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# Theoretical Study of the Structure and Bonding in Bridgehead Diphosphines

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The molecular structures of a representative selection of medium-sized bicyclic diphosphines (i.e., diphosphanes) were studied by means of the ab initio second-order Møller−Plesset (MP2) method. The calculated results matched the available X-ray crystallographic data reasonably. A distinctive structural aspect is that all the 1,5-diphosphabicyclo[3.3.3]undecane systems, the 1,6-diphosphabicyclo[4.4.4]tetradecane free base, and its axially disubstituted derivatives adopt the *out,out*-conformation, whereas the monosubstituted [4.4.4] species prefer the *out,in*-arrangement. The intrabridgehead interaction was described in terms of polarity, bond order index, force constant, vibrational frequency, and nature of the critical point of the total electron density. The electronic structures of the [3.3.3] and [4.4.4] diphosphanes were theoretically investigated by means of their NMR spectroscopic properties. The chemical shifts and indirect nuclear spin−spin coupling constants, computed by density functional theory (DFT)-based methods, were in satisfactory agreement with the experimental values. In particular, the theoretical results yielded a consistent account of the strong orientational effects of the phosphorus lone pair and coordination on $\delta(^{31}P)$, $J(^{31}P-^{31}P)$, and $J(^{31}P-C)$ that show remarkable changes of sign and magnitude within this class of compounds.

## Introduction

There is considerable interest in the interaction between bridgehead atoms in medium-sized polycyclic compounds, because it has provided a variety of stable compounds that display unusual structures, spectroscopic properties, and reactivities. From a qualitative standpoint, these features can be attributed to the partial bonding between the bridgehead atoms inside the caged structure. During the past two decades, a number of medium-ring bicyclic $\mu$-hydrido-bridged carbocations,[1,2] diamines,[3,4] phosphatranes,[5] and diphosphanes[6−12] have been prepared and characterized.

In our previous papers, theoretical investigations of the molecular structure and spectroscopic properties of representative samples of bicycloalkyl carbocations ($C^{+}-H_{\mu}\cdots C$ interaction),[13] caged diamines (N···N axial interaction),[14] and phosphatranes (P···N axial interaction)[15] have been reported. Here, the theoretical analysis is addressed to diphosphanes (P···P axial interaction) of the bicyclo[3.3.3]undecane (**1**) and bicyclo[4.4.4]tetradecane series (**2**). The most noteworthy structural aspect of these molecules is the strong dependence of the intrabridgehead $P_1$- -$P_2$ distance on the length of the alkanic $[CH_2]_x$ bridges and the nature of the apical (Z) groups bound to phosphorus.

Given the variety of steric arrangements, a theoretical investigation into the molecular and electronic structures of the [3.3.3] and [4.4.4] diphosphanes therefore seemed useful. Here, we report calculations of the preferred conformations using the ab initio MP2 method. Because the NMR observables are very efficient monitors of the complex interplay of structural and electronic effects operating in these molecules, their $^{31}P$ chemical shifts and spin−spin indirect coupling constants $J(^{31}P-^{31}P)$ and $J(^{31}P-^{13}C)$ were studied by calculations at the density functional theory (DFT) level.

## Computational Details

Second-order Møller−Plesset (MP2) full geometry optimizations employed the 6-31G(d) basis set with the *Gaussian 98* suite of programs.[16] Harmonic frequency calculations were performed for all of the optimized structures to establish that the stationary points are minima. The force constant extraction and normal-mode analysis were then obtained according to the Wilson FG matrix method[17] using standard internal coordinates and including the intrabridgehead interaction as an individual stretching coordinate. Localization of the molecular orbitals was performed by means of the Pipek−Mezey procedure,[18] and bond order indices were calculated from the definition of Sannigrahi and Kar.[19] The critical-point (CP) analyses of the scalar fields $\rho$ and $\nabla^2\rho$ were carried out according to Bader's atom-in-molecules (AIM) theory.[20]

The NMR absolute shielding constants ($\sigma$ values) were calculated at the three-parameter Lee−Yang−Parr (B3LYP)/DFT level with the continuous set of gauge transformations (CSGT) method[21] using the basis sets of Schäfer et al.,[22] TZP for H and TZ2P for the heavy atoms. The calculated magnetic shieldings were converted into the $\delta$ chemical shifts by noting that at the same level of theory the $^{1}H$ and $^{13}C$ absolute shieldings in tetramethylsilane (TMS) are 30.95 and 181.38, respectively, and the $^{31}P$ absolute shielding in $PH_3$ is 586.52.

The indirect nuclear spin−spin coupling constants were obtained by means of standard response-theory methods at the B3LYP/DFT level using the Dalton software[23] and the cc-pVDZ basis set.[24] The calculation of the *J* tensor took into account all four contributions of the nonrelativistic Ramsey theory[25] (i.e., in addition to the Fermi contact term, the diamagnetic spin−orbit, paramagnetic spin−orbit, and spin−dipole terms).

