

HP₄⁻ and (CH₂)₂P₃⁻ Anions Form Four-membered Rings with an Allyl Moiety - An *ab initio*/NMR study

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Abstract On the energy hypersurfaces of the anions HP₄⁻ and CH₂P₃⁻ at the RMP2(fc) /6-31+G(d) level, the isomers with triphosphaallyl moiety are the lowest energy structures. For these free 1-X-2,4-(P_B)₂-3-P_A⁻ anions characteristic ³¹P NMR chemical shifts, $\delta^{31}\text{P}$, are predicted to be (for X = PH, **1**, $\delta^{31}\text{P}(\text{P}_A) = 517$, $\delta^{31}\text{P}(\text{P}_B) = 424$, and $\delta^{31}\text{P}(\text{P}_X) = 50$; for X = CH₂, **4**, $\delta^{31}\text{P}(\text{P}_A) = 611$, $\delta^{31}\text{P}(\text{P}_B) = 450$). The observed $\delta_{\text{exp}}^{31}\text{P}$ values for HP₄⁻ (Na/K, DME) completely disagree with the $\delta^{31}\text{P}$ calculated at GIAO/MP2/6-311+G(d) //RMP2(fc) /6-31+G(d) for structure **1**. The rotational average of the phosphinidyltriphosphirene structures (P₃-PH, **3**) agree better with the $\delta_{\text{exp}}^{31}\text{P}$ than those with a bicyclo[1.1.0]hydrogentetraphosphanide backbone, **2**. MO analysis can rationalize the extreme *endo/exo* effect ($\Delta\delta^{31}\text{P} = 455$ ppm) on the chemical shift in the exocyclic PH group of **3**. The lowest energy geometry of the anion **3** has E_{rel} of 31 kJ mol⁻¹ relative to **1**. The most favored **3** + Na⁺ structure is only 15 kJ mol⁻¹ above the lowest energy HP₄Na minimum, **2** + Na⁺ with Na⁺ in *endo* and H in *exo* orientation of the bicyclo-P₄ framework (E_{rel} of **1** + Na⁺ is 13 kJ mol⁻¹). In most HP₄Na structures the Na⁺ changes the ³¹P NMR chemical shifts towards higher field with respect to the bare anions.

Keywords *Ab initio* calculations, Phosphorus heterocycles, Small ring systems, ³¹P NMR

Introduction

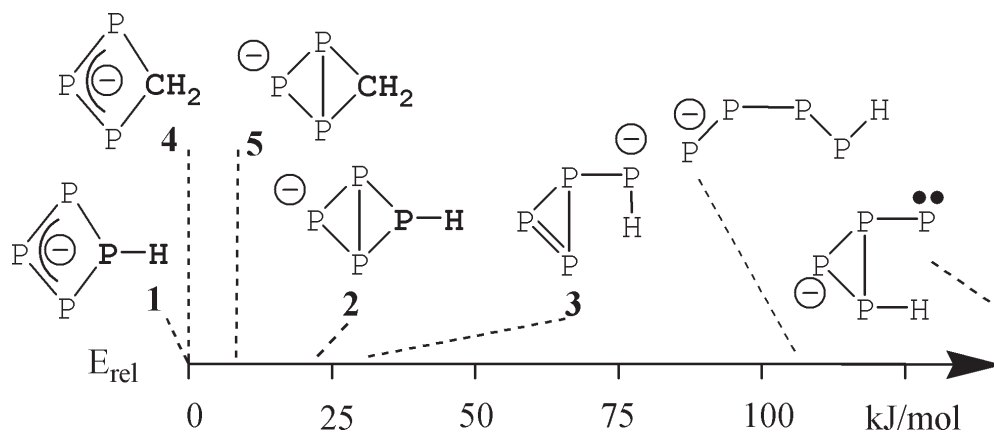
On the way from the perfect deltahedron, P₄ (T_d)-- to polyphosphanes the intermediate species with less triangles has enticed various experimental and theoretical studies.[1-3] The HP₄⁻ anion attracted special interest due to its puzzling ³¹P NMR chemical shift and the disagreement between

theoretical [4] and empirical [5] assignment of the P-H orientation (empirical *endo* vs theoretical *exo* preference) of bicyclo[1.1.0]tetraphosphanide (**2endo** and **2exo** in Figures 1 and 2). The reported NMR chemical shift of the anionic phosphorus in HP₄⁻ (71.3 ppm) is about in the middle of the range of phosphanides (with formal σ²-P moiety): -335 for solvated ^tBuPHLi to +732 for (^tBu₃SiP)₂P Na(solv). Furthermore $\delta^{31}\text{P}$ of HP₄(Na/K) is similar to that of the phospholide anion,[6] cyclo-(CH)₄P⁻ (77.2 ppm). In this context the structural assignment to a bicycle is questionable. A monocyclic structure with an allylic -PPP- moiety, characterized by a 3 center π bond, appears to be a reasonable alternative. Recent experimental research in phosphoallyls shows that the

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Dedicated to Professor Paul Ragué von Schleyer on the occasion of his 70th birthday

Figure 1 Relative energies at MP2(fc)/6-31+G(d) in kJ mol^{-1} of HP_4^- and CH_2P_3^- anion structures. The high energy isomers (linear H-PPPP, $E_{\text{rel}} = 119 \text{ kJ mol}^{-1}$ and the 1-phosphinidino-phosphiren-2-ylid, $E_{\text{rel}} = 166 \text{ kJ mol}^{-1}$) are neglected in this study



allyl structure is preferred over the three-membered ring for phosphanides.[7] This raises the question whether the bicyclic form is really the best structure for HP_4^- . Therefore in the following, relative energies for HP_4R structures (with R = negative charge, and Na) are presented together with their MO analysis. The discussion places these results in the context of similar investigations in HP_4R systems with R = H,[8,9] and Li [4] as *substituent*. The sodium ion pair structures are considered to obtain an impression of the counterion effect on the structural preference and the NMR chemical shifts of the HP_4^- isomers. For a comprehensive set of phosphanides including the cyclo- $\text{P}_3(\text{CH}_2)^-$, which is isovalent to **1**, their geometries and computed chemical shifts are presented. These provide an estimate for the agreement between experimental $\delta^{31}\text{P}$ and the corresponding values from MP2/NMR calculations, which neglect the solvent as well as the counterion effect. The experimental $\delta^{31}\text{P}(\text{HP}_4(\text{Na/K}), \text{DME})$ are reinterpreted based on these results.

