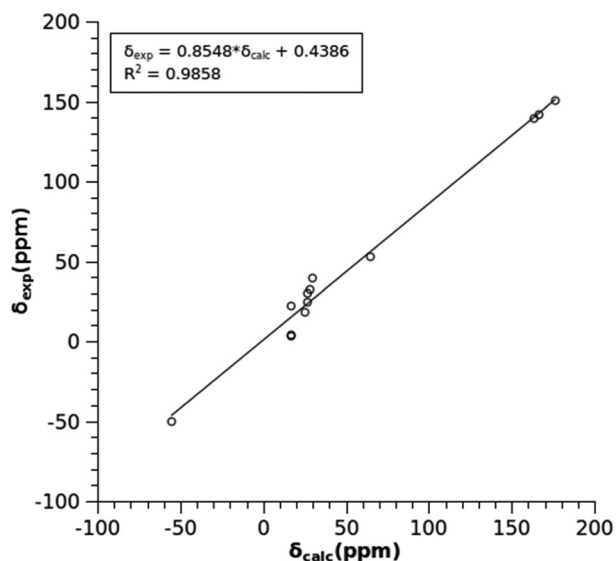
Fig. 6 Experimental chemical shifts *vs.* calculated using solution model 1 for the compounds listed in Table 3.

Fig. 7 Experimental chemical shifts *vs.* calculated using solution model 2 for the compounds listed in Table 3.

exemplified by a closer look at system **22**. After gas-phase geometry optimization at the MPW1K/6-31G(d) level 10 individual conformations have been identified as true minima. Chemical shift calculations at the GIAO-MPW1K/6-311++G(2d,2p) level and single point calculations at the MP2(FC)/6-31+G(2d,p)//MPW1K/6-31G(d) level have subsequently been performed for all ten structures in order to calculate ^{31}P NMR shifts and relative free energies ΔG_{298} in the gas phase and in solution (model 1). The results of this exercise as collected in Table 4 show the first three conformers

22_1 to **22_3** (shown graphically in Fig. 9) to be energetically accessible at a temperature of 298.15 K. It is quite remarkable to see that the ^{31}P NMR shifts calculated in the gas phase and in the presence of the PCM continuum model (for CHCl$_3$ as the solvent) hardly differ. The shifts vary largely for individual conformers from +50.7 ppm (conformer **22_2**) to +102.4 ppm (conformer **22_8**). The difference between the Boltzmann-averaged ^{31}P NMR shifts predicted for the gas phase (+61.5 ppm) and for CHCl$_3$ solution (+64.7 ppm) is thus solely due to changes in the Boltzmann-weights of individual
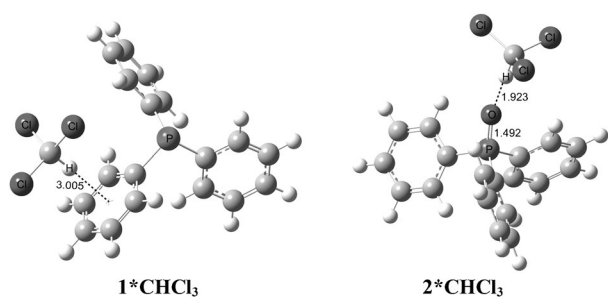
Fig. 8 Energetically most favorable complexes of PPh₃ (**1**) and OPPh₃ (**2**) with CHCl₃ as obtained at the MP2(FC)/6-31 + G(2d,p)// MPW1K/6-31G(d) level of theory.

Fig. 9 Structures of the three most stable conformations of system **22**.

conformers. In addition to relative energies obtained at the MP2(FC)/6-31 + G(2d,p)//MPW1K/6-31G(d) level Table 4 shows also values from single-point calculations at the MPW1K/6-311++G(2d,2p)//MPW1K/6-31G(d) level of theory which accompany the chemical shift calculations. Boltzmann-averaged ³¹P NMR shifts found using DFT energies are also listed in Table 4.