## Results and Discussion

**Molecular Structures.** First, it must be mentioned that, depending on the orientation of the phosphorus bridgeheads into

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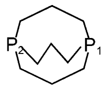
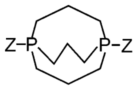
or out of the molecular cavity, there are three topological forms of bicyclic diphosphanes: the *out,out*-, *out,in*-, and *in,in*-isomers (*in* and *out* stand for inside- and outside-pyramidalized phosphorus, respectively). Whenever appropriate, all alternative structures for a given species were computed, but only the global minimum structure is presented in detail here.

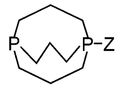
Recently, Alder et al.[11] have reported DFT/B3LYP calculations on the molecular structures of **1**, **1**(H)$^+$, **2**, and **2**(H)$^+$.



**1**



**1** (Z = H$^+$, Me$^+$,O)



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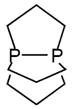
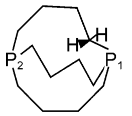
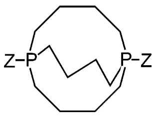


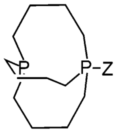
**1**$^{++}$



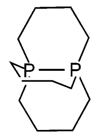
**2**



**2** (Z = H$^+$, Me$^+$,O)



**2** (Z = H$^+$, Me$^+$, F$^+$, O)



**2**$^{++}$

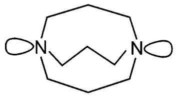
In this context, the peculiar importance of the electron correlation in the structures computed for diphosphanes must be stressed. Indeed, previous calculations[26,27] on the related phosphatranes ZP[E(CH$_2$)$_2$]$_3$N, with E = NR and O, have shown that both Hartree–Fock (HF) and DFT/B3LYP methods gave P- -N$_{ax}$ distances considerably longer than the X-ray values. A better agreement between theoretical and experimental values was obtained from MP2 computations.[15] Therefore, the ab initio MP2 procedure was adopted here for all diphosphanes **1**, (Z)P-[(CH$_2$)$_3$]$_3$P(Z), and **2**, (Z)P[(CH$_2$)$_4$]$_3$P(Z). X-ray structural determinations have been reported only for **1**,[9] **2**$^{2+}$,[6] and **2**(H)$^+$.[11] For these molecules, the theoretical results are in substantial agreement with the experimental values. In particular, the discrepancies between theoretical and experimental $r$(P- -P) are 0.03 (MP2) and 0.06 (DFT) Å for **1**, 0.09 (MP2) and 0.14 (DFT) Å for **2**(H)$^+$, 0.02 (MP2) Å for **2**$^{2+}$, and 0.02 (MP2) Å for **1**(Me)$_2^{2+}$ and **2**(Me)$^+$ (for the latter species, by reference with the X-ray parameters of **1**(CH$_2$Ph)$_2^{2+}$ and **2**(CH$_2$Ph)$^+$,[7,12] respectively). A noteworthy point is the observation of a significantly different intrabridgehead Si- -N$_{ax}$ distance for some structurally related molecules, namely silatranes, in the gas phase versus the crystalline state.[28–30] Thus, the crystal packing forces may also be responsible for some shortening of the P- -P distance in the solid state of diphosphanes of the [3.3.3] and [4.4.4] series; this is likely to be particularly important when the structure is polar (e.g., for mono-oxides, **2**(Z=O)$^+$). Of course, the MP2 theoretical results mimic the gas-phase environment, while the available experimental data refer to the solid state. By keeping these factors in mind, the MP2 molecular structures of all the compounds investigated should be reliable. A selection of relevant structural parameters (P$_1$- -P$_2$ distance, sum of the valence bond angles at P, bond order index, stretching force constant, vibrational frequency, and nature of the intrabridgehead CP) are listed in Table 1.

