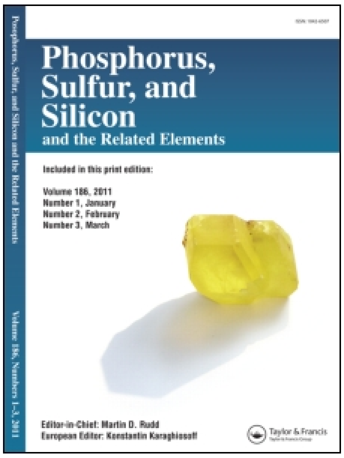

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Applications of Modern NMR Methods to Organophosphorus Chemistry

G. Hägele[a,b]; M. Murray[a]; C. Papadopoulos[a,b]
[a] School of Chemistry, University of Bristol, England [b] Institut für Anorganische Chemie and Strukturchemie, Heinrich Heine Universität, Düsseldorf, Germany

To cite this Article Hägele, G. , Murray, M. and Papadopoulos, C.(1993) 'Applications of Modern NMR Methods to Organophosphorus Chemistry', Phosphorus, Sulfur, and Silicon and the Related Elements, 77: 1, 89 — 92

To link to this Article: DOI: 10.1080/10426509308045626

URL: http://dx.doi.org/10.1080/10426509308045626

Phosphorus, Sulfur, and Silicon, 1993, Vol. 77, pp. 89–92
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APPLICATIONS OF MODERN NMR METHODS TO ORGANOPHOSPHORUS CHEMISTRY

GERHARD HÄGELE*, MARTIN MURRAY, and CHARALABOS PAPADOPOULOS*.

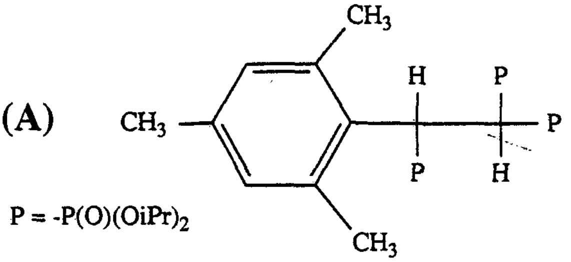
School of Chemistry, University of Bristol, BS8 1TS, England
and * Institut für Anorganische Chemie und Strukturchemie, Heinrich Heine Universität,
Düsseldorf, Germany.

Abstract: Methods for the analysis of complex mixtures of phosphorus compounds are illustrated by measurements on a mixture of isopropyl esters of mesityl substituted polyphosphonic acids and a hydrolysis product of phosphonitrilic chloride trimer. One and two dimensional methods are described, using both homonuclear and heteronuclear (P-H and H-C) correlations to obtain information hidden in normal spectra and relative signs of coupling constants.

Recent advances in nmr instrumentation have radically changed the desirable strategy for applying the method to structural studies of new compounds. Thus the techniques available for dealing with overlapping spectra are now so powerful that it is no longer as necessary, or perhaps even desirable, to insist on pure samples for nmr measurement. Since the main disadvantage of many of the techniques to be described is the time that they take, there are obvious advantages to be gained from measuring mixed samples, since data can then be acquired for more than one compound at the same time.

We illustrate this principle, as well as a number of modern and extremely powerful nmr experiments, on a sample which was ostensibly the hexakis isopropyl ester of 1-mesitylethane 1,2,2-triphosphonic acid (A). A ^{31}P spectrum immediately showed that

(A)



two major impurities were present in the sample, which were apparently a diphosphorus species (**B**) and a monophosphorus species (**C**). The intensity of the ^{31}P signals of (**B**) indicated that it was present in about 50% of the molar concentration of (A), but in the ^{1}H spectrum of the mixture the CH and CH_3 signals of (**B**) had about the same intensity as those of (**A**), indicating that (**B**) must have two-fold symmetry. The molar concentration of (**C**) was less than half that of (**B**).

