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THE PROTON MAGNETIC RESONANCE SPECTRA OF *PARA*-SUBSTITUTED TRIARYLPHOSPHINE OXIDES

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Abstract—The high resolution PMR spectra of thirteen *para*-substituted triarylphosphine oxides have been determined. Analysis of the observed spectra as ABX leads to a determination of the P^{31}-H coupling constants for protons *ortho* and *meta* to the phosphorus nucleus. The PMR parameters obtained are discussed with reference to the interaction of the phosphono group with the aromatic ring and in relationship to other arylphosphorus compounds.

INTRODUCTION

AN INCREASING number of studies of the PMR spectra of organophosphorus compounds have been reported[1,2] and the application of PMR spectra to structural problems have become common in organophosphorus chemistry.[3] These studies have been restricted to the resonances of aliphatic and olefinic protons and have been concerned primarily with the determination of chemical shifts and P^{31}-H spin-spin coupling constants and their variation with the P^{31}-H distance and the charge or covalency of the P^{31} nucleus.[1,4] The only report to date regarding aromatic proton resonances is contained in the comprehensive study of Hendrickson *et al.*[1] No detailed analyses were carried out, but it was shown that the strongest peak in the aromatic multiplets for a number of triphenylphosphonium salts fell in the region $\tau = 2{\cdot}23$–$2{\cdot}42$ ppm; the similarity between these multiplets and those arising from phenyl groups on carbonium ions[5] was pointed out.

This paper describes the high resolution PMR spectra of a number of *para*-substituted triarylphosphine oxides. The nature of the spectra is such that analyses can be carried out readily and the *ortho* and *meta* P^{31}-H coupling constants have been determined for thirteen compounds.

EXPERIMENTAL AND ANALYSES

The triarylphosphine oxides were prepared in this laboratory[6] and were shown to be of a high degree of purity by elemental and spectroscopic analyses. Because of the limited solubility of the phosphine oxides, the spectra reported in Table 1 were determined on saturated solutions; however, in three instances in which solubility allowed meaningful concentration variation (comps 1, 7, 13), both chemical shift and coupling constant values were shown to be concentration independent. Dimethylsulfoxide (DMSO) and $CDCl_3$ were employed as solvents depending upon the solubility

[1] J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron* **20**, 449 (1964).
[2] G. Martin and A. Besnard, *C.R. Acad., Sci., Paris* **257**, 898 (1963) and earlier Refs.
[3] F. A. Cotton and R. A. Schunn, *J. Amer. Chem. Soc.* **85**, 2394 (1963); W. G. Bentrude and E. R. Witt, *Ibid.* **85**, 2522 (1963); S. J. Fitch, *Ibid.* **86**, 61 (1964).
[4] J. B. Stothers and J. R. Robinson, *Canad. J. Chem.* **42**, 967 (1964).
[5] R. S. Berry, R. Dehl, and W. R. Vaughan, *J. Phys. Chem.* **34**, 1460 (1961).
[6] H. H. Hsieh, Ph.D. Thesis, University of Pittsburgh, 1964; H. H. Hsieh and C. E. Griffin, to be published.

TABLE 1. PMR SPECTRA OF TRIARYLPHOSPHINE OXIDES[a]

			$(p\text{-}YC_6H_4)_n(C_6H_5)_{3-n}P \rightarrow O$					
	Y	n	Solvent	ω_A	ω_B	J_{AB}	J_{AX}	J_{BX}
1.	HO	3	DMSO	444	413	8·5	11·1	2·3
2.	HO	2	DMSO	445	414	8·5	11·0	2·5
3.	HO	1	DMSO	444	413	8·5	11·5	2·3
4.	$(CH_3)_2N$	3	DMSO	438	413	8·8	11·0	2·3
5.	$(CH_3)_2N$	2	DMSO	437	411	8·8	11·1	2·4
6.	$(CH_3)_2N$	1	DMSO	—	411	8·7	—	2·3
7.	CH_3O	3	DMSO	451	423	8·9	11·0	2·3
			$CDCl_3$	452	412	8·7	11·2	2·1
8.	CH_3O	2	$CDCl_3$	454	415	8·6	11·0	2·3
9.	CH_3O	1	$CDCl_3$	453	414	8·9	11·3	2·4
10.	CH_3	3	$CDCl_3$	452	432	8·1	11·3	3·1
11.	Br	3	DMSO	461	477	8·6	10·5	3·4
12.	HOOC	3	DMSO	472	491	8·0	11·3	2·8
13.	CH_3OOC	3	DMSO	468	487	8·0	11·2	3·0

[a] All frequencies are given in c/s at 60 Mc/s from internal TMS reference.

behavior of the particular phosphine oxide; variation in coupling constant values with changes in solvent were essentially negligible and fell within the limits of experimental error (see compd 7).[7]

The spectra were determined at 27° (probe temp) using a Varian Associates Model A-60 spectrometer. Peak frequencies are reported in c/s with reference to internal TMS; the coupling constant data were taken from the averages of two forward and two reverse runs at a spectrum sweep width of 50 c/s. The estimated probable errors for chemical shift and coupling constant data are 1·0 and 0·1 c/s, respectively, although the average deviations are much smaller.