**TABLE 1: Theoretical Characteristics of the Interbridgehead Interaction[a]**

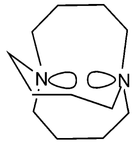
| | $r$(P$_1$P$_2$) | Σα(P$_1$) | Σα(P$_2$) | boi | $k$ | $\omega$ | PED[b] | CP |
|---|---|---|---|---|---|---|---|---|
| **1** | 4.096[c] | 316.6 | | 0.004 | 0.48 | 210 | 43 | (3, +3) |
| **1**$^{2+}$ | 2.159 | 356.4 | | 0.939 | 1.51 | 521 | 46 | (3, −1) |
| **1**(H)$^+$ | 3.786 | 341.5 | 319.1 | 0.023 | 0.47 | 194 | 42 | (3, +3) |
| **1**(H)$_2^{2+}$ | 3.629 | 338.6 | | 0.012 | 0.53 | 208 | 40 | (3, +3) |
| **1**(Me)$^+$ | 3.832 | 338.3 | 318.5 | 0.021 | 0.48 | 190 | 42 | (3, +3) |
| **1**(Me)$_2^{2+}$ | 3.705[d] | 335.2 | | 0.011 | 0.54 | 193 | 41 | (3, +3) |
| **1**(O)$_2$ | 3.917 | 324.5 | | 0.008 | 0.58 | 206 | 40 | (3, +3) |
| **2** | 4.934 | 301.1 | 319.2 | $0.000_1$ | 0.48 | 198 | 12 | (3, +3) |
| **2**$^{2+}$ | 2.181[e] | 339.8 | | 0.882 | 1.50 | 458 | 48 | (3, −1) |
| **2**(H)$^+$ | 2.670[f] | 355.8 | 320.6 | 0.378 | 0.52 | 206 | 38 | (3, −1) |
| **2**(H)$_2^{2+}$ | 4.706 | 345.2 | | $0.000_1$ | 0.53 | 179 | 45 | (3, +3) |
| **2**(Me)$^+$ | 2.787[g] | 351.4 | 319.7 | 0.347 | 0.50 | 197 | 42 | (3, −1) |
| **2**(Me)$_2^{2+}$ | 4.805 | 341.2 | | $0.000_1$ | 0.56 | 173 | 46 | (3, +3) |
| **2**(F)$^+$ | 2.426 | 359.3 | 323.3 | 0.598 | 0.72 | 227 | 32 | (3, −1) |
| **2**(O) | 3.081 | 333.4 | 316.5 | 0.086 | 0.50 | 209 | 44 | (3, −1) |
| **2**(O)$_2$ | 5.089 | 328.8 | | $0.000_1$ | 0.61 | 178 | 44 | (3, +3) |

[a] Distance in Å, sums of C–P–C bond angles in °, bond order index and stretching force constant in mdyn Å$^{-1}$, vibrational frequency in cm$^{-1}$, and critical point. [b] Potential energy distribution, % of the stretching coordinate in the vibrational mode. [c] Experimental value 4.07 Å, ref 9. [d] Experimental value 3.69 Å of **1**(CH$_2$Ph)$_2^{2+}$, ref 7. [e] Experimental value 2.17 Å, ref 6. [f] Experimental value 2.58 Å, ref 11. [g] Experimental value 2.81 Å of **2**(CH$_2$Ph)$^+$, ref 12.

Of the three possible isomers (*out,out*, *out,in*, and *in,in*), both free bases **1** and **2** strongly prefer the *out,out*-conformation. Thus, the lengthening of the three [CH$_2$]$_n$ bridges does not induce the inward inversion of the lone-pair orbitals, as occurs in the related [3.3.3] (**3**) and [4.4.4] (**4**) diamines.[4,14,31,32]



**3**



**4**

Furthermore, a notable difference is that the lowest-energy conformation of diphosphane **1** is symmetrical ($C_{3h}$), whereas the preferred conformation of the still-elusive diphosphane **2** is completely unsymmetrical with one α-C–H group tipped inside the cage. An unusual structural aspect of diphosphane **2** is that the endo-H atom is sterically compressed. Indeed, the relevant bond distances in this CH$_2$ group are predicted to be 1.082 Å for C–H (endo) and 1.095 Å for C–H (exo); this sizable difference should be reflected in the $^1$H NMR and IR spectra of diphosphane **2**. On the other hand, the full inward inversion of both P atoms is shown by the dicationic propellanes **1**$^{2+}$ and **2**$^{2+}$. In these systems, the P- -P distance is slightly shorter than in the related, neutral molecule 1,6-diphosphabicyclo[4.4.0]-decane, 2.19 Å,[33] despite the two adjacent formal positive charges. The electrostatic repulsion is therefore compensated by the greater s-character in the P–P bond orbitals: 28% in **1**$^{2+}$ and 33% in **2**$^{2+}$ versus 18% in the simple [4.4.0] diphosphine. As expected, a normal “bond” critical point, classified as CP(3, −1), is connected to the axial P–P bond. The related bond order index, 0.94 in **1**$^{2+}$ and 0.88 in **2**$^{2+}$, is also normal for a single bond. For comparison, it can be mentioned that the calculated bond order index is 0.93 in P$_2$H$_4$ and 1.94 in P$_2$H$_2$.

There are significant structural differences between the [3.3.3] and [4.4.4] diphosphine series, and a unique picture cannot be provided for the P$_1$- -P$_2$ interaction. In the [3.3.3] series, apart from dication **1**$^{2+}$, the P- -P distance ranges from 4.096 Å in **1** to 3.629 Å in **1**(H)$_2^{2+}$, with the average value being similar to twice the van der Waals radius of phosphorus (3.8 Å). No change of the geometry at the two (pyramidal) bridgehead atoms is undergone by base **1** upon coordination of a Z group at one apical position. Of course, the high strain energy in the *in,in*-conformation imposes the *out,out*-conformation in the axially disubstituted species $\mathbf{1}(Z)_2{}^{2+}$ also. A local depletion of charge along the $P_1$- -$P_2$ direction (i.e., a "cage" CP(3, +3)) occurs for all compounds **1**(Z), indicating that there is not an effective $P_1$- -$P_2$ bond in these molecules. The bond order index, less than 0.03, is diagnostic of a very weak through-space interaction between these two atoms.