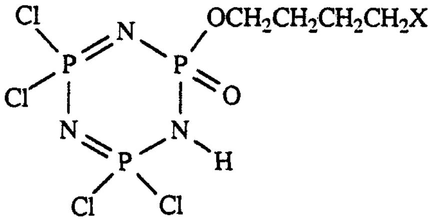
A first indication of the identity of (**B**) was given by a doublet of doublets in the ^1H nmr spectrum at ca. 7.1 ppm, which was partly obscured by the solvent signal (C_6D_6). The solvent signal was easily removed by the WEFT technique, which exploits the longer relaxation time of the solvent signal. The doublet of doublets (J = 20 and 28 Hz) was shown to arise from coupling to the two ^{31}P nuclei of (**B**) by the absence of any cross-peaks in the ^1H-^1H COSY spectrum, and the shift of the proton indicates that an olefinic group is present.

The main advantage of the COSY spectrum however was to reveal the position of the second ethane skeleton proton of (A), which is obscured by the many isopropyl CH signals (six from (A) and two from (**B**)). The effect of the three ^{31}P nuclei, which all couple to both protons, is to shift the "box" produced in the COSY spectrum by the two protons by J_{HP} in each dimension, such that the relative sign of the two HP coupling constants can be immediately determined. In the current case, where the two protons are on different carbons, the two HP couplings are always a two bond and a three bond coupling, which always have opposite sign (^2J -ve and ^3J +ve). Where similar couplings to a "passive" third proton are observed, the determination of relative signs is only possible in a COSY45 or ECOSY experiment, as the 90° pulse used in COSY90 or DQF experiments changes the spin state of the passive third nucleus 50% of the time. The ECOSY experiment[1], being suitable for phase-sensitive measurement, is therefore now our standard COSY type experiment.

The main disadvantage of ECOSY is that the phase cycling requires a minimum of 12 accumulations per t_1 increment, and since it is a phase-sensitive experiment twice this number, i.e. 24 accumulations are needed. With a typical (on our JEOL ALPHA spectrometer) number of column points of 512, this gives a typical accumulation time of 3 hours, often far more than the sensitivity requirements of the experiment would demand. This needs to be compared with the minimum of 4 scans (therefore ca. 1 hour) of the DQF experiment, or the minimum of 1 scan (therefore ca. 15 minutes) of HOHAHA (TOCSY) or pulsed field gradient COSY.

Despite the success of the ECOSY experiment in revealing the chemical shift, couplings and signs of couplings of the "hidden" proton, the couplings can only be measured with limited accuracy because of the poor digital resolution of the 2D spectrum. This problem can be overcome by 1-dimensional methods derived from 2D spectroscopy, such as 1D COSY and HOHAHA difference methods. The former method suffers from the disadvantage that signals appear in "anti-phase", i.e. with one component of a doublet positive, the other negative. This is especially confusing with complex multiplets such as observed in the present case. A much better experiment is the HOHAHA difference experiment, where selective presaturation of a signal coupled to the hidden signal, followed by subtraction from a spectrum without presaturation, reveals a spectrum of only those signals in the same coupling network as the irradiated signal. In this case the well isolated signal at δ 3.40 is ideally suited for selective presaturation, and a high resolution spectrum of the hidden signal at δ 4.55 is obtained.

A second example where we have exploited the HOHAHA difference experiment arose in our studies of the hydrolysis of phosphonitrilic chloride trimer[2]. Among the many species observed in the reaction in tetrahydrofuran are some which show proton coupling. The major one of these was assigned by Gabler and Haw[3] to a P-O-P linked dimer, but we showed that a proton signal at δ 3.82 is responsible for the coupling to phosphorus, and a HOHAHA difference spectrum obtained by irradiating this signal reveals that it arises from a reaction product of the t.h.f. solvent, probably of structure (**D**).