Computational details

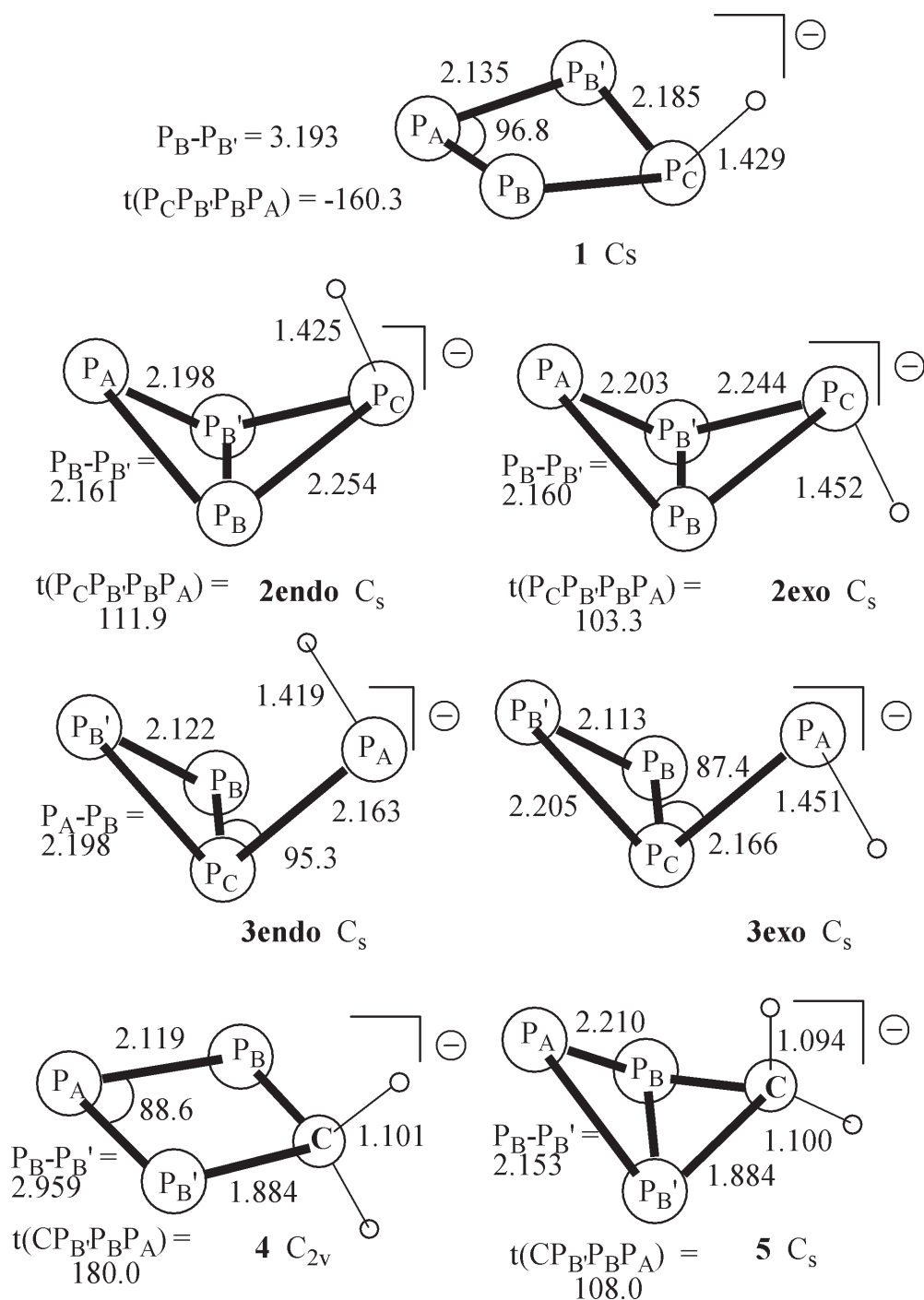
The geometries of HP_4^- , $\text{P}_3(\text{CH}_2)^-$ and related molecules were optimized at the MP2(fc)/6-31+G(d) level. The basis set includes diffuse functions, which are required for sufficient description of anionic molecules. The HP_4^- geometries are presented in Figure 2, whereas details of the $\text{P}_3(\text{CH}_2)^-$ and HP_4Na calculations are in the supplementary material. Throughout this paper, bond lengths are given in Ångström, bond angles in degrees, and relative energies in kJ mol^{-1} . Relative energies are with respect to **1** for the HP_4^- anions and with respect to **11** for the HP_4Na geometries. The ^{31}P NMR chemical shifts, $\delta_{\text{calc}}^{31}\text{P}$, were computed at the GIAO/MP2/6-311+G(d), GIAO/MP2/6-31+G(d) and for comparison also at GIAO/B3LYP/6-31+G(d) with PH_3 in 6-31G(d,p) geometry as theoretical reference. All calculations including calculation of the Wiberg bond index [10] were carried out using the GAUSSIAN 98 [11] set of programs.

Results and discussion

Minimum structures of HP_4^- and CH_2P_3^-

For HP_4^- only one “Baudler Structure” [12], **2** in this study, exists. Nevertheless, several other structures are minima on this energy hypersurface with **1** as the lowest energy isomer ($E_{\text{rel}}(\mathbf{2}) = 23.3 \text{ kJ mol}^{-1}$). While the optimized geometries of **1** to **3** are shown in Figure 2, the linear H-PPPP⁻ minimum with *s-cis* conformation ($E_{\text{rel}} = 119 \text{ kJ mol}^{-1}$) and the phosphinidine structure (cyclo-(P)(PH)(P-P)⁻, $E_{\text{rel}} = 166 \text{ kJ mol}^{-1}$) are neglected due to their high energies. In all structures considered the phosphorus atoms can be classified in three types: P_A , the formally anionic phosphorus, P_B and $\text{P}_{B'}$, two symmetry equivalent phosphorus atoms, and P_C , a $\sigma^3\text{-P}$. The allyl conjugation of the $\text{P}_B\text{-P}_A\text{-P}_{B'}$ fragment in **1** and **4** is characterized by $\text{P}_A\text{-P}_B$ bond lengths of 2.135 and 2.119 Å, respectively, which are similar to that in the acyclic H-PPP-H⁻ anion [7] (2.096 Å at MP2/6-31+G(d) and 2.09(2) Å in the crystal structure of $[\text{Bu}_3\text{Si-PPP-Si}^+\text{Bu}_3\cdot\text{Na}(\text{THF})_4]$). While reducing the $\text{P}_B\text{-P}_A\text{-P}_{B'}$ bond angle in the allyl system from 108.2° of the acyclic compound [7] to 96.8° in **1** induces an elongation of the $\text{P}_A\text{-P}_B$ bond by 0.04 Å, stronger bending in **4** ($\text{P}_B\text{-P}_A\text{-P}_{B'} = 88.6^\circ$) means less lengthening of the $\text{P}_A\text{-P}_B$ ($\Delta = 0.02 \text{ Å}$). From **1** to **2**, the $\text{P}_A\text{-P}_B$ bond changes its character from a partial π -bond to a single bond. Due to the π donor character of the occupied p-AO at P_A , which is orthogonal to the $\text{P}_A\text{P}_B\text{P}_{B'}$ plane, the $\text{P}_C\text{-P}_B$ and $\text{P}_C\text{-P}_{B'}$ bond are elongated while the $\text{P}_A\text{-P}_B$ and $\text{P}_A\text{-P}_{B'}$ bonds shrink compared to bicyclo $\text{H}_2\text{P}_4^-(\text{HP-P} = 2.229 \text{ Å in the } \textit{exo,exo} \text{ isomer})$. For HP_4^- the non-Baudler structure **1** is preferred even more over **2** than for $\text{P}_3(\text{CH}_2)^-$ with $E_{\text{rel}}(\mathbf{5}) = 10.6 \text{ kJ mol}^{-1}$ (relative to **4**). An impression of the location of the negative molecular charge can be obtained from the Mulliken charges, q_M . As expected for an allylic delocalization, the anionic charge of **1** is not localized at P_A since the HOMO has two nodal planes at P_A ($q_M(\text{P}_A)$ is only -0.08, while $q_M(\text{P}_B)$ is -0.44). In **3** the negative molecular charge should be located in the exocyclic phosphanido group. Nevertheless, $q_M(\text{P}_A)$ and $q_M(\text{H})$ are to-

Figure 2 MP2(fc)/6-31+G(d) optimized geometries of the HP_4^- and $CH_2P_3^-$ anion structures considered. Bond length in Å, bond angles in degree



gether only -0.53 electron charges. A similar distribution of the anionic charge between P_A and the remaining molecule occurs in **2**: $q_M(P_A, \mathbf{2exo}) = -0.60$, $q_M(P_A, \mathbf{2endo}) = -0.63$. The charge delocalization is reflected by shortened P_A-P_B and widened P_B-P_C bonds in **2** compared to bicyclo H_2P_4 ($HP-P = 2.229$ Å in the *exo,exo* isomer). The donor character of $p-AO(P_A)$ towards P_C in the bicycle **2** is small ($WBI(P_A-P_C) < 0.2$). While the partial P_A-P_C bonding reflects the descent from the P_4 cage, the cluster character should vanish in **3** since

two bonds of white phosphorus are opened and only one deltahedron remains.