In the [4.4.4] series, apart from dication $\mathbf{2}^{2+}$, *r*(P- -P) varies from 5.089 Å in **2**(O) to 2.426 Å in $\mathbf{2}(F)^+$ (i.e., much more than the variation observed along series **1**). The shorter distances are close to those of normal P−P single bonds (2.1−2.2 Å). The distinctive point is that the linkage of a Z group to one P atom is accompanied by the inward inversion of the nonquaternized P atom; hence, $P_1$ relaxes toward planarity (or trigonal bipyramidal geometry), and $P_2$ becomes inwardly pyramidalized. In particular, the flattening at $P_1$ follows the trend $\mathbf{2}(O) < \mathbf{2}(Me)^+ < \mathbf{2}(H)^+ < \mathbf{2}(F)^+$. Thus, the formal trigonal bipyramidal geometry is progressively adopted around the $P_1$ atom well-suited to form a coordinate bond with $P_2$. A "bond" CP(3, −1) is, indeed, found for $\mathbf{2}(H)^+$, $\mathbf{2}(Me)^+$, $\mathbf{2}(F)^+$, and **2**(O). The related bond order index, ranging from 0.09 in **2**(O) to 0.60 in $\mathbf{2}(F)^+$, parallels the variation of the P- -P distance. In turn, as for the [3.3.3] series, the stereochemistry of dications $\mathbf{2}(Z)_2{}^{2+}$ demands the *out,out*-conformation. In particular, the tetracoordinate P atoms show nearly ideal tetrahedral geometry in the dioxo adducts.

It is worth noting that, in agreement with the structural relationships reported for silatranes[34] and phosphatranes,[15] there is a strong correlation between the intrabridgehead $P_1$- -$P_2$ distance and the deviations $\Delta P$'s from coplanarity of the phosphorus atoms and their three equatorial carbons. ($\Delta P$ is assumed positive for outward pyramidalization and negative for inward pyramidalization.) Use of the appropriate MP2 data provides for the [3.3.3] series

$$r(P_1\text{- -}P_2) = 2.585 + 1.088\Delta P_1 + 0.978\Delta P_2$$
$$(r \text{ and } \Delta P \text{ in angstroms; 7 points; average deviation 0.007 Å})$$

and for the [4.4.4] series

$$r(P_1\text{- -}P_2) = 3.482 + 1.199\Delta P_1 + 1.573\Delta P_2$$
$$(r \text{ and } \Delta P \text{ in angstroms; 8 points; average deviation 0.054 Å})$$

Of course, the $P_1$−$P_2$ normal single bonds in the propellane dications show larger force constants, about 1.5 mdyn/Å, and stretching frequencies, 521 $cm^{-1}$ in $\mathbf{1}^{2+}$ and 458 $cm^{-1}$ in $\mathbf{2}^{2+}$. By comparison, the P−P stretching frequency of $P_2(Me)_4$ is 455 $cm^{-1}$ (trans conformer) or 429 $cm^{-1}$ (gauche conformer).[35] On the other hand, the higher $P_1$- -$P_2$ intrabridgehead stretching frequency is predicted at 227 $cm^{-1}$ for $\mathbf{2}(F)^+$, whereas the lower frequency, 173 $cm^{-1}$, is computed for $\mathbf{2}(Me)_2{}^{2+}$. The potential energy distribution shows that the contribution of the $P_1$- -$P_2$ stretching coordinate to the associated IR mode varies from 48% in $\mathbf{2}^{2+}$ to 12% in **2**. The "cage pulsation" normal modes calculated for $\mathbf{1}^{2+}$ and $\mathbf{2}(F)^+$ are depicted in Figure 1, where the displacements of the hydrogen atoms are omitted for clarity.

Another important point is the observation of a significantly different stability of the three oxidation states of diphosphines **1** and **2** compared to the related diamines **3** and **4**. Indeed, all three oxidation states of **3** and **4** are stable species.[36,37] In particular, those of **4** are isolable as stable solids that, according to X-ray diffraction studies, have a $D_3$ structure with inward pyramidalization at the bridgehead atoms and an N···N distance of 2.806 Å in **4**, 2.295 Å in $\mathbf{4}^{+\bullet}$, and 1.532 Å in $\mathbf{4}^{2+}$.[37] Interestingly, the three-electron(3e)/two-electron(2e) bond length ratio of $\mathbf{4}^{+\bullet}$ and $\mathbf{4}^{2+}$ is close to $^3/_2$. The situation is quite different for the related phosphorus systems, because only **1** and dication $\mathbf{2}^{2+}$ are stable species. The isolation of reactive dication $\mathbf{1}^{2+}$ is problematic, while radical cations $\mathbf{1}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$ are extremely short-lived.[9] The free diphosphine **2** has not yet been synthesized. The structural patterns predicted by our ab initio (U)-MP2 calculations are