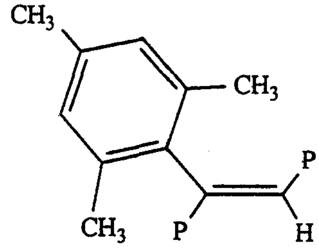


(D)

X = Cl or OR

The effects of phosphorus coupling on COSY spectra are also observed in ^{13}C-^{1}H correlation experiments, though we have now replaced this experiment by the more sensitive "inverse" ^{1}H-^{13}C experiment using ^{1}H observation. It is this experiment which reveals the identity of (**B**), since the ^{13}C nucleus (at δ 133.3) which correlates to the proton at δ 7.1 has one large ^{31}P coupling (179Hz), indicating that a P-C=CH-P group is present. The *trans* configuration of the two phosphorus nuclei is proved by the large (90Hz) value of $^{3}J_{PP}$. (**B**) has presumably arisen from (A) in the distillation by loss of diisopropylphosphonate in a retro-Pudovik type of reaction.

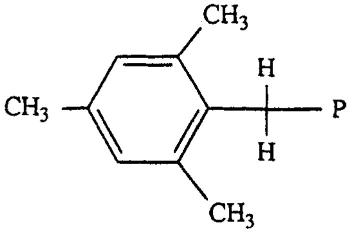
(B)



Although the above techniques allow the H-P coupling constants to be observed, they cannot determine which phosphorus is responsible for each of the couplings. For these assignments, which are also necessary to determine from which molecule the various proton signals arise, we use a ^{31}P-^{1}H correlation experiment. This is directly comparable to the ^{13}C-^{1}H experiment, though we have amended the decoupling scheme for the special requirements of polyphosphorus compounds. The standard CH experiment is decoupled in both ^{13}C and ^{1}H dimensions, and is usually set up to exploit correlations through the rather large (ca. 140Hz) one-bond C-H couplings, which are always positive. In the P-H case the P-H couplings are more interesting, as they may be positive or negative, and a single proton may have couplings to several phosphorus nuclei. Our amended experiment is only decoupled in the ^{31}P dimension, and a 45° ^{31}P pulse is used to obtain relative signs of P-P and P-H coupling constants. A problem remains the large range of P-H coupling constants which occur; in practice it is usually better to set up the experiment for a larger value, as even very small couplings (7 bonds in the case of the 4-methyl groups of the mesityl groups) can give detectable correlations when the coupling constant is set to 24 Hz, whereas couplings which are multiples of twice the set value can lead to cancellation of the correlations. We are currently attempting to overcome the problem of the variation of coupling constants by implementing a 3 dimensional experiment, in which the coupling constant will represent the third dimension of the matrix.

It was the ^{31}P-^{1}H correlation experiment which revealed the identity of (C), since the phosphorus signal showed correlations to a mesityl group, one kind of isopropyl group, and a doublet (δ 3.11, J_{HP} 18Hz), which had already been shown in the ^{1}H-^{13}C correlation experiment to be correlated with a doublet (δ 29.4, $^{1}J_{CP}$ 140Hz) which must be a P-bonded carbon. This shows that (C) is the di-isopropyl ester of mesitylmethane phosphonic acid.

(C)



The sensitivity of the ^{31}P-^{1}H correlation is such that it revealed details of a further species, present in ca. 1% concentration, which is apparently the *cis* isomer of (**B**), which had previously been overlooked because of its low concentration, and the fact that one of the phosphorus signals is at δ -1.3, outside the range selected for the ^{31}P-^{1}H correlation experiment.

References:

1. C.Griesinger, O.W.Sørensen, and R.R.Ernst, **J.Chem.Phys.**, **85**, 6837, (1986).
2. M.Murray, I.M.Rillie, and G.Woodward, **Phosphorus, Sulfur, and Silicon, 65**, 83, (1992).
3. D.G. Gabler and J.F. Haw, **Inorg. Chem.**, **29**, 4018 (1990).