SHORT PAPER

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An experimental study of the $^{4h}J(^{31}P–^{31}P)$ coupling constant and the $^{12}C/^{13}C$ isotope effect on ^{31}P in an iminophosphorane-substituted proton sponge

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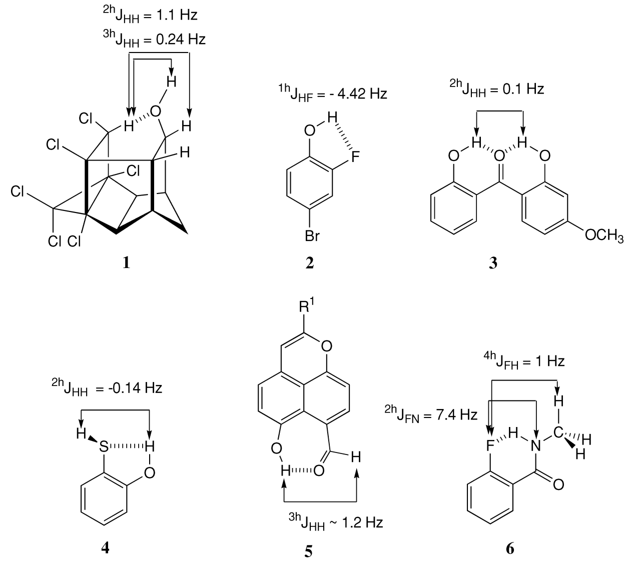
The ^{13}C NMR spectra of the bromide of the protonated iminophosphorane -substituted sponge **7** were recorded at different fields. Together with the use of ^{13}C satellites of the ^{31}P NMR spectrum, these experiments allow determination of a reasonable set of chemical shifts and coupling constants. The most interesting are a $^{4h}J_{PP} = 1.6$ Hz, determined directly from the ^{31}P NMR spectrum, which probably involves the hydrogen bond, and a $^{2}\Delta^{31}P(^{13}C)$ isotope shift of 9 ppb.

Keywords: isotope shifts, coupling constants through hydrogen bonds, proton sponges

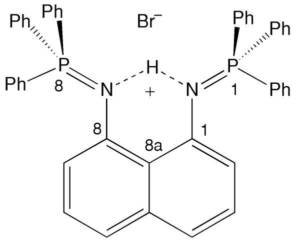
For many years, long-range coupling constants have been described and some of them tentatively assigned to couplings through hydrogen bonds (HBs). We have collected some examples in Scheme 1: **1**,[1] **2**,[2], **3**,[3] **4**,[4], **5**,[5] and **6**.[6] Other examples have been reported by Rae, Weigold, Contreras and Biekofsky.[6]



Scheme 1 Examples of couplings through hydrogen bonds

For several of these examples, a coupling through the covalent bonds of the skeleton cannot be excluded; moreover, the geometry (or even the existence) of the HB was not determined unambiguously, for instance, by crystallography. Some years ago, two of us (J.E. and P.M.) described another example of a coupling through a hydrogen bond involving two ^{31}P atoms, and reported the X-ray structure of the compound.[7] The increasing interest on these couplings[8–11] prompted us to seek to establish, through *ab initio* calculations, the reality of the $^{31}P–^{31}P$ coupling through the hydrogen bond and not through the naphthalene ring, *i.e.* a $^{4h}J_{PP}$ *vs* a $^{6}J_{PP}$.[7,12] The substrate used was a protonated iminophosphorane-substituted proton sponge **7** (other related compounds behave similarly). In the quoted work, compound **8** was used as a model to measure some coupling constants.[7] Following Hansen we have labelled the fused carbons of the naphthalene ring, **4a** and **8a**.[13]