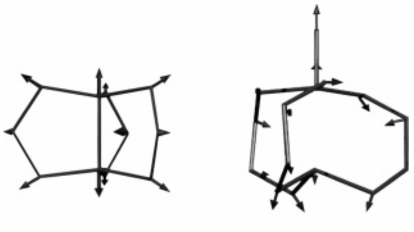


**Figure 1.** Relative atomic displacements computed for the "cage pulsation" normal mode of $\mathbf{1}^{2+}$ and $\mathbf{2}(F)^+$.

| **1** | $\mathbf{1}^{+\bullet}$ | $\mathbf{1}^{2+}$ | **2** | $\mathbf{2}^{+}$ | $\mathbf{2}^{2+}$ |
|---|---|---|---|---|---|
| $C_{3h}$ (*out,out*) | $C_3$ (*out,out*) | $C_{3h}$ (*in,in*) | $C_1$ (*out,out*) | $C_3$ (*in,out*) | $D_3$ (*in,in*) |
| P···P 4.096 | 3.669 | 2.159 | 4.934 | 2.576 | 2.181 Å |

| **3** | $\mathbf{3}^{+\bullet}$ | $\mathbf{3}^{2+}$ | **4** | $\mathbf{4}^{+\bullet}$ | $\mathbf{4}^{2+}$ |
|---|---|---|---|---|---|
| $C_{3h}$ (*out,out*) | $C_{3h}$(*in,in*) | $C_{3h}$(*in,in*) | $D_3$(*in,in*) | $D_3$(*in,in*) | $D_3$(*in,in*) |
| N···N 3.005 | 2.287 | 1.573 | 2.764 | 2.275 | 1.535 Å |

Thus, the theoretical 3e/2e bond length ratios are 1.70, 1.18, 1.45, and 1.48 for $\mathbf{1}^{+\bullet}/\mathbf{1}^{2+}$, $\mathbf{2}^{+\bullet}/\mathbf{2}^{2+}$, $\mathbf{3}^{+\bullet}/\mathbf{3}^{2+}$, and $\mathbf{4}^{+\bullet}/\mathbf{4}^{2+}$, respectively. Radical cation $\mathbf{1}^{+\bullet}$ adopts the *out,out*-conformation asymmetrically stretched along the $C_3$ axis, with atomic spin densities of 0.95 on the flattened ($\Sigma\alpha = 347.3°$) phosphorus and 0.01 on the pyramidalized ($\Sigma\alpha = 321.6°$) phosphorus. Radical cation $\mathbf{2}^{+\bullet}$ instead prefers the *in,out*-conformation, with atomic spin densities of 0.77 on P (*out*; near-planar, $\Sigma\alpha = 359.1°$) and 0.18 on P (*in*; tetrahedral, $\Sigma\alpha = 323.3°$). These geometries are a clear hint to the extreme reactivity of the radical cations $\mathbf{1}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$. On the other hand, the nearly planar nitrogens of $\mathbf{3}^{+\bullet}$ ($\Sigma\alpha = 358.4°$) and the tetrahedral nitrogens of $\mathbf{4}^{+\bullet}$ ($\Sigma\alpha = 338.5°$) are consistent with their hyperfine couplings of 14.7 and 34.4 G, respectively.[36,37]

Last, it is noteworthy that the present bonding analysis in diphosphanes is fully consistent with the thorough conclusions of Magnusson,[38] and Reed and von Ragué Schleyer.[39] The d functions of phosphorus play a polarizing and correlating role (mainly angular correlation) in the configuration interaction (CI) wave function. Thus, in the supposedly hypervalent species **2**(Z), the $P_1$- -$P_2$ intrabridgehead bonding is found to be strongly ionic. Indeed, the calculated electron density in this bonding is partitioned 11% on $P_1$ and 89% on $P_2$ in $\mathbf{2}(H)^+$, 10% on $P_1$ and 90% on $P_2$ in $\mathbf{2}(Me)^+$, and 19% on $P_1$ and 81% on $P_2$ in $\mathbf{2}(F)^+$. The composition of the P valence orbitals involved in the intrabridgehead bonding interaction is quite different: in $\mathbf{2}(F)^+$, for example, $P_1(sp^{3.97}d^{0.68})$ and $P_2(sp^{0.75})$. For comparison, the phosphorus atoms use $sp^{2.06}$ hybrid orbitals in the $P_1$−$P_2$ normal single bond of $\mathbf{2}^{2+}$.

