

Complete Analysis of the 100 MHz ^1H NMR Spectrum of Triphenylphosphine

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The high-resolution ^1H NMR spectrum of triphenylphosphine (I) has long been a puzzling problem to the spectroscopist. Since the first report of its appearance as a singlet at 25 MHz¹ it has been shown that both 60 and 100 MHz spectra of solutions of (I) in most common organic solvents appear as a doublet with no further details.^{2,3} Using ^1H - $\{^{31}\text{P}\}$ spin decoupling Shaw *et al.*² concluded that the ^1H - ^{31}P spin coupling constants are all of almost similar magnitude with an average value of 3.5 Hz. From the benzene- d_6 ASIS (aromatic solvent induced shift) spectrum Keat³ obtained a value $^3J_{\text{P-H}_3} = 7.1$ Hz applying ^1H - $\{^1\text{H}\}$ spin decoupling to the more widely spaced multiplets for the *ortho* and *meta*, *para* protons in this solvent; other spectral parameters remained undetermined.

In this note we wish to report that it is possible to resolve a sufficient number of transitions in the 100 MHz benzene- d_6 ASIS spectrum of (I) for a complete analysis to be performed. The ^1H NMR spectrum (Fig. 1) may be analysed as the AA'BB'C part of an AA'BB'CX ($X = ^{31}\text{P}$) spin system since long-range couplings between protons on different rings are negligible in aromatic phosphines.⁴ The analysis was performed using a modified version of the iterative computer program LAOCN3.⁵ Assignments of experimental frequencies were obtained after a series of trial-and-error calculations in which only the chemical shift difference between the *meta* and *para* protons was slightly changed. Values used for the $J_{\text{H-H}}$'s and $J_{\text{H-P}}$'s in these initial calcu-

lations were estimated from our results on corresponding couplings in heteroaromatic phosphines,⁴ *i.e.* J_{HH} 's as for benzene⁶ and $^nJ_{\text{H-P}} = K \times ^nJ_{\text{H-H}}$ ($^nJ_{\text{H-H}}$ for benzene) using conversion factors $K = 0.9, 1.0,$ and 1.1 for $n = 3, 4,$ and $5,$ respectively. After a few sets of iterative calculations in which all parameters affecting the ^1H spectrum were varied, an assignment of a total of 106 theoretical transitions was reached. The r.m.s. error between observed and calculated frequencies was 0.013 Hz and the final NMR parameters (all in Hz; $\nu_0 = 100.1$ MHz; chemical shifts referred to internal TMS) are listed in Table 1; the corresponding simulated spectrum is presented in Fig. 1. Further iterative calculations showed that the $J_{\text{H-P}}$'s all have the same sign, *i.e.* positive as determined for $^3J_{\text{H-P}}$ in some *para*-substituted triphenylphosphines.⁷

The magnitudes of the $^nJ_{\text{H-P}}$'s in (I) are very similar to the corresponding $^nJ_{\text{H-H}}$ values in benzene⁶ in agreement with results for other phosphines.⁴ Also the ^{31}P (III) substituent effect

Table 1. Proton chemical shifts, ^1H - ^{31}P and ^1H - ^1H spin-spin coupling constants in triphenylphosphine.^a

$\nu_{\text{H}_2} = \nu_{\text{H}_6}$	737.18	$^3J_{\text{H}_2-\text{H}_3} = ^3J_{\text{H}_6-\text{H}_5}$	7.66
$\nu_{\text{H}_3} = \nu_{\text{H}_5}$	705.10	$^4J_{\text{H}_2-\text{H}_4} = ^4J_{\text{H}_4-\text{H}_6}$	1.28
ν_{H_4}	704.19	$^5J_{\text{H}_3-\text{H}_5} = ^5J_{\text{H}_3-\text{H}_5}$	0.64
$^3J_{\text{P-H}_2} = ^3J_{\text{P-H}_6}$	7.58	$^4J_{\text{H}_2-\text{H}_6}$	1.71
$^4J_{\text{P-H}_3} = ^4J_{\text{P-H}_5}$	1.49	$^3J_{\text{H}_3-\text{H}_4} = ^3J_{\text{H}_4-\text{H}_5}$	7.47
$^5J_{\text{P-H}_4}$	0.69	$^4J_{\text{H}_3-\text{H}_5}$	1.40

^a As a 55% w/w solution in benzene- d_6 . All values are in Hz. Chemical shifts are downfield from internal TMS (3% w/w). The errors of both chemical shifts and coupling constants are estimated from the probable errors to be within ± 0.03 Hz.