The ten gas-phase conformers of **22** were subsequently used to calculate ³¹P NMR shifts with solvent model 2, in which explicit chloroform molecules were placed in close vicinity of the phosphorous atom and π-bond, where intermolecular solute/solvent interaction is most likely. The solvent–substrate complexes obtained after geometry optimization illustrate, however, that no close contacts are possible between CHCl₃ solvent molecules and the central phosphorous atom due to severe steric effects. The two energetically most favorable complexes identified in these studies are shown in Fig. 10. Relative energies and individual ³¹P NMR shifts for all complexes are collected in Table 5. Surveying the chemical shifts calculated for individual conformers in Table 5 we note again a large dispersion of shift values. The Boltzmann-averaged chemical shift (based on MP2(FC)/6-31 + G(2d,p) free energies) obtained with solution model 2 for chloroform
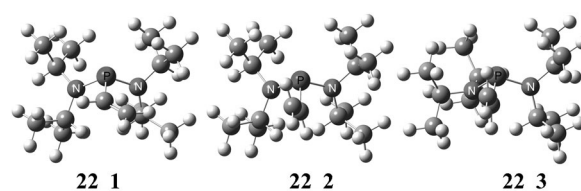
is +62.8 ppm. Whether to use other relative energies in the Boltzmann-averaging procedure was tested by using free energies derived from MPW1K/6-311++G(2d,2p) single point calculations, but the relative weights of individual conformers are not decisively different with this choice (Table 5). How much of this effort is required? Selecting from Table 5 only those CHCl₃ complexes derived from the three most stable gas-phase conformations **22_1** through **22_3** the Boltzmann-averaged chemical shift was found to be hardly changed at +62.6 ppm (see ESI†). For this smaller set of structures basis set effects in the MP2(FC) energy calculations were also explored, but the changes in the predicted chemical shift were rather minor.
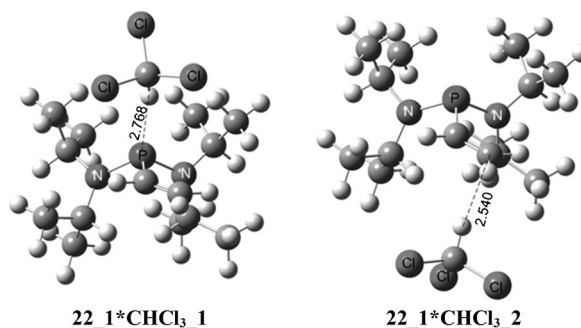

Fig. 10 Complexes between the most stable conformation of system **22** and chloroform.

Table 4 Chemical shifts and energetic characteristics for all conformations of the system **22** calculated for the gas phase and in solution (CHCl₃, solution model 1)

| | Chem. shift[a]/ppm | | Free energies/kJ mol⁻¹ | | | |
| | | | MPW1K | | MP2 | |
Conformation	Gas-phase[b]	Solution model 1[c]	$\Delta G_{298}{}^d$	$\Delta G_{298,\text{CHCl}_3}{}^e$	$\Delta G_{298}{}^f$	$\Delta G_{298,\text{CHCl}_3}{}^g$
22_1	+66.6	+66.3	1.7	0.0	0.0	0.0
22_2	+50.7	+51.2	0.0	1.0	1.1	3.8
22_3	+87.0	+87.2	12.7	11.4	6.9	7.3
22_4	+85.6	+86.4	13.7	12.8	14.1	15.0
22_5	+80.0	+80.8	15.4	14.1	16.5	16.9
22_6	+84.7	+84.3	21.6	18.1	19.7	17.9
22_7	+100.5	+100.3	20.6	17.6	19.9	18.6
22_8	+102.4	+102.6	19.6	19.2	17.4	18.7
22_9	+80.4	+80.8	15.5	18.4	17.8	22.4
22_10	+87.3	+87.5	39.9	35.9	32.0	29.6
$\langle\delta\rangle^h$			+56.3	+60.6	+61.5	+64.7