**Chemical Shifts.** The $^{31}P$ chemical shifts calculated by the CSGT formalism with the B3LYP functional are collected in Table 2. It must be noted that highly accurate predictions of the $\delta(^{31}P)$ observables require very large basis sets and higher orders of perturbation theory or coupled-cluster methods.[40−42]

**TABLE 2: Theoretical and Experimental $^{31}$P NMR Chemical Shifts Relative to PH$_3$**

| | $\delta$(P$_1$) | | | $\delta$(P$_2$) | | |
|---|---|---|---|---|---|---|
| | *out* | *in* | exptl | *out* | *in* | exptl |
| **1** | −35.7 | | −30.1[a] | | | |
| **1**$^{2+}$ | | 83.1 | 60.7[a] | | | |
| **1**(H)$^{+}$ | 9.2 | | (−6.0)[b] | −54.5 | | (−6.0)[b] |
| **1**(H)$_2^{2+}$ | −0.5 | | | | | |
| **1**(Me)$^{+}$ | 34.3 | | | −51.5 | | |
| **1**(Me)$_2^{2+}$ | 29.7 | | 35.9[a] | | | |
| **1**(O)$_2$ | | | 52.9[a] | | | |
| **2** | −31.9 | | | | 13.3 | |
| **2**$^{2+}$ | | −12.9 | −10.6[c] | | | |
| **2**(H)$^{+}$ | −98.3 | | −83.1[a] | | 0.7 | −12.3[a] |
| **2**(H)$_2^{2+}$ | 21.8 | | | | | |
| **2**(Me)$^{+}$ | −32.9 | | −25.9[d] | | −11.6 | −13.1[d] |
| **2**(Me)$_2^{2+}$ | 53.2 | | | | | |
| **2**(F)$^{+}$ | −61.5 | | −63.2[a] | | −6.5 | −7.8[a] |
| **2**(O) | 34.5 | | 53.6[a] | | −36.3 | −44.5[a] |
| **2**(O)$_2$ | 55.7 | | 70.7[d] | | | |

[a] Reference 9. [b] Average value, ref 11. [c] Reference 6. [d] Reference 12.

**TABLE 3: Theoretical and Experimental $J(^{31}P-^{31}P)$ Indirect Nuclear Spin−Spin Coupling Constants (Hz)**

| | $J$(P$_1$- - P$_2$) | | | |
|---|---|---|---|---|
| | *out,out* | *out,in* | *in,in* | exptl |
| **1** | 0.6 (0.3)[a] | | | |
| **1**$^{2+}$ | | | 73.6 (0.8) | |
| **1**(H)$^{+}$ | 3.6 (−1.8) | | | |
| **1**(H)$_2^{2+}$ | 13.4 (0.0$_1$) | | | |
| **1**(Me)$^{+}$ | 3.6 (−1.3) | | | |
| **1**(Me)$_2^{2+}$ | 10.3 (−0.0$_4$) | | | (±)5.0[b] |
| **1**(O)$_2$ | 6.6 (−0.0$_3$) | | | |
| **2** | 0.3 (−0.4) | | | |
| **2**$^{2+}$ | | | −25.3 (11.5) | |
| **2**(H)$^{+}$ | | −147.5 (4.8) | | (±)178.0[c] |
| **2**(H)$_2^{2+}$ | 1.5 (−0.0$_2$) | | | |
| **2**(Me)$^{+}$ | | −82.9 (3.8) | | (±)57.0[d] |
| **2**(Me)$_2^{2+}$ | 1.1 (−0.0$_2$) | | | |
| **2**(F)$^{+}$ | | −169.8 (6.9) | | (±)198.0[c] |
| **2**(O) | | 107.0 (1.3) | | (±)108.0[c] |
| **2**(O)$_2$ | 0.9 (−0.0$_1$) | | | |

[a] The results given in parentheses are the noncontact contributions. [b] Experimental value of **1**(Me,CH$_2$Ph)$^{2+}$, ref 9. [c] Reference 9. [d] Reference 12.

Another critical point concerns the $^{31}$P shielding scale. Indeed, the standard reference compound for $^{31}$P is 85% aqueous H$_3$PO$_4$, whose shielding cannot be accurately estimated by theory. A more convenient reference is PH$_3$, but its gas-to-liquid shift as large as 28 ppm[43] must be also taken into account. Therefore, following the suggestion advanced recently by van Wüllen,[44] the $^{31}$P absolute magnetic shielding calculated for a substance S was converted here to the chemical shift relative to 85% H$_3$PO$_4$ by using the relation

$$\delta(\mathrm{S, calc}) = \sigma(\mathrm{PH_3, calc}) - \sigma(\mathrm{S, calc}) - 266.1$$

where −266.1 is the gas-phase chemical shift of PH$_3$.[44] Thus, the DFT-CSGT results (Table 2) reasonably account for the experimental condensed-phase values. Indeed, a regression analysis of the theoretical and experimental data (15 points) gives an equation