A P-P double bond characterizes **3**, phosphinidino-phosphirene, with E_{rel} of 30.8 and 40.1 kJ mol^{-1} . For the parent cyclo-(PH)(P)₂ the double bond length was calculated to be 1.981 [13] at RHF/DZP and is 2.033 Å at the level of this study. The corresponding $P_B-P_{B'}$ bond in **3** is distinctly longer (2.122 and 2.113 Å, Figure 2) due to the negative hyperconjugation of the $p-AO(P_A)$ which matches the sym-

Table 1 Experimental and GIAO/MP2(fc)/6-311+G(d)//MP2(fc)/6-31+G(d) calculated [a] ^{31}P NMR chemical shifts of compounds [b] with anionic P_3 moiety (relative energies [c] of HP_4^- in kJ mol^{-1})

Structure	E_{rel} [c]	P_A [b]	P_B [b]	P_C [b]
$[\text{P}(\text{PR})_2](\text{Na}, 4 \text{ THF}), \text{exp.}$ [d]	—	732.5	212.5	—
$[\text{P}(\text{PR})_2]^-$, <i>alltrans</i> [d]	—	595	168	—
$[\text{cyclo-P}(\text{PR})_2]^-$, <i>trans</i> [d]	—	-275	-255	—
$[\text{cyclo-P}(\text{PR})_2]^-$, <i>cis</i> [d]	—	-251	-281	—
$\text{HP}_4(\text{Na/K}, \text{DME}), \text{exp.}$ [e]	—	+71.3	-355.1	-329.5
$\text{HP}_4^-, \mathbf{1}$	0.0	517	424	50
$\text{HP}_4^-, \mathbf{2endo}$	24.7	221	-322	350
$\text{HP}_4^-, \mathbf{2exo}$	23.3	-16	-360	-120
$\text{HP}_4^-, \mathbf{3endo}$	41.1	377	-268	-261
$\text{HP}_4^-, \mathbf{3exo}$	30.8	-78	-247	-286
$\text{P}_3(\text{CH})_2^-$, exp. [f]	—	272.0	262.9	—
cyclo-1,2,3- $\text{P}_3(\text{CH})_2^-$, C_{2v}	0.0	279 ^e	264 ^e	—
bicyclo- $\text{P}_3(\text{CH})_2^-$, C_s	220.0	301 ^g	-170 ^g	—
cyclo-1,2,3- $\text{P}_3(\text{CH}_2)^-$, C_{2v}	0.0	611	450	—
bicyclo- $\text{P}_3(\text{CH}_2)^-$, C_s	10.6	23	-355	—

[a] Chemical shifts calculated using PH_3 in MP2/6-31G(d,p) geometry as theoretical reference with $^{31}\text{P} = -240$ and $\sigma^{31}\text{P} = 616.8$ ppm

[b] P_A is dicoordinate and occurs once; P_B occurs twice and is attached to P_A ; P_C is tricoordinate and occurs once

[c] At MP2(fc)/6-31+G(d) the total energy of **1** is -1363.92945 Hartree

[d] The substituent R is H in the computed molecules and $^t\text{Bu}_3\text{Si-P}$ in the experiment.[18] [e] Reference 5. [f] Reference 14

[g] Chemical shifts calculated at GIAO/MP2/6-311G(d) using PH_3 in MP2/6-31G(d,p) geometry as theoretical reference with $\sigma^{31}\text{P} = 616.9$ ppm

metry of the $\pi^*(\text{P}_B-\text{P}_B)$ group orbital. This is supported by calculation of the transition structure for rotation around the P_A-P_C bond in which the double bond length is about as long as in the parent HP_3 (2.033 Å). The consequences of the remarkable $\text{P}_A-\pi^*(\text{P}_B-\text{P}_B)$ conjugation for the predicted ^{31}P NMR signals are discussed in the following section together with a scan over $\delta^{31}\text{P}$ of different model phosphanides.

NMR chemical shifts

For the P_4H^- structures considered the high level ab initio calculations of the phosphorus NMR chemical shifts, $\delta_{\text{calc}}^{31}\text{P}$, of all P atoms are presented in Table 1. After comparing the characteristic $\delta^{31}\text{P}$ of P_A in **1** - **5** with the $\sigma^2\text{-P}$ in various phosphid anions (Table 2) the effect of molecular motion is considered. At last, $\delta_{\text{calc}}^{31}\text{P}$ for the P_4HNa complexes at a *practicable* level of theory are considered to estimate the effect of the sodium cation (Table 3).

From Table 1 it becomes clear that none of the sets of calculated chemical shifts for single structures ($\delta^{31}\text{P}(\text{P}_A, i)$, $\delta^{31}\text{P}(\text{P}_B, i)$, and $\delta^{31}\text{P}(\text{P}_C, i)$ values for $i = \mathbf{1}, \mathbf{2endo}, \mathbf{2exo}, \mathbf{3endo},$ and $\mathbf{3exo}$) alone matches the experimental data set. While P_C in structure **1** comprising a triphosphaallyl moiety ($\delta_{\text{calc}}^{31}\text{P}(\text{P}_C, \mathbf{1}) = 50$ ppm, Table 1) has about the chemical shift assigned to the anionic phosphorus in an assumed bicyclic structure, the $\delta_{\text{calc}}^{31}\text{P}$ of the other nuclei are more than 700 ppm