[a] Relative to PPh₃. [b] GIAO-MPW1K/6-311++G(2d,2p). [c] MPW1K/6-311++G(2d,2p)+PCM/UAHF/MPW1K/6-311++G(2d,2p). [d] MPW1K/6-311++G(2d,2p), free en. corr.: MPW1K/6-31G(d). [e] MPW1K/6-311++G(2d,2p)+PCM/UAHF/MPW1K/6-311++G(2d,2p), free en. corr.: MPW1K/6-31G(d). [f] MP2(FC)/6-31+G(2d,p)//MPW1K/6-31G(d), free en. corr.: MPW1K/6-31G(d). [g] MP2(FC)/6-31+G(2d,p)//MPW1K/6-31G(d)+PCM/UAHF/MPW1K/6-311++G(2d,2p), free en. corr.: MPW1K/6-31G(d). [h] Boltzmann-averaged chemical shift.

Table 5 Chemical shifts and energetic characteristics for solvent–solute complexes of **22** with $CHCl_3$ as employed for solvent model 2

| | | Free energies/kJ mol^{-1} | | | |
| | | MPW1K/6-311++G(2d,2p) | | MP2(FC)/6-31+G(2d,p) | |
Complex	Chem. shift^a/ppm	$\Delta G_{298}{}^b$	$\Delta G_{298,\text{CHCl}_3}{}^c$	$\Delta G_{298}{}^d$	$\Delta G_{298,\text{CHCl}_3}{}^e$
22_1*CHCl₃_1	+62.4	0.0	0.0	0.0	0.0
22_1*CHCl₃_2	+65.9	5.8	4.5	4.9	3.5
22_2*CHCl₃_1	+52.1	2.9	5.7	4.0	6.7
22_2*CHCl₃_2	+50.8	3.9	1.8	11.8	9.7
22_3*CHCl₃_1	+82.7	13.6	14.9	9.8	11.1
22_7*CHCl₃_2	+98.7	15.9	13.5	14.9	12.6
22_3*CHCl₃_2	+85.1	17.0	13.4	17.7	14.1
22_4*CHCl₃_1	+83.4	13.8	15.6	16.2	18.0
22_9*CHCl₃_1	+76.6	14.1	15.8	17.8	19.5
22_6*CHCl₃_1	+78.2	19.0	19.1	19.5	19.6
22_7*CHCl₃_1	+94.5	17.3	17.6	19.9	20.1
22_5*CHCl₃_1	+78.1	15.0	17.3	18.5	20.8
22_5*CHCl₃_2	+78.9	18.5	13.9	26.0	21.4
22_8*CHCl₃_1	+95.3	19.3	21.3	19.5	21.5
22_4*CHCl₃_2	+84.1	17.9	13.8	25.8	21.7
22_6*CHCl₃_2	+84.3	26.0	22.6	26.9	23.6
22_9*CHCl₃_2	+78.7	18.0	14.6	27.2	23.9
22_8*CHCl₃_2	+101.0	24.5	21.6	29.3	26.3
22_10*CHCl₃_1	+83.0	42.1	40.4	34.2	32.5
22_10*CHCl₃_2	+86.3	45.2	41.6	40.7	37.1
$\langle\delta\rangle^f$		+59.5	+59.4	+61.6	+62.8

^{a} Relative to PPh₃, GIAO-MPW1K/6-311++G(2d,2p)+PCM/UAHF/MPW1K/6-311++G(2d,2p). ^{b} MPW1K/6-311++G(2d,2p), free en. corr.: MPW1K/6-31G(d). ^{c} MPW1K/6-311++G(2d,2p)+PCM/UAHF/MPW1K/6-311++G(2d,2p), free en. corr.: MPW1K/6-31G(d). ^{d} MP2(FC)/6-31+G(2d,p)//MPW1K/6-31G(d), free en. corr.: MPW1K/6-31G(d). ^{e} MP2(FC)/6-31+G(2d,p)//MPW1K/6-31G(d)+PCM/UAHF/MPW1K/6-311++G(2d,2p), free en. corr.: MPW1K/6-31G(d). ^{f} Boltzmann-averaged chemical shift.