Compound **8** shows a "normal" spectrum: carbons C(8) and C(1) are coupled to the P(8) phosphorus with $^{2}J(^{13}C-^{31}P) = 3.5$ Hz and $^{4}J(^{13}C-^{31}P) = 1.5$ Hz.[7] In our article on compound **7**, we also pointed out that the multiplicity observed at 50 MHz in $CDCl_3$ for the signal belonging to carbons C(1) and C(8) implied that a coupling constant of *ca* 3 Hz had to exist between the two phosphorus atoms.[7] Moreover, we noted that the simulated spectrum is rather insensitive to small variations of this coupling. The importance of that type of coupling through the hydrogen bond led us to resume the study of compound **7**. The isotopomer containing one ^{13}C atom at position 1' presents a ABX system where X is C(1') and A and B are the two phosphorus atoms P(1) and P(8) between which exists a small anisochrony due to the $^{12}C/^{13}C$ isotope effect. Note that the system is of the ABX type even if the carbon is coupled only to one phosphorus, whenever a coupling exists between the two phosphorus nucleii. This is a special ABX system in which $J_{AX} >> J_{BX}$ because of the large $^{1}J_{PC}$ coupling, and J_{AB} is the P–P coupling which is expected to be small compared to $^{1}J_{PC}$ in this molecule. The AB part of this system is thus made of two AX subspectra with $\Delta\nu^{\pm} = \nu_A - \nu_B \pm 1/2\,(J_{AX} - J_{BX})$.[14] One half of each of these subspectra gives on each side of the central peak a doublet the splitting of which is exactly equal to J_{AB} if this constant is not zero We report in Figs 1 and 2, respectively, the ^{13}C NMR signal of C(1)/C(8) and the ^{31}P NMR signal of **7**.



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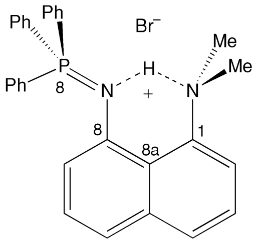

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* To receive any correspondence.

† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

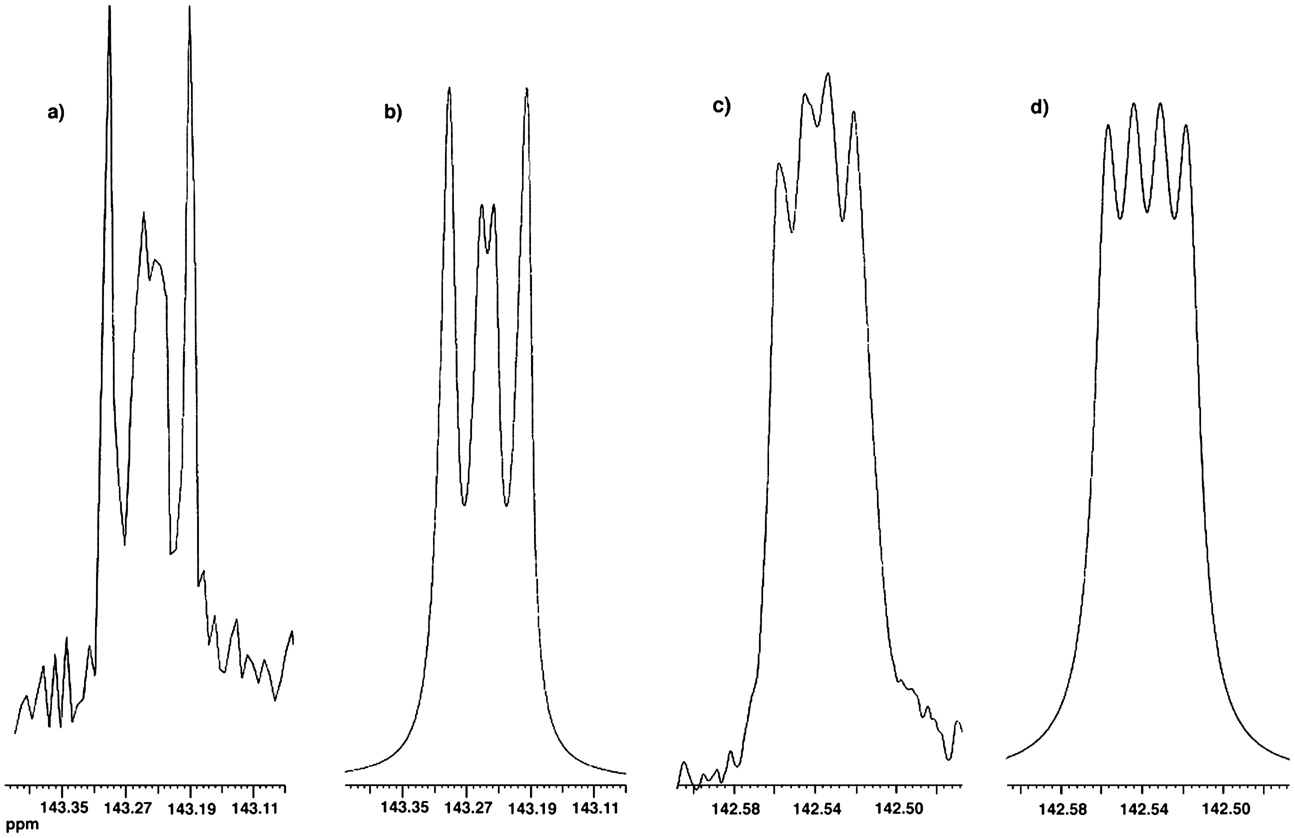


Fig. 1 Signal of C(1)/C(8): a) experimental at 50.1 MHz; (b) simulated at 50.1 MHz; (c) experimental at 125.7 MHz; (d) simulated at 125.7 MHz.

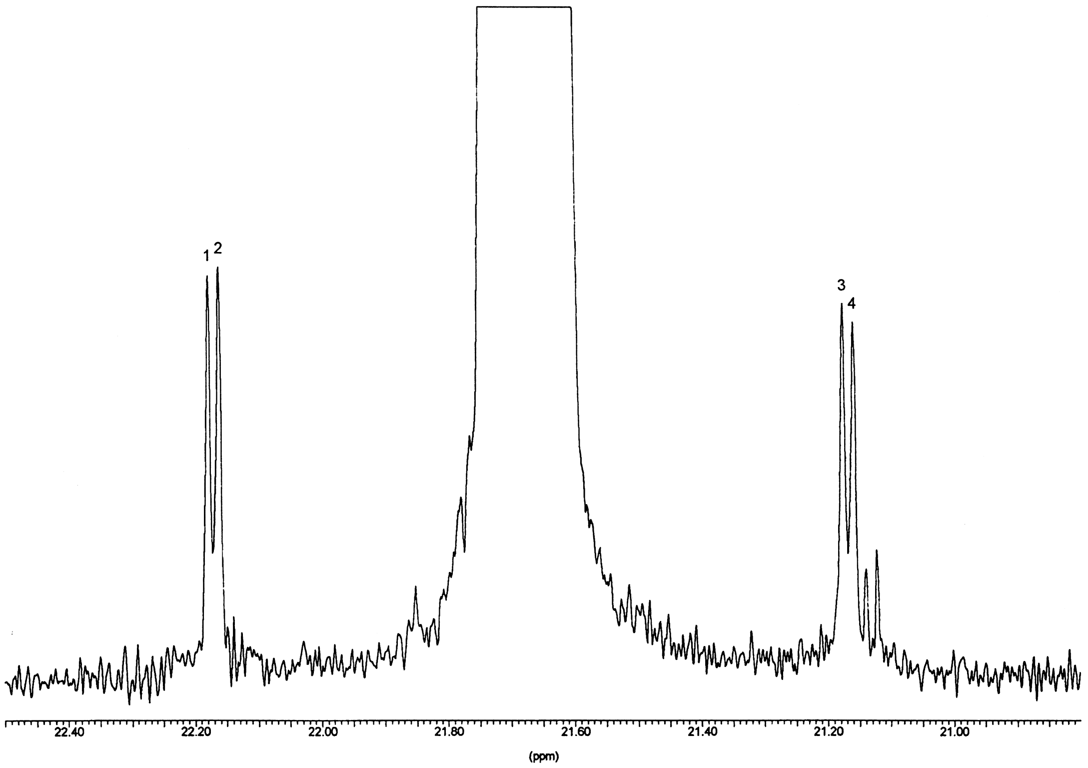
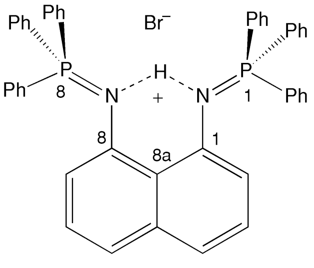


Fig. 2 Signal of P(1)/P(8) at 101.25 MHz (frequencies of satellites in Hz: **1** 2245.73, **2** 2244.06, **3** 2144.17, **4** 2142.50).