downfield from the remaining $\delta_{\text{calc}}^{31}\text{P}$. For the bicyclic P_4H^- structures, **2endo** and **2exo**, the $\delta_{\text{calc}}^{31}\text{P}$ values for the two P_B nuclei agree reasonably well with the experimental P_B value (deviations of 33 for **2endo** and -5 for **2exo**). In disfavor of these structures, the $\delta_{\text{calc}}^{31}\text{P}(\text{P}_C, \mathbf{2})$ differ by 210 and 680 ppm from $\delta_{\text{exp}}^{31}\text{P}(\text{P}_C)$. The experimental $\delta^{31}\text{P}(\text{P}_A, \mathbf{2})$ is in the middle between the two corresponding calculated values. Nevertheless, *endo/exo* isomerization is not likely to be fast enough to provide an averaged signal for the bicyclic structures. In contrast, for the rotamers **3endo** and **3exo** averaging is likely at room temperature (rotational barrier: 53 kJ mol^{-1} at MP2(fc)/6-31+G(d) level) and thereby provides a $\delta_{\text{calc,av}}^{31}\text{P}(\text{P}_A)$ close to the experiment. For the two P_B and the one P_C of **3** the calculated NMR shifts deviate from the corresponding $\delta_{\text{exp}}^{31}\text{P}$ by less than 105 ppm. In conclusion, differentiation between the allylic, **1**, and the other cyclic isomers based on the $\delta_{\text{calc}}^{31}\text{P}$ values appears to be justified even if the effect of a coordinated sodium cation is neglected (the $\delta^{31}\text{P}(\text{P}_B)$ at GIAO/MP2/6-31+G(d) for the $[\mathbf{1}^*\text{Na}]$ complexes differ from those of **1** by 47 for **6** and zero for **7**; while $\delta^{31}\text{P}(\text{P}_B, \mathbf{1}) > 300$ is distinctly different to the $\delta^{31}\text{P}(\text{P}_B, \mathbf{2})$ and $\delta^{31}\text{P}(\text{P}_B, \mathbf{3}) < -200$ ppm). Nevertheless, for a confirmative assignment of the experimental $\delta^{31}\text{P}$ to either **2** or **3** the effect of Na^+ should be considered. Comparison of the experimentally known data corresponding to the anions PH_2^- , $\text{P}(\text{SiH}_3)_2^-$, and $\text{P}(\text{PH}_2)(\text{SiH}_3)^-$ with the $\delta_{\text{calc}}^{31}\text{P}$ in Table 2 gives the impression that the sodium cation changes $\delta^{31}\text{P}$ towards lower field.

Table 2 Calculated [a] NMR chemical shifts [b,c] of the σ^2 -P with the α substituents [d] X and Y in acyclic and cyclic structures comprising the phosphanide moiety

Molecule	X	Y	$\delta^{31}\text{P}$ MP2 [b]	$\delta^{31}\text{P}$ DFT [c]	$\delta_{\text{exp}}^{31}\text{P}$ [e-m]
PH_2^-	H	H	-358	-350	-283 [e]
PH-Me^-	CH_3	H	-157	-128	—
PMe_2^-	CH_3	CH_3	17	53	—
PH-SiH_3^-	SiH_3	H	-361	-338	-335.4 [f]
$\text{P(SiH}_3)_2^-$	SiH_3	SiH_3	-399	-380	-300 ± 5 [g]
PH-PH_2^-	PH_2	H	-168	-151	17.4 [h]
$\text{P(PH}_2)(\text{SiH}_3)^-$	PH_2	SiH_3	-319	-288	-176.8 [i]
$\text{P(PH}_2)_2^-$	PH_2	PH_2	-209	-177	—
P(PH)_2^-	PH	PH	501	685	732.5 [j]
cyclo- P(PH)_2^-	PHR [d]	PHR [d]	-285	-236	— [j]
2 <i>exo</i> bicyclo- HP_4^-	PRR' [d]	PRR' [d]	-48	-17	—
2 <i>endo</i> bicyclo- HP_4^-	PRR' [d]	PRR' [d]	166	200	—
1 cyclo- HP_4^-	PR [d]	PR [d]	426	668	—
4 cyclo- $\text{P}_3(\text{CH}_2)^-$	PR [d]	PR [d]	516	729	— [k]
5 bicyclo- $\text{P}_3(\text{CH}_2)^-$	PR [d]	PR [d]	-10	37	— [k]
cyclo- P_5^-	PR [d]	PR [d]	-[b]	495	467.2 [l]
cyclo- $\text{P}(\text{CH})_4^-$	CH_2R [d]	CH_2R [d]	51	54	77.2 [m]
cyclo- $\text{P}_3(\text{CH}_2)^-$	PR [d]	PR [d]	237	330	272.0 [k]

[a] Based on RMP2(fc)/6-31+G(d) optimized geometries

[b] GIAO/MP2/6-31+G(d) calculated magnetic shieldings transformed to $\delta^{31}\text{P}$ with the theoretical reference $\sigma^{31}\text{P}(\text{PH}_3)$ in MP2/6-31G(d,p) geometry = 648.4 ppm. The P_5^- could not be calculated due to computational limitations

[c] GIAO/B3LYP/6-31+G(d) calculated magnetic shieldings transformed to $\delta^{31}\text{P}$ with the theoretical reference $\sigma^{31}\text{P}(\text{PH}_3)$ in MP2/6-31G(d,p) geometry = 589.0 ppm

[d] Substituent R, R' are endocyclic σ^2 or σ^3 phosphorus

[e] Value for NaPH_2^* monoglym [16]

[f] Values for $^t\text{Bu}_3\text{Si-PH}$ anion with Li^+ as counterion in THF solution (2 THF directly coordinate to the cation); for the corresponding sodium solution $\delta^{31}\text{P} = -327.7$ [17]

[g] Values for $(\text{Me}^3\text{Si})_2\text{P}$ with Li^+ as counterion and various solvents [18]

[h] In the terminal groups of $[\text{n}-(\text{PPh})_3]^{2-} (\text{K}^+)_2$ [19]

[i] Value for $^t\text{Bu}_3\text{Si-P}-(\text{P}_3\text{R}_2)$ with Na^+ as counterion [17]

[j] Value for $(^t\text{Bu}_3\text{Si-P})_2\text{P}^-$ with Na^+ as counterion (4 THF directly coordinate to Na^+) [17]

[k] Value for cyclo- $(\text{P})_3(\text{CH}_2)^-$. The early assignment to CH_2P_3^- was refuted [14]

[l] Value for $\text{P}_5(\text{Na}, [18]\text{crown-6, THF})$ solution and 470.2 ppm for the reaction solution [20]

[m] Value for $\text{C}_4\text{H}_4\text{P}^-$ with Li^+ as counterion in THF solution [6]

While in the following the substituent effects in R_2P^- anions is discussed together with the $(\text{P}_3)(\text{H})\text{P}^-$ structures, **3***endo* and **3***exo*, the sodium cation effect in $[\text{P}_4\text{H}^*\text{Na}]$ complexes are considered in the last section.

The $\delta^{31}\text{P}$ of the anionic phosphorus, P_A^- , in a comprehensive set of model molecules (Table 2) reveals some special features of the saturated phosphorus substituents (CH_3 , SiH_3 , and PH_2): while the effect of methyl groups is roughly additive for CH_3 ($\Delta\delta$, the difference with respect to the $\delta^{31}\text{P}$ value in PH_2^- , is about 201 for the first and 174 ppm for the second alkyl group) and small for both SiH_3 , the effect of the first PH_2 (+190) is opposite to that of the second phosphino group (-42 ppm). This upfield effect on $\delta^{31}\text{P}$ of the second phosphane substituent is also known experimentally from the series PH_3 , P_2H_4 and $\text{n-P}_3\text{H}_5$. Furthermore, the substituent effect on $\delta^{31}\text{P}$ is not additive in $\text{SiH}_3\text{-P-PH}_2$ with 'mixed' substitution: the obtained $\Delta\delta$ is only +39 ppm instead of +187 ppm extrapolated from first substituent effects.