$$\delta(\mathrm{obs}) = 0.965\delta(\mathrm{calc}) + 3.924$$

with a correlation coefficient of 0.963. The mean absolute error is 10 ppm in a range as large as 154 ppm, and a gas-to-liquid shift of ~10 ppm cannot be ruled out for the present molecules. Instead, no significant correlation is found between $\delta(^{31}$P) and $r$(P- -P) or $\Delta P$ (deviation from planarity). Therefore, this NMR parameter cannot be used as a univocal monitor of the intrabridgehead bonding in both these series. Of course, the large movement of the $^{31}$P resonance within these series of molecules reflects the complex interplay of many stereoelectronic factors (the change of geometry, disappearance of the P lone pair, and apical substitution), which one can hardly disentangle. However, the main trends in the $^{31}$P chemical shifts are consistently predicted by theory. In particular, the extreme cases **2**(H)$^{+}$ (most shielded value of −83.1)[9] and **2**(O)$_2$ (least shielded value of 70.7)[12] and the downfield displacement with the sequence Z = H$^{+}$, F$^{+}$, Me$^{+}$, and O in the [4.4.4] series are fairly reproduced by theory. Furthermore, the shielding caused by protonation is predicted to be much stronger when going fron **2** to **2**(H)$^{+}$ than from **1** to **1**(H)$^{+}$.

Other important NMR features are the low-field $^{1}$H(−P) signal of the protonated bases and the high-field $^{13}$C peak of the methylated bases. It is very satisfying to remark that the DFT-CSGT chemical shifts compare quite favorably with the available spectroscopic data: for **2**(H)$^{+}$, $\delta(^{1}$H) experimental 5.64,[9] theoretical 5.51; for **1**(Me)$_2^{2+}$, $\delta(^{13}$C) experimental 12.7,[9] theoretical 10.4; for **2**(Me)$_2^{2+}$, $\delta(^{13}$C) experimental 21.6,[12] theoretical 21.0. Furthermore, the overall agreement between theoretical and experimental $\delta(^{13}$C) values of the [CH$_2$]$_3$ and [CH$_2$]$_4$ bridges in both series of molecules is very good. Thus, on the whole, the theoretical predictions for the chemical shifts lends further support to the MP2-optimized structures.

Finally, it is worthwhile to mention the sizable difference predicted for the $^{1}$H NMR resonances of the tipped α-CH$_2$ group in *out,out*-diphosphane **2**: the endo and exo protons should resonate at 2.95 and 0.90 ppm, respectively.

**Indirect Nuclear Spin−Spin Coupling Constants.** The main results of the DFT calculations are presented in Table 3. Before the discussion is started, it must be stressed that highly accurate predictions of the $J$ property require very large basis sets, in particular for the Fermi contact (FC) term, and more sophisticated exploitation of electron correlation effects.[45−47]

In the pattern of $J$(PP) values computed for the [3.3.3] and [4.4.4] series, the following aspects are noteworthy. First, the FC term predominates over the other terms in all the species investigated. The sum of the noncontact terms is always very small except in **2**$^{2+}$ (FC −25.3 Hz, noncontact 11.5 Hz). This pattern is quite different from that calculated for the simple “normal” diphosphines P$_2$H$_4$ (FC −177.38 Hz, noncontact terms 29.57 Hz) and P$_2$H$_6^{2+}$ (FC −0.75 Hz, noncontact terms 25.81 Hz).

Very small values of $J$(PP) are predicted for all cases of *out,-out*-conformation, as expected for long-range coupling constants betwen the bridgehead nuclei (i.e., formally $^{4}J$ in the [3.3.3] series and $^{5}J$ in the [4.4.4] series). Larger values for $J$(PP) are shown by the species having the *out,in*- or *in,in*-structure. In this case, the (formally) one-bond coupling constant $J$(PP), however, shows a strong dependence upon the nature of the apical Z substituent, the formal charge on the phosphorus atoms, and the length of the alkanic bridges. One peculiar point of the *out,in*-species of the [4.4.4] series is, indeed, the reversal of sign of $J$(PP) on passing from **2**(Z = H, Me, F)$^{+}$ to **2**(O). In the first three adducts, $J$(PP) is negative, whereas it is positive in the oxide adduct. Therefore, the present theoretical results definitely complement the experimental measurements of Alder et al.,[9,12] who only determined the absolute value of this coupling constant and not its sign.

Another important theoretical prediction concerns the dicationic propellanes $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$. Despite their almost equal P−P bond lengths, 2.16 Å in $\mathbf{1}^{2+}$ and 2.18 Å in $\mathbf{2}^{2+}$, $^1J$(PP) is different in sign and magnitude: +74 Hz in $\mathbf{1}^{2+}$ and −25 Hz in $\mathbf{2}^{2+}$. This finding confirms the conclusion that along all the diphosphanes investigated there is no simple correlation between P- -P distance and *J*(PP) value.

