Nuclear Magnetic Resonance Coupling Constants for a Bis(dioxaphosphorinanyl)

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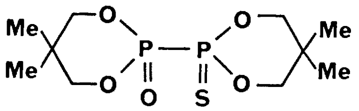
Summary $^1H-\{^{31}P\}$ heteronuclear double resonance experiments on compound (I) show that $^1J_{PP}$ and all $^3J_{HP}$ and $^4J_{HP}$ have the same sign, presumably positive.

THE effect of substituents on spin–spin coupling constants between two directly-bonded phosphorus nuclei has been the subject of controversy recently.[1–6] In most cases the sign of $^1J_{PP}$ is unknown. The limited amount of information available has led to an incorrect prediction[2,5] for the sign of $^1J_{PP}$ for P_2F_4. Theoretical calculations have also[3,4] been incorrect as to sign. The topic is of importance because (P,P) coupling is unique in that it is the only type of homonuclear coupling for second-row elements of the Periodic Table that it is feasible to study in detail. This arises because the ^{31}P nucleus occurs in 100% natural abundance and has a spin quantum number of $\frac{1}{2}$, and also because phosphorus has a rich chemistry.

We have carried out heteronuclear $^1H-\{^{31}P\}$ double resonance experiments on bis-(P^1-oxo-P^2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinanyl) (I), prepared as described by Stec and Zwierzak.[7] The spin system for this molecule is in principle complicated, but in practice a semi-first-order treatment suffices to explain the observed spectral features. At 100 MHz the equatorial protons [for a solution of (I) in $CDCl_3$] give rise to a region of the spectrum containing many transitions. The low-frequency and high-frequency extremes of this region show a doublet of triplets pattern. The doublet splitting is due to $^4J_{HP}$ and the triplet splitting arises from the AA′MM′ nature of the four CH_2 protons of a given ring. Each of the doublet of triplets mentioned may be assigned to the equatorial protons of a given ring for specified spin states of the appropriate geminal proton and of the nearer ^{31}P nucleus. Irradiation with 'tickling' or partial decoupling radiofrequency powers[8] at *ca.* 40 MHz allows the investigation of the ^{31}P region of the spectrum, including a breakdown according to sub-spectral principles.[9] Thus the relative signs of $^3J_{HP}$, $^4J_{HP}$, and $^1J_{PP}$ are found. Our experiments show that all these coupling constants have the same sign. The magnitude of $^1J_{PP}$ was found only approximately by this procedure to be 475 ± 40 Hz. Since $^3J_{HP^V}$ is well-known to be positive through intervening carbon and oxygen,[10,11] we conclude that $^1J_{PP}$ is also positive in (I).



(I)

Prior to this work, only one sign of $^1J_{PP}$ between two quinquevalent (tetra-co-ordinate) phosphorus atoms was known,[2] that for the ion $HP_2O_5^{3-}$. This was also suggested to be large and positive but the evidence for the sign was less convincing than in the present example since it was based on a sign for $^2J_{HP}$ through phosphorus in a case with which there were no close parallels with well-established signs. In contrast to these two positive values for $^1J_{PP}$, several negative signs [1,5,12,13] have been measured for cases involving two tervalent ^{31}P nuclei or one tervalent and one quinquevalent phosphorus. The present result therefore supports the contention of Rudolph and Newmark[5] that $J_{P^{III}P^{III}}$ may be in general negative whereas $^1J_{P^VP^V}$ may be in general positive (through some of the latter class of compounds such as $Me_2P(:S)P(:S)Me_2$, have low magnitudes for $^1J_{PP}$, which may therefore be of either sign). This may in some respects parallel the case for $^1J_{CP}$.[14] The trend of $^1J_{PP}$ with the nature of substituents remains a matter for speculation at present.

Note added in proof. A value of $^1J_{PP} = +720$ Hz has recently been measured for $Me_3P \rightarrow PF_5$ (C. W. Schultz and R. W. Rudolph, personal communication).

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