The deviation of $\delta^{31}\text{P}$ for R_2P^- is probably partially due to the Na^+ coordinating to the anion in solution. Since experimental values are all at lower field (+26 with $\text{R} = \text{H}$, $\text{R}' = \text{SiH}_3$; +75 with $\text{R} = \text{R}' = \text{H}$; +99 ppm with $\text{R} = \text{R}' = \text{SiH}_3$), the sodium effect can be expected to reduce the magnetic shielding of phosphorus. For all saturated substituents the GIAO/B3LYP chemical shifts of $\text{RR}'\text{P}^-$ are in reasonable agreement with the corresponding GIAO/MP2 values (B3LYP shifts deviate by +8 to +36 ppm from the MP2 results both obtained with the 6-31+G(d) basis set). In contrast, for the unsaturated substituents (cf. values in the lower part of Table 2) the GIAO/B3LYP chemical shifts show larger deviations from the GIAO/MP2 data. At both levels the reported $\delta^{31}\text{P}$ for the phospholide, cyclo- $(\text{CH})_4\text{P}$, is in reasonable agreement with $\delta_{\text{calc}}^{31}\text{P}$ (26 ppm deviation at GIAO/MP2 and 29 ppm at GIAO/B3LYP). Coincidentally, the $\delta^{31}\text{P}$ of $(\text{CH}_3)_2\text{P}^-$ and the phospholide are quite similar. In case of

Table 3 GIAO/MP2(fc)/6-31+G(d) //MP2(fc)/6-31+G(d) calculated [a] ^{31}P NMR chemical shifts and relative energies [b] (in kJ mol^{-1}) of HP_4^- anions and HP_4Na complexes [c]

Structure [b]	E_{rel} [b]	P_A [c]	P_B [c]	P_C [c]
HP_4^- , 1	0.0	426	350	15
HP_4^- , 2endo	24.7	166	-318	303
HP_4^- , 2exo	23.3	-48	-350	-130
HP_4^- , 3endo	41.1	319	-288	-263
HP_4^- , 3exo	30.8	-98	-259	-280
6 , C_s	16.7	407	397	17
7 , C_s	12.9	320	350	2
8 , C_s	30.2	89	-333	330
9 , C_s [d]	46.5	128	-308	319
10 , C_s	117.1	241	-286	172
11 , C_s	0.0	-120	-364	-141
12 , C_s	26.2	-91	-367	-63
13 , C_s	89.2	438	-204	-324
14 , C_s	72.1	-20	-189	-317
15 , C_I	65.9	157	- [e]	-252
16 , C_s	15.4	-35	-257	-311
exp. [f], C_s	—	71	-355	-330

[a] Chemical shifts calculated using PH_3 in MP2/6-31G(d,p) geometry as theoretical reference with $\delta^{31}\text{P} = -240$ and $\sigma^{31}\text{P} = 648.4$ ppm

[b] Point groups of the geometry obtained without symmetry constraint. The total energy of **1** is -1363.92945 Hartree. The total energy of **11** is -1525.78079 Hartree

[c] P_A is the anionic phosphorus (occurs once); P_B occurs

twice and is attached to P_A ; P_C is tricoordinate and attached to hydrogen.

[d] In the shallow potential area the C_s structure has one imaginary vibration mode with only $i15$ cm^{-1} .

[e] For the P_B attached to Na^+ $\delta^{31}\text{P}$ is -4 and for the other P_B $\delta^{31}\text{P}$ is -42 ppm

[f] Double intensity reported for P_B . [5]

the monocyclic $(\text{P})_3(\text{CH}_2)^-$ isomers **4** and **5** the predicted $\delta^{31}\text{P}$ should not be compared with values from an early investigation, [15] because refined measurements showed that the investigated compound is actually the five-membered $(\text{P})_3(\text{CH}_2)^-$ ring. [14] The $\delta^{31}\text{P}(P_A)$ calculated for the $(\text{P})_3(\text{CH}_2)^-$ ring at GIAO/MP2 is in better agreement (-35 ppm deviation) than the GIAO/B3LYP value (+58 ppm, cf. Table 2). The $\delta_{\text{calc}}^{31}\text{P}$ in the lower part of Table 1 show that computations would have excluded the initially assumed $\text{P}_3(\text{CH}_2)^-$ structure immediately. Nevertheless, if $\text{P}_3(\text{CH}_2)^-$ had really been detected, its chemical shift (+611 ppm for P_A) would have set a landmark for many years. The small deviation between $\delta_{\text{exp}}^{31}\text{P}$ and $\delta_{\text{calc}}^{31}\text{P}$ for $\text{P}_3(\text{CH}_2)^-$ (less than 5 ppm) does not justify the conclusion that the observed anion is 'free', because the appropriate 6-311+G(d) basis set could not be applied for this 'large' molecule. GIAO/B3LYP NMR calculations indicate that the sodium changes both $\delta_{\text{calc}}^{31}\text{P}$ towards lower field by about 40 ppm). The good agreement with the measurement confirms that the relatively high field $\delta^{31}\text{P}(P_A)$ belongs to a triphosphaallyl anion moiety as in **1** and **4**.

If P_A is the central atom of an allyl conjugate moiety, its chemical shifts (about 250 to 700 ppm) are distinctly different than for the P_A in the R_2P^- anions with $\text{R} = \text{H}, \text{CH}_3$, or SiH_3 (-400 to -200 ppm). While this is obviously due to the different valence ($\sigma^2, \lambda^3\text{-P}$ vs $\sigma^2, \lambda^2\text{-P}$), the unusual chemical

shift calculated for the $\sigma^2\text{-P}$ in the phosphirene ring of **3endo** and **3exo** are related to a much more complex molecular orbital, MO, structure. Since simplified depictions of the valence MOs of phosphorus with 2p type AOs instead of 3p AOs (e.g. Figure 1 in an article [8] about the P_4H_2 MOs) give correct symmetries but may present a misleading overlap, the MOs in Figure 3 are presented as 3D objects in the supplementary material. The MOs of the bicyclic structure as well as the phosphirene derivative can be constructed based on the $\text{P}_B\text{-P}_B$ fragment with two orthogonal π bond group orbitals (relative orientations of the π bonds specified in Figure 3; $P_A\text{-P}_C$ parallel X axis, $\text{P}_B\text{-P}_B$ parallel Y axis). As in the previous P_4H_2 study [8] the group orbitals of PH and P^- can be added to this group to form the bicyclic structures P_4H_2 , **2endo** and **2exo**. The phosphinophosphirane **3** is obtained by adding the bare end of the anionic P-PH^- fragment to P_BP_B . The HOMO of P_4H_2 (*exo,exo*; a_1 in C_{2v}) as well as the 29th MOs (HOMO-3) of the P_4H^- isomers **2endo** and **2exo** are not only characterized by the π bonding $3p_z$ AOs at P_B and P_B , but also comprise $3p_z$ AOs at P_A and P_C (P_A , respectively). At the MP2 level the MNDO order [8] of symmetry orbitals in tetraphospha-bicyclo[1.1.0]butane is only confirmed for the HOMO and HOMO-1 (Figure 3). The $4a_1$ MO [8] with $\sigma(\text{P}_B\text{P}_B)$ character is not HOMO-2 but HOMO-4 with a b_2 (L_{p_z} at PH groups, antibonding) and a MO with a_2 symmetry