One additional technical issue arises for ion pair system **21**, where ^{31}P NMR calculations can be performed either for the full ion pair or for the phosphonium portion alone. Gas and solution phase calculations have been performed for both of these choices. The results compiled in Fig. 11 clearly illustrate that accurate predictions require the consideration of the full system. The difference for the theoretical and experimental chemical shifts of the phosphane atom P_1 is small, while it is quite large for the phosphonium atom P_2. Similar results have been obtained for system **18**, where application of solution model 2 to the bare phosphonium cation (PPh₃Me$^+$) leads to a calculated chemical shift of +27.4 ppm, which is 5.2 ppm

larger than the experimental value of +22.2 ppm. Consideration of the full ion pair through inclusion of the iodide counter ion shifts the predicted chemical shift for **18** considerably to +23.1 ppm, just 0.9 ppm away from the experimental value.

Conclusions

(1) The MPW1K functional in combination with the GIAO scheme represents a good basis for gas-phase and condensed-phase calculations of ^{31}P NMR chemical shifts for large molecular systems. Predictions with other hybrid functionals (such as B98 or B3LYP) appear to be less reliable, while predictions at the MP2 level are significantly more expensive.

(2) The IGLO-III and 6-311++G(2d,2p) basis sets in combination with GIAO-MPW1K provide ^{31}P NMR chemical shift predictions with good accuracy. Smaller basis sets provide systematically inferior predictions.

(3) The ^{31}P NMR shifts calculated for individual conformers vary largely, emphasizing the need for Boltzmann-averaging over the full conformational space of the system.

(4) ^{31}P NMR chemical shifts in solution are best predicted by including explicit solvent molecules at the stage of geometry optimization and by performing the GIAO shift calculations in the presence of the PCM/UAHF continuum solvation model.

(5) Accurate prediction of ^{31}P NMR chemical shifts of ion pair systems require consideration of the full system.

Finally, in view of the considerably different chemical shifts obtained with different reference compounds it appears that accurate predictions can only be made through relative shift calculations of two structurally and chemically closely related
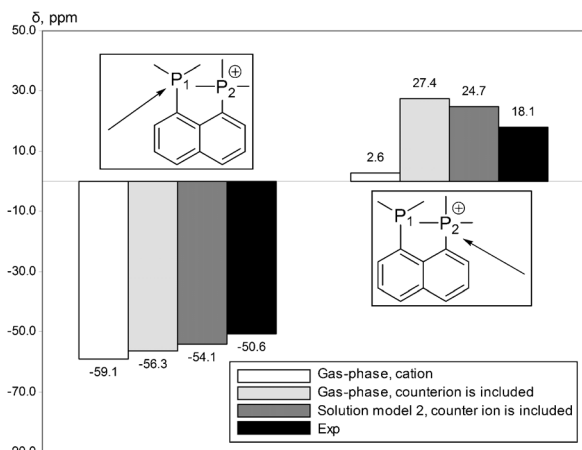

Fig. 11 ^{31}P NMR chemical shifts (relative to PPh₃) calculated for ion-pair system **21** in the presence and the absence of the iodide counter ion.

systems. This requirement may reflect the fact that several factors are not accounted for in the current computational approach. This includes the known concentration- and temperature-dependence of experimentally measured ^{31}P spectra as well as the neglect of solvent magnetic polarizability effects in the current form of the PCM continuum solvation model.[39]

Acknowledgements

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75 The significantly different slope parameters of 0.855 (Fig. 6) and 0.870 (Fig. 7) as compared to the slope parameter in the gas phase studies of 0.929 (Fig. 5) are due to the smaller range of chemical shifts considered in the solution studies.