Some interesting information has also been obtained on the one-bond phosphorus−carbon coupling constants in all the compounds considered. The DFT calculations of $^1J$(PC), indeed, gave results in good agreement with the available experimental data.[9,12] According to theory, the FC interaction is largely responsible for both the sign and magnitude of the various $^1J$(PC) values. In particular, the $^1J$(PC) values for trivalent phosphorus are predicted to be negative, whereas those for quaternized phosphorus are expected to be positive, in line with the available experimental data on organophosphorus compounds.[48] This pattern is exemplified by the following: **1**, $^1J(\mathrm{P_1-}C\mathrm{H_2})$ experimental (±)21,[11] theoretical −22.8 Hz; $\mathbf{1}(\mathrm{Me})_2^{2+}$, $^1J(\mathrm{P_1-}C\mathrm{H_2})$ experimental (±)44,[9] theoretical 45.2, and $^1J(\mathrm{P_1-}C\mathrm{H_3})$ experimental (±)58,[9] theoretical 58.0 Hz; $\mathbf{2}(\mathrm{H})^+$, $^1J(\mathrm{P_1-}C\mathrm{H_2})$ experimental (±)90,[9] theoretical 89.2 Hz; and $\mathbf{2}(\mathrm{Me})^+$, $^1J(\mathrm{P_1-}C\mathrm{H_2})$ experimental (±)82,[12] theoretical 82.2 Hz. The picture instead is not univocal for the inward-pyramidalized phosphorus atom in the group of *out,in*-adducts in the [4.4.4] series. Indeed, $^1J(\mathrm{P_2-}C\mathrm{H_2})$ is predicted to be positive for $\mathbf{2}(\mathrm{H})^+$, $\mathbf{2}(\mathrm{Me})^+$, and $\mathbf{2}(\mathrm{F})^+$, and negative for **2**(O). This behavior reflects the different degree of partial bonding between the two bridgehead atoms in the **2**(Z) adducts, as discussed above.

Finally, it is worth mentioning the strong orientational effect of the $\mathrm{P_2}$ lone pair on the formally geminal coupling constant between $\mathrm{P_2}$ and the axial carbon in the methylated derivatives: *out,out*-$\mathbf{1}(\mathrm{Me})^+$, $^2J(\mathrm{P_2-}C\mathrm{H_3})$ theoretical 2.2 Hz; *out,in*-$\mathbf{2}(\mathrm{Me})^+$, $^2J(\mathrm{P_2-}C\mathrm{H_3})$ experimental (±)32,[12] theoretical 34.0 Hz; *out,out*-$\mathbf{2}(\mathrm{Me_2})^{2+}$, $^2J(\mathrm{P_2-}C\mathrm{H_3})$ theoretical −0.1 Hz. It is noteworthy that, in the monomethylated derivative *out,in*-$\mathbf{2}(\mathrm{Me})^+$, the geminal $^2J(\mathrm{P_2-}C\mathrm{H_3})$ coupling constant is quite similar to the directly bonded $^1J(\mathrm{P_1-}C\mathrm{H_3})$ coupling constant (experimental (±)38,[12] theoretical 33.0 Hz), despite the wide difference in the P- -C distances: $\mathrm{P_1-}C\mathrm{H_3}$ of 1.84 Å and $\mathrm{P_2}$- -$C\mathrm{H_3}$ of 4.63 Å.

## Concluding Remarks

A detailed, theoretical compendium of structural and NMR spectroscopic data of a representative selection of medium-sized bicyclic diphosphanes has been presented. The main interest has been focused on the intrabridgehead interaction between the bridgehead phosphorus atoms in bicyclo[3.3.3]undecane and bicyclo[4.4.4]tetradecane systems. The molecular structure and bonding have been thoroughly investigated by the ab initio MP2 method. On the whole, the correspondence between theoretical results and X-ray available data is satisfactory. The [4.4.4] diphosphanes are more flexible energetically with respect to a shortening/lengthening of the P- -P distance than the [3.3.3] congeners. Indeed, all the [3.3.3] systems, the [4.4.4] neutral base, and its axially disubstituted derivatives adopt the *out,out*-conformation, whereas the monosubstituted [4.4.4] species prefer the *out,in*-arrangement. The special properties of the intrabridgehead bonding have been comprehensively described in terms of bond order index, force constant, vibrational frequency, and analysis of the critical points according to the AIM theory. The presence of a CP(3, −1) between the bridgehead centers has been determined only in the monosubstituted species of the [4.4.4] series and not in the free bases [3.3.3] and [4.4.4]. The unique electronic structure of diphosphanes has been further investigated with their NMR properties. The computational results, obtained at the ab initio and DFT levels, have provided detailed complementary information, which makes up for the lack of experimental measurements. The stereo and substituent dependence of the variations in the $^{31}$P NMR chemical shift, as well as of the indirect nuclear spin−spin coupling constants $J(^{31}\mathrm{P}-^{31}\mathrm{P})$ and $J(^{31}\mathrm{P}-^{13}\mathrm{C})$, has been satisfactorily accounted for by the DFT calculations. In particular, the reversal of sign of $J(^{31}\mathrm{P}-^{31}\mathrm{P})$ has been predicted on passing from the [4.4.4] adducts with Z = H$^+$, Me$^+$, or F$^+$ to the [4.4.4] oxide adduct and from the [3.3.3] to the [4.4.4] propellane dication.

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