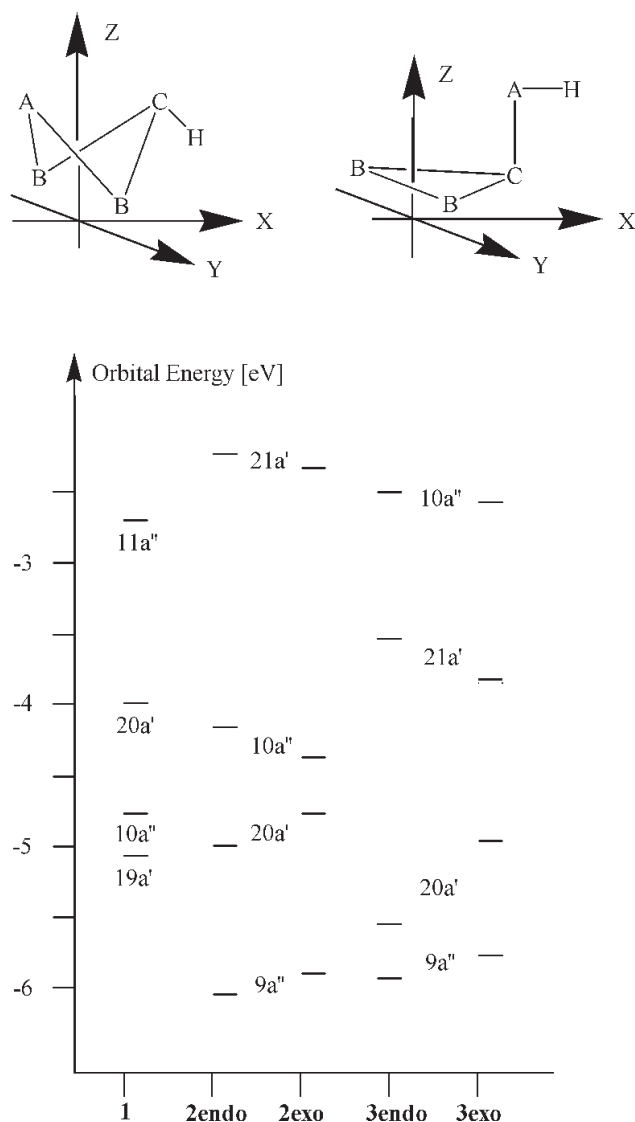


Figure 3 MO energies in eV at MP2(fc)/6-31+G(d) // MP2(fc)/6-31+G(d) of the HP_4^- anions **1-3**

($\pi^*(P_B P_{B'})$ combined bonding with $3p_y$ AOs at the PH groups) forming HOMO-3 and HOMO-2.

In contrast to bicyclic P_4H_2 , the bicyclic P_4H^- isomers **2endo** and **2exo** have no $\pi(P_B P_{B'})$ character of their HOMOs but are primarily a $3p$ AO at P_A . Despite the negative charge of **2** and different MOs, the chemical shifts of P_B are predicted to be quite similar to those of the bridgehead phosphorus in *exo,exo* P_4H_2 ($\delta_{\text{calc}}^{31P} = -378$ ppm at GIAO/MP2/6-311+G(d) level). As the folding angle of the triangles of the bicycle increases from 103.6° to 113.5° (*endo,exo* to *endo,endo* P_4H_2) and from 103.3° to 111.9° (**2exo** to **3endo**) the $\delta^{31P}_{\text{bridgehead}}$ changes by about 45 ppm downfield in both structures. In bicyclo P_4H_2 as well as in **2** the $\delta_{\text{calc}}^{31P}$ of the PH groups are more sensitive to the *endo* or *exo* orientation of the PH bond than the bridgehead phosphorus. Remarkably, the *endo/exo* effect is larger in **2** ($\delta^{31P}(P_C, \mathbf{2endo})$ is

470 ppm downfield relative to $\delta^{31P}(P_C, \mathbf{2exo}$, 440 ppm at the GIAO/MP2/6-31+G(d) level) where only one P-H bond changes the orientation, than between the *exo,exo* and the *endo,endo* conformer of bicyclo P_4H_2 ($\delta^{31P}(\text{PH}; \text{exo,exo}) = -227$, $\delta^{31P}(\text{PH}; \text{endo,endo}) = 22$, at the GIAO/MP2/6-31+G(d) level). An indicator for the difference between these otherwise quite similar structures is the Wiberg Bond index, WBI, of the P-P bond of tetrahedral P_4 , which is opened in **2**; the $\text{WBI}(P_A-P_C, \mathbf{2})$ is 0.18, while it is only 0.03 for P_C-P_C in *exo,exo* P_4H_2 . Which MOs reflect this rudimental bond of tetrahedral P_4 in the different isomers, *endo* and *exo*? Since the P-H bond, which changes its orientation, lies in the mirror plane of the C_s symmetric molecules **2**, these MOs with a'' character should show less differences between *endo* and *exo* than those of a' symmetry character (Figure 3) with electron density in the plane comprising P_A, P_C and H. While the order of the symmetry MOs are the same for **2endo** and for **2exo**, the MO energies differ: ($\epsilon(\mathbf{2exo}) - \epsilon(\mathbf{2endo})$ in eV: -0.09 for $21a'$, -0.22 for $10a''$, 0.22 for $20a'$, and 0.16 for $9a''$). In MO $10a'$ the *endo/exo* difference is most pronounced: at the $P_A P_B P_{B'}$ moiety is a combination of π bonding $3p_z(P_B)$, $3p_z(P_{B'})$ with a $3p_x$ AO at P_A ; at the PH group is a $3p$ AO of P_C in the direction of the threefold axis of the trigonal pyramidal bonded phosphorus. While the Lp contribution at P_C has a $3p_z$ AO character in **3exo** and combines bonding with the $\pi(P_B, P_{B'})$ group orbital, it is of $3p_x$ type in **3endo** and is antibonding with respect to $\pi(P_B, P_{B'})$. In MO $20a'$ of **2endo** the coefficients of the magnetically shielding Lp at P_C is smaller than that in **2exo**. This partially rationalizes that P_C is so much less shielded (downfield) in **2endo** than in **2exo**. A simple explanation of this remarkable effect by a charge-shift relation is obviously wrong for **2** (Mulliken charges, δ^{31P} pairs: +0.05/-120 for P_C, exo ; -0.60/-16 for P_A, exo ; -0.63/221 for P_A, endo ; -0.08/350 for P_C, endo) as well as for **3** (-0.40/-78 for P_A, exo ; -0.48/377 for P_A, endo).

The *endo/exo* orientation of the exocyclic PH group in **3** effects only P_A considerably. Does this mean that the phosphirene moiety is not involved? Again, the WBI are considered to get hints: $\text{WBI}(P_A P_C) = 0.98$ and 0.90 for $P_B P_C$ are in agreement with single bonds; remarkably, $\text{WBI}(P_B P_{B'})$ is much closer to 1 than to 2 (1.33 **3endo**, 1.32 **3exo**); strikingly, there are one third bonds between P_A and $P_B, P_{B'}$ respectively ($\text{WBI} = 0.38$ in **3endo**, 0.37 in **3exo**). These bonds towards the $P_B P_{B'}$ fragment rationalize the $\delta^{31P}(P_B)$ at -268 (**3endo**) and -247 (**3exo**), which are distinctly different from those of molecules with an unperturbed π_{pp} bond (*trans*-H-P=P-H with $\delta^{31P} = 407$, δ^{31P} of σ^2 -P in 1-X-phosphirenes with X = H: 276 X = PH_2 : 300, and X = SiH_3 : 287 calculated at GIAO/MP2/6-311G(d) on MP2/6-31G(d) geometries). The MOs $21a'$, $20a'$, and $19a'$ of the C_s symmetric geometries contribute to this conjugation of $P_B P_{B'}$ with the exocyclic PH group in both isomers, **3endo** and **3exo**. Since the order and shape of the symmetry orbitals in **3endo** and **3exo** appear to be the same, the large *endo/exo* effect in $\delta^{31P}(P_A)$ seems puzzling. The *endo/exo* effect occurs also in the isovalent 1-thio-phosphirene, but $P_B P_{B'}$ is less pronounced (the sulfur in the *endo* isomer is 148 ppm less shielded than in the *exo* form). Since the set of MOs for P_3 -SH only differ in their AO coef-