Figure 1 represents the experimental and simulated ^{13}C signal of C(1)/C(8) at 50.1 and 125.7 MHz (the simulations at 62.9 and 100.6 MHz are not reported) and Fig. 2 the ^{31}P signal at 101.25 MHz. The $^{31}P/^{31}P$ coupling constant is obtained from the two ^{13}C satellites of the ^{31}P signal which belong, as explained above, to the isotopomer with a ^{13}C at the *ipso* carbon C(1′).



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C(1)/C(8)	142.608	$^{2}J_{PC} = 3.55$ Hz, $^{4}J_{PC} = 1.38$ Hz
C(2)/C(7)	114.88	$^{3}J_{PC} = 8.7$ Hz
C(3)/C(6)	121.00	
C(4)/C(5)	125.64	
C(4a)	136.52	$^{4}J_{PC} = 1.3$ Hz
C(8a)	120.92	$^{3}J_{PC} = 11.6$ Hz
C(1′)	123.67	$^{1}J_{PC} = 101.6$ Hz
C(2′)/C(6′)	132.73	$^{2}J_{PC} = 10.6$ Hz
C(3′)/C(5′)	129.71	$^{3}J_{PC} = 13.0$ Hz
C(4′)	134.10	$^{4}J_{PC} = 2.9$ Hz
P(1)[^{12}C]	21.6838	$^{4h}J_{PP} = 1.6$ Hz

The value of $^{4}J_{PP}$ is smaller than the published one[7] but still consistent with the calculations.[12] The calculated values are larger than the measured ones, either because the calculations were carried out in a simplified model or, more probably, because in the model a symmetric situation was assumed.

Following Heckmann *et al.*[15] we will define the isotope effect on C(1) in ppb $^{n}\Delta^{31}P(^{13}C) = \delta^{31}P(^{12}C) - \delta^{31}P(^{13}C)$, where n is the number of bonds between ^{31}P and $^{12/13}C$. In our case, from the spectra at different fields, we found for P(1)/P(8) a value of |8.8| ppb which corresponds to P(8)[^{13}C] = 21.6750 ppm; this value is the difference of two isotope effects, $^{2}\Delta^{31}P(^{13}C)$ and $^{4}\Delta^{31}P(^{13}C)$. Heckmann has recently reported a $^{4}\Delta^{31}P(^{13}C)$ of – 7 ppb,[15] although in a very different system, $[(CH_3)_2CH]_3Si\text{-}O\text{-}C{\equiv}P$. We can safely assume that $^{2}\Delta^{31}P(^{13}C)$ is larger than $^{4}\Delta^{31}P(^{13}C)$ and therefore that the observed isotope effect corresponds to the former.

It is important to note that if the sum of $^{2}J_{PC}$ and $^{4}J_{PC} = 4.93$ Hz is known with a ±0.02 Hz precision, each value is subject to some error as happens with $^{2}\Delta^{31}P(^{13}C)$. It is difficult to specify the error of the reported values because they resulted from the visual comparison of the simulated spectra with the experimental ones at different fields. To our own surprise, small variations of J or $^{2}\Delta^{31}P(^{13}C)$ modify some of the spectra. The reported values are the best compromise over many attempts. An average error of ±0.1 Hz is a conservative estimation.

Experimental

The sample of compound **7** was the same that we had already used, the compound being stable in the solid state.[7] Compound **7** is moderately soluble in $CDCl_3$, therefore we have used a saturated solution without taking any special care (for instance, the solution was not degassed). The ^{13}C NMR spectra were recorded at 50.1 (Bruker AM-200), 62.9 (Bruker DRX-250), 100.6 (Varian Inova 400) and 125.7 MHz (Varian Unity 500). The ^{31}P NMR spectrum at 101.25 MHz was recorded on a Bruker DRX-250 spectrometer with a digital resolution of 0.06 Hz/point. An external sample of 85% H_3PO_4 was introduced in the tube to obtain the phosphorus chemical shift and removed afterwards. The ^{13}C spectra were obtained with a digital resolution of 0.047 Hz (at 125.7 MHz) and the chemical shifts referenced to the $CDCl_3$ signal at 77.00 ppm. The simulation programs used were gNMR versions 3.65 and 4.0, Cherwell Scientific Publishing, Oxford, UK and NMRSIM 2.61 from Bruker.

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