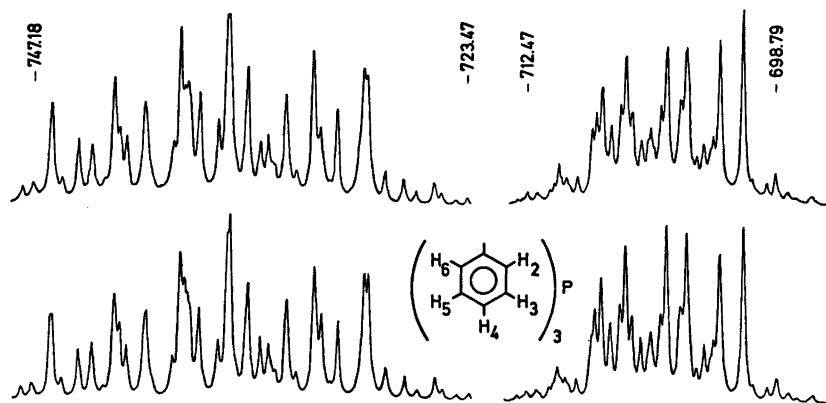


Fig. 1. Experimental (upper) and simulated (lower) 100.1 MHz ^1H NMR spectrum of triphenylphosphine in benzene- d_6 . The frequency scale (Hz) is downfield from internal TMS.

on the ${}^nJ_{\text{H-H}}$'s is negligible as expected.⁴ The magnitudes (and signs) of ${}^nJ_{\text{H-P}}$ in (I) are of interest in connection with studies of effects of ring substituents on these parameters. *Ortho* substituents have been found to have a large influence on both $J_{\text{H-P}}$ and $J_{\text{C-P}}$ in aromatic phosphines through a twisting of the ring planes with respect to the orientation of the phosphorus lone pair of electrons.⁸ CNDO/2 calculations of ${}^nJ_{\text{H-P}}$ in phenylphosphine for different conformations of the $-\text{PH}_2$ substituent with respect to the ring plane⁹ support these experimental results. Calculations for a dihedral angle (between the ring plane and the C-P-X plane, X=lone pair) of 70° , *i.e.* in the region of the most stable conformation expected for triphenylphosphine,¹⁰ gives values (${}^3J_{\text{H}_2-\text{P}}=6.69$ Hz, ${}^4J_{\text{H}_3-\text{P}}=1.71$ Hz and ${}^5J_{\text{H}_4-\text{P}}=0.97$ Hz) in good agreement with the experimental results reported here for triphenylphosphine.

Experimental. ${}^1\text{H}$ NMR spectra were recorded at 100.1 MHz in the continuous wave mode on a Varian XL-100-15 spectrometer and at a temperature of 31° . Spectra were recorded using internal ${}^1\text{H}$ lock (TMS), a sweep width of 0.5 Hz/cm and a sweep rate of 0.01 Hz/sec. Relative line positions are the average of values for the two sweep directions and are believed to be correct to within ± 0.03 Hz. Solutions were prepared in 5 mm o.d. tubes using benzene- d_6 as solvent and TMS as internal standard and lock signal source. The solutions were carefully degassed by the freeze-pump-thaw technique and sealed under vacuum.

Calculations were performed on the CDC 6400 computer system at R.E.C.A.U., University of Aarhus.

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On the Structure of Deuterated Iminodiacetic Acid Hydrochloride, $\text{C}_4\text{H}_4\text{D}_3\text{NO}_4\cdot\text{DCl}$

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The crystal structure of iminodiacetic acid hydrochloride, $\text{C}_4\text{H}_7\text{NO}_4\cdot\text{HCl}$ (denoted IDAC), has been reported previously.¹ These crystals decompose within two months at room temperature after being removed from the mother liquor. However, a more stable compound is obtained when the acid hydrogen atoms are replaced by deuterium. This compound (denoted DIDAC) is prepared by repeated recrystallizations of IDAC from $\text{D}_2\text{O} + \text{DCl}$ (containing more than 99.5 % D). The crystal structure of DIDAC has been determined in order to study if the observed difference in the stabilities of the two compounds can be correlated with any structural differences.

Powder photographs of DIDAC were taken as described in Ref. 1. The spectra could be indexed using the lattice parameters of IDAC. The unit cell dimensions were then improved by least-squares refinement. The orthorhombic unit cell dimensions are $a=12.380$ (1),* $b=5.718$ (1), and $c=5.111$ (1) Å.

A single crystal with the dimensions $0.25 \times 0.20 \times 0.17$ mm was mounted in a thin-walled glass capillary and used for the collection of X-ray intensity data on a four-circle diffractometer of type CAD-4. Experimental conditions and data reduction are described in Ref. 1. The systematically absent reflexions indicated the same space groups as for IDAC, $Pmmn$ or $Pm2_1n$.

The atomic parameters of the non-hydrogen atoms from IDAC were used as starting parameters in a least-squares refinement assuming the space group to be $Pmnm$. After including an isotropic extinction parameter in the refinement,² a difference map, calculated from data with $\sin \theta/\lambda < 0.5 \text{ \AA}^{-1}$, revealed the remaining atoms. In the further calculations, the H and D atoms were given a fixed isotropic temperature factor (3.0 \AA^2). The refined value of the extinction parameter, 2.5×10^4 , corresponds to a mosaic spread of $2.4''$ or a domain size of 3.8×10^{-4} cm. Weights used in the last cycle of refinement, $w=1/(\sigma_c^2 + 0.0001|F_o|^2 + 4.0)$, gave $R=0.074$, $R_w=0.096$ and a smooth weighting scheme. The resulting positional and thermal parameters are given in Table 1. Tables with $|F_o|$, $|F_c|$, $\sin^2 \theta_o$, and $\sin^2 \theta_c$ can be obtained from the author.

* Figures within parentheses represent e.s.d.'s in the least significant digits.