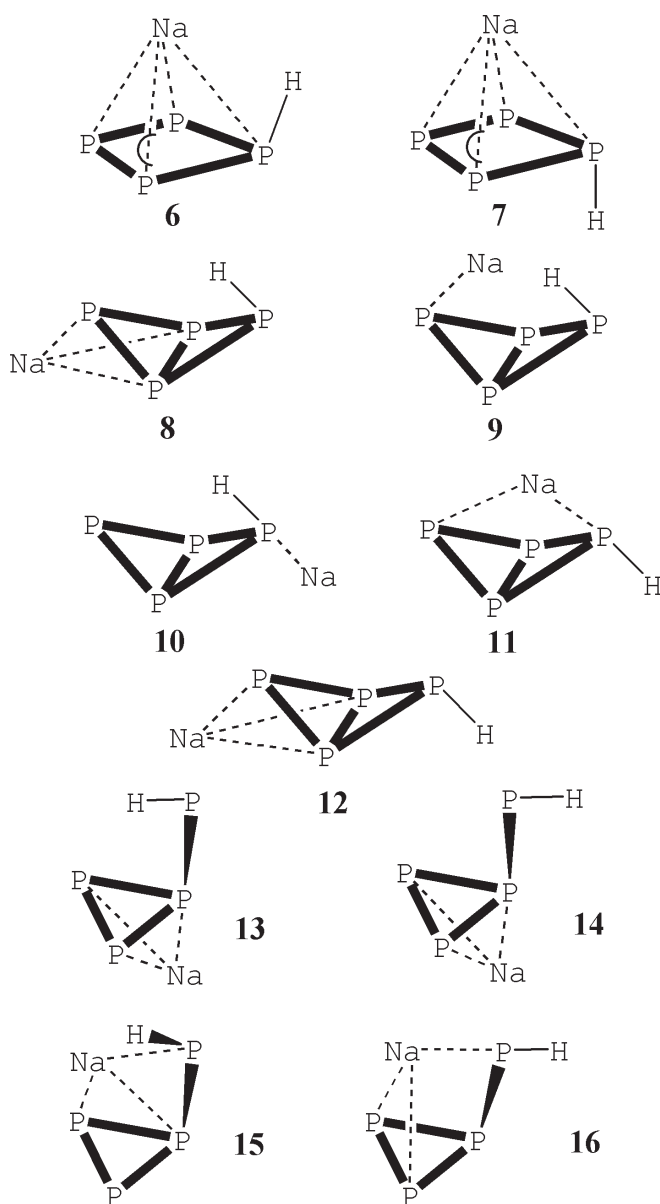


Figure 4 Structures of HP_4Na

ficients but not in their character from those in the P_3 -PH isomers, **3**, it is reasonable that both molecules show the outstanding *endo/exo* effect in the chemical shift of the exocyclic group. Since the a'' symmetric MOs are not likely to change much from *endo* to *exo*, the following consideration focuses on the a' MOs, MO 20a' and MO 21a' especially.

The HOMO-2, 20a', and HOMO-1, 21a', can be constructed from a $\pi(P_B P_B)$ and a fragment orbital of the $P_C P_A H$ part. While for both isomers of **3** in MO 21a' the $\pi(P_B P_B)$ is in z direction (with the $P_B P_B P_C$ plane as nodal plane) the $\pi(P_B P_B)$ in MO 20a' is basically oriented in x direction (nodal plane perpendicular to the line from P_C to the middle of P_B and P_B). The $P_C P_A H$ fragment in 20a' mainly contributes a p_x AO at P_C to the MO, so that P_A , for which the *endo/exo* effect

is obtained, is only slightly involved. In contrast, MO 21a' shows a principally different electronic structure at P_A in the *endo* than in the *exo* isomer. The 'normal' fragment orbital of $P_C P_A H$ appears in the *exo* isomer: a $\sigma(P_C P_A)$ mixing with the $s(H)$ AO so that the outer lobe at P_A mixes bonding with $s(H)$. Like in a hydrogen bridged structure, the $P_C P_A H$ fragment orbital in **3endo** is composed of a $\sigma(P_C P_A)$ with the $s(H)$ conjugate to the central lobe of the P-P σ bond orbital. The combination of the $P_B P_B$ and the $P_C P_A H$ group orbitals has antibonding character in MO 21a' (shortening the $P_B P_B$ but widening $P_B P_C$) in the *endo* as well as the *exo* isomer of **3**. Nevertheless, the hydrogens P_A - P_C bridging valence in the *endo* isomer in contrast to having P-H bond character is probably the main reason for the remarkably different magnetic properties of P_A in **3endo** compared to **3exo**. As mentioned above, only the calculated shifts of P_B and P_C of **3endo** and **3exo** are in reasonable agreement with the measured values, while both $\delta^{31}P(P_A)$ deviate distinctly: one too high, the other too low. Since the exocyclic group of **3** is able to rotate, an average $\delta^{31}P(P_A)$ value should be considered, which comes close to the experimental chemical shift.

The predicted set of $\delta^{31}P$ values for the lowest energy HP_4^- isomer, **1**, is similar to those for the experimentally known compounds with the triphosphaallyl moiety (Table 1), but they do not match the experimental data for $HP_4(Na/K)$ solution. In disfavor of the bicyclic structure, the $\delta_{calc}^{31}P$ of **2exo** also shows distinct deviations ($\Delta\delta^{31}P = -119$ to $+200$ ppm) from the experimental value. Remarkably, $\delta_{calc}^{31}P$ of the until now ignored structure **3** resembles the experimental results if rotational averaging is considered. Nevertheless, a question of interest is whether the remaining deviations, are due to coordination of a cation to the anionic phosphorus?

Counterion effect

Since in the experimental work the HP_4^- anions were generated in Na^+ -containing solution and HP_4Na^+ was detected in the mass spectrometer, the counterion effect of one sodium was studied (structures **6** to **16**, Figure 4). Coordinating Na^+ to the lone pair of the anionic phosphorus, $Lp(P_A)$, and additionally to the tricoordinate P_C of **2exo** has the most stabilizing effect. The amount of stabilization can be estimated to be 35 kJ mol^{-1} from comparing the relative energies of **1** with **2exo** ($E_{rel} = 23$) and **6** or **7** ($E_{rel} = 12.9 \text{ kJ mol}^{-1}$) with **11**. Coordination of sodium to one $Lp(P_A)$ and the P_B - P_B π bond is less effective but provides the minimum **11**, which is about as stable as **6** or **7**, the π complexes of **1** with Na^+ . Within the set of HP_4Na with the bicyclo P_4 framework structure **11** is followed by **12** and **8** on the energy scale. In **8** and **12**, Na^+ is attached to P_A in an *exo* position and the *exo* preference of the P-H bond is slightly larger (4.0 kJ mol^{-1}) than in **2** (1.4 kJ mol^{-1}). The higher relative energy of **9** can be rationalized by steric hindrance of hydrogen and sodium being both in *endo* conformations. Isomer **10** has no P_A -Na contact but only coordination of Na^+ to a neutral tricoordinate phosphorus and is therefore relative high in energy ($117.1 \text{ kJ mol}^{-1}$). The energetic ordering of the sodium complexes is found as fol-

lows: $11 < 12 < 8 < 9 \ll 10$. In contrast to the HP_4Li study [4] based on RHF/DZP optimizations, the ‘endo + Na^+ ’ has only one valence isomer, **8**. Nevertheless, the relative energies ($0.0 < 43.9 < 48.9 < 49.8 \ll 154.8$ kJ mol $^{-1}$) of the corresponding HP_4Li structures [4] reflect similar stabilization effects as in the HP_4Na isomers **8–12** (Table 3). With the exception of **16**, the HP_4Na structures based on the HP_4^- framework of **3** have relatively high energies (65.9 for **15** to 89.2 kJ mol $^{-1}$ for **13**). This indicates that Na^+ coordination to the triphosphirene ring is not very efficient, although it has a π bond group orbital.

