

Phosphorus-31 Two-dimensional N.M.R. Spectroscopy: Broadband Homonuclear Decoupling in Polyphosphorus Compounds

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The ^{31}P two-dimensional n.m.r. spectrum of a mixture of selenides of 1,1,2-tris(diphenylphosphino)ethane can be used to effect broadband homonuclear decoupling of very large splittings, and permits ready assignment of the resonances from individual species.

Heteronuclear J - and δ -resolved two-dimensional n.m.r. spectra¹ have been extensively used for a number of pairs of

nuclei,² including ^{11}B - ^1H , ^{13}C - ^1H , and ^{31}P - ^1H , but homonuclear two-dimensional experiments have hitherto been confined

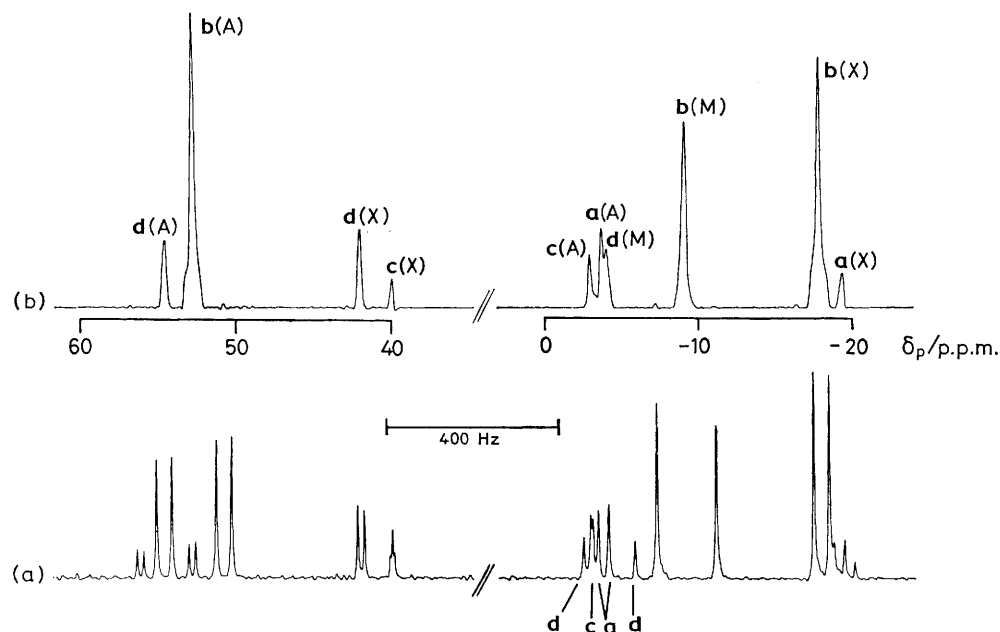


Figure 2. Proton decoupled one-dimensional phosphorus-31 spectra at 36.2 MHz of the mixture (1a–d). (a) Normal spectrum with chemical shift dispersion and full pattern of multiplicities due to phosphorus spin coupling interactions. (b) 45° projection of J -correlated two-dimensional spectrum giving broadband homonuclear decoupling so that the line positions depend solely upon the chemical shifts and reflect the ten different phosphorus environments in the mixture.

gives a one-dimensional spectrum⁸ in which all effects due to homonuclear coupling have been eliminated; that is, the effect of broadband decoupling has been produced, as shown in Figure 2(b). This trace consists of ten lines, each corresponding to a distinct phosphorus chemical shift, and it is noteworthy that several of the homonuclear couplings which have been collapsed in this way exceed 100 Hz; very difficult or impossible to achieve by ordinary r.f. decoupling. Furthermore, the nature of the two-dimensional experiment is such that much larger homonuclear couplings, certainly up to the known maximum for J_{P-P} of ca. 1000 Hz, could be eliminated in the same way. Perhaps the most valuable feature of this approach is its ability to display unequivocally the chemical shifts associated with different phosphorus sites in systems of considerable complexity. The spectra have all the simplicity normally associated with proton-decoupled carbon-13 n.m.r. spectra at natural abundance and are correspondingly easy to interpret. These experiments can tolerate some degree of second-order character in the spin-system, since even in these circumstances the positions of many of the lines depend upon simple multiples of the various coupling constants, though their intensities may be perturbed.⁸ The 45° projection therefore gives lines at the various chemical shift positions and the

broadband-decoupled spectrum again facilitates assignments, even though there are additional weaker resonances at other (calculable) positions. For example, for $J/\delta = 0.1$ these extra peaks have intensities which are ca. 10% of the main peaks, and are unlikely to lead to confusion.

Low temperature (200 K) spectra gave no indication of inhibition of rotation about the central C–C bond in (1a–e), but it is clear from models that there is considerable steric crowding, and consequently that certain conformations are likely to be strongly favoured. The various ^{31}P – ^{31}P couplings are of interest in this connection. The large values of $^2J(\text{P}^{\text{III}}\text{–}\text{P}^{\text{V}})$ in (1b) and (1d) indicate predominance of a conformation in which the dihedral angle between the P^{III} –lone pair direction and the P^{V} –bridge–C bond is close to zero, since in the less hindered molecule $\text{Ph}_2\text{P}(\text{Se})\text{CH}_2\text{PPh}_2$ this coupling⁷ is considerably smaller (85.1 Hz). Similarly, the variations in $^3J_{P-P}$ when at least one phosphorus atom is trivalent may also arise mainly from lone-pair orientation effects.

It has been pointed out⁸ that for complex proton spectra the use of two-dimensional methods cannot in general replace the need for high magnetic fields. However, for ^{31}P the chemical shift range is much greater, and the additional information from a two-dimensional experiment will make a lower field

Table 1. ^{31}P n.m.r. parameters of (1).

(1)	$E_{A,d}$			$\delta(^{31}\text{P})/\text{p.p.m.}^b$			$ J(^{31}\text{P}\text{–}^{31}\text{P}) /\text{Hz}^c$		
	A	M	X	A	M	X	AM	AX	MX
a ^f	l.p.	l.p.	l.p.	–3.6	–3.6	–19.5	?	25.0	25.0
b	Se	l.p.	l.p.	52.8	–9.1	–18.0	142.2	36.6	0
c	l.p.	l.p.	Se	–2.9	–2.9	39.8	?	5.3	5.3
d	Se	l.p.	Se	54.7	–3.9	41.8	124.1	15.7	0
e ^{f,g}	Se	Se	Se	45.8	45.8	42.3	8.1 ^e	18.1	18.1

^a l.p. = electron lone pair. ^b ± 0.1 p.p.m. to high frequency of 85% H_3PO_4 . ^c ± 0.2 Hz, signs not yet determined. ^d The species with $E_A = E_M = \text{Se}$, $E_X = \text{l.p.}$ has not yet been characterised. ^e Determined from ^{77}Se satellites in the ^{31}P spectrum. ^f A satisfactory elemental analysis has been obtained for a pure sample of this species. ^g Not present in the mixture, but included for completeness.

¹ $J[^{31}\text{P}(\text{A})\text{–}^{77}\text{Se}] = -776.6$ and $^1J[^{31}\text{P}(\text{X})\text{–}^{77}\text{Se}] = -737.3$ Hz.

spectrometer completely adequate for many complicated systems including polydentate ligands and their complexes, especially as the broadband-decoupling facility makes it possible to read off directly from the spectrum the chemical shifts associated with the different phosphorus sites.

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