The $\delta^{31}\text{P}$ data for the HP_4Na structures listed in Table 3 confirm that the isomer with the triphosphaallyl moiety was not observed [5] in the experiment. The changes of $\delta^{31}\text{P}$ from **1** to **6** or **7** are astonishingly small: for P_A -19 and -106 ppm, for P_C +2 and -13, and for P_B +47 (**1** to **6**) and no change from **1** to **7**. In contrast, the allylic P_A - P_B bond length is more sensitive to the counterion than to the link group X in cyclo-1,2,3-(P) $_3\text{X}$ (with X = PH, CH_2 , as compared to the acyclic R-PPP-R [7] anion). Therefore, compensation of effects is likely to be responsible for the moderate changes of $\delta^{31}\text{P}$ for **1**, **6**, and **7**. The effect of π -coordination of Na^+ on $\delta^{31}\text{P}$ is larger for **3** (e.g. $\delta^{31}\text{P}(\text{P}_B)$ changes from -288 (**3endo**) to -204 ppm in **13**). Noteworthy, coordination of Na^+ to the π bond at the anti position to the phosphido group has quite a large effect on $\delta^{31}\text{P}$ of the remote phosphorus ($\delta^{31}\text{P}(\text{P}_A)$: 319 in **3endo** and 438 in **13**). On the other hand, coordination of Na^+ to either side of the π bond of **3exo** gives rise to small down field changes ($\delta^{31}\text{P}(\text{P}_A)$: -98 (**3exo**) to -20 (**14**) and -35 for **16**). Is the effect of the Na^+ additive? In GIAO/MP2 calculations with the 6-31G(d), which is a smaller basis set than used throughout this study, the $\delta^{31}\text{P}(\text{P}_A)$ is 50 for a HP_4Na_2^+ structure in which the sodiums are placed as in **14** and **16**. Therefore, further research for **3** might focus on $[\text{HP}_4^- \cdot \text{Na}^+]_\infty$ chains with this building block.

The bicyclo- P_4 based HP_4Na structures have a $\delta^{31}\text{P}(\text{P}_B)$ in the small range of -367 to -285 ppm. This means that the counterion effect on the central P_B is quite small. Even in **8** and **12**, where Na^+ is close to P_B ($\text{Na}-\text{P}_B = 2.922$ Å in **8** and 2.918 in **12**), $\delta^{31}\text{P}(\text{P}_B)$ is about the same as in the parents **3endo** and **3exo**. In all HP_4Na with bicyclo- P_4 backbone $\delta^{31}\text{P}$ of the anionic phosphorus, P_A , changes to higher field when Na^+ is coordinated to it. This effect ranges from $\Delta\delta^{31}\text{P}(\text{2endo to 9}) = -38$ to $\Delta\delta^{31}\text{P}(\text{2exo to 8}) = -77$ ppm. With the exception of **10**, Na^+ is never coordinated to P_C , in the [**2** *Na] complexes] Consequently, $\delta^{31}\text{P}(\text{P}_C)$ is only slightly affected by the counterion] Since Na^+ interacts only in **11** with the $\text{Lp}(\text{P}_A)$ the counterion effect on $\delta^{31}\text{P}(\text{P}_A)$ is larger in **11** than in **8–10** and **12** (Tables 1 and 3). In general, the Na^+ has a small effect on the NMR chemical shifts of P_A and P_C in the conjugate system and systematically changes $\delta^{31}\text{P}$ to lower field in the phosphanidophosphirene, so that the *endo/exo* difference remains. Nevertheless, the computed effects of Na^+ on $\delta^{31}\text{P}$ in HP_4^- ions are in agreement with the re-assignment of the experimental values to the phosphirenylphosphide structure, **3**.

Summary

The energy difference between the bi- and monocyclic (P) $_3\text{X}$ anions with X = PH, or CH_2 are in agreement with the ‘allyl preference’, which was recently reported for the acyclic triphosphide, R-PPP-R.] The $\delta^{31}\text{P}$ values predicted for the preferred structure of the HP_4^- anion does not agree with the reported NMR chemical shifts for $\text{HP}_4(\text{Na/K})$. Even when considering the counterion effect, the computed $\delta^{31}\text{P}$ values disagree with an assignment to **1** to a four-membered ring structure. Out of a variety of HP_4Na structures, which comprise a bicyclo[1.1.0] P_4H , **2**, or a P_3 -PH, **3**, structure, the latter provides better agreement with the $\delta_{\text{exp}}^{31}\text{P}$ values. The $\delta_{\text{calc}}^{31}\text{P}$ of the exocyclic PH group in **3** shows distinct deviations (306 in **3endo**, -149 ppm in **3exo**) from the probably related experimental chemical shift, $\delta_{\text{calc}}^{31}\text{P}(\text{P}_A)$. Nevertheless, due to a low rotation barrier between **3endo**, and **3exo**) an average $\delta^{31}\text{P}(\text{P}_A)$ has to be considered in favor of structure **3**.

From the $\delta_{\text{calc}}^{31}\text{P}$ values for a comprehensive set of phosphanide molecules at the MP2 and the DFT levels and the HP_4Na calculations conclusions can be drawn on the performance of the NMR methods and the counterion effect: a) *Ab initio* NMR method: for localized structures, the DFT-derived $\delta^{31}\text{P}$ differ by only +8 to +36 ppm from the MP2 values. However, deviations of up to 242 ppm occur for structures with π_{pp} bonds. b) Counterion effect: probably due to the neglect of counterion effects, most $\delta_{\text{calc,MP2}}^{31}\text{P}$ values are at higher field than $\delta_{\text{exp}}^{31}\text{P}$ of related compounds. This is confirmed as a trend by the $\delta_{\text{calc}}^{31}\text{P}$ of HP_4Na structures. We are aware of the difficulties related to the synthesis of phosphanide compounds but hope that the presented chemical shifts can be of help in identifying the fascinating triphosphaallyl moiety (e.g. in cyclo- $\text{P}_3(\text{CH})_2^-$) if they appear *intermediately* in the experiment.

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Supplementary material available 3D coordinates of the molecules from Table 1 - 3 in XYZ format with the calculated isotropic magnetic shielding as fourth coordinate; 3D representation of the MOs with 20a' and 21a' symmetry of **3endo** and **3exo** in VRML format; Gaussian output of **1**, **2endo**, **2exo**, **3endo** and **3exo**.

The SHARC files, containing computed magnetic shielding tensors, are available from the author upon request (please contact Alk Dransfeld:

dransfld@ccc.uni-erlangen.de).

For more information on NMR-SHARC see

<http://www.ccc.uni-erlangen.de/sharc/>

or <http://www.quantchem.kuleuven.ac.be/sharc/>

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