The spin systems of the *para*-substituted triarylphosphine oxides are of the type designated as A_2B_2X;[8] in the spectra of the symmetrically substituted compounds (1, 4, 7, 10–13), all 8 signals of the AB part were cleanly resolved and the A and B portions of the aromatic proton resonances did not overlap. It was therefore possible to treat the spectra as a typical AB pattern modified by coupling with the X (P^{31}) nucleus[9] and an analysis was carried out on this basis. Spin-spin coupling between protons on opposite sides of the aromatic ring was not resolved under the conditions of resolution employed, but probably contributed to peak broadening. For the seven symmetrically substituted compounds excellent agreement was obtained between the observed spectra and spectra calculated on the basis of transition energy and intensity expressions for the ABX case.[10] For the remaining compounds in Table 1, the AB pattern was superimposed on the multiplet pattern of the unsubstituted phenyl groups; in all cases except 6, the eight AB lines were cleanly resolved. For compound 6, the downfield portion (H_A) was largely obscurred by phenyl proton resonances. The primary resonance line for triphenylphosphine oxide appears at 452 c/s (in DMSO). In Table 1, protons *ortho* to phosphorus are designated H_A even though they do not give rise to the more downfield signals in all cases (11–13).

[7] A solvent dependence for phosphorus-proton couplings has been noted by Martin and Besnard[3] in a number of organophosphorus compounds and a similar dependence for geminal P—H couplings in benzyl phosphonium salts has been noted in this laboratory (M. Gordon and C. E. Griffin, to be published).

[8] J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance*, McGraw-Hill, New York, N.Y. (1959).

[9] For other examples of the analysis of similar A_2B_2X spectra, R. E. Richards and T. Schaefer, *Proc. Royal Soc.* [A], **246**, 429 (1958); T. Schaefer and W. G. Schneider, *Canad. J. Chem.* **37**, 2078 (1959); R. J. Abraham and H. J. Bernstein, *Ibid.* **39**, 905 (1961); and Ref. 8.

[10] H. J. Bernstein, J. A. Pople, and W. G. Schneider, *Canad. J. Chem.* **35**, 65 (1957).

DISCUSSION

The spectra observed for the triarylphosphine oxides are consistent with expectation; studies of the absorption spectra and acidities of phosphine oxides and phosphonic acid derivatives have established the phosphoryl group to be a moderately strong electron acceptor substituent.[11] Consequently, on the basis of previous studies of the effects of substituents on aromatic proton resonances, the downfield shift of protons *ortho* to phosphorus relative to protons *ortho* to electron donor substituents such as methoxy and hydroxy would be anticipated.[8,12] The magnitude of the internal shift (ω_A-ω_B) is such (25–40 c/s for comps 1–10) that relatively simple spectra interpretable by ABX analyses result. The magnitude of the internal shift provides further evidence for the nature of the electron acceptor properties of the phosphoryl group. The internal shift for compound 7 in $CDCl_3$ is 0·67 ppm; Smith[12] reports internal shifts of 0·81 ppm for *p*-methoxybenzaldehyde and 1·10 ppm for *p*-methoxybenzoic acid in the same solvent and 0·60 ppm for *p*-bromoanisole in carbon tetrachloride. These comparisons and further comparisons with the internal shift data for para-substituted phenols[13] indicate the phosphoryl group to be a considerably weaker electron acceptor than carbonyl functions and roughly comparable in net effect to bromine, conclusions consistent with the findings of other workers.[11] It is recognized that the deshielding effect of a substituent on an *ortho*-proton is only qualitatively related to the inductive and resonance effects of the substituent[8,12] and that other factors such as the diamagnetic anisotropy of the substituent[12] and internal hydrogen bonding may influence the shielding. Consequently, this internal shift interpretation can only be considered as indicative of the electron acceptor properties of the phosphoryl group.

Although chemical shift and coupling constant values were shown to be concentration independent and coupling constant values were essentially solvent independent on the basis of these limited studies, chemical shifts for H_A and H_B did show a solvent dependence, the dependence being greater for H_B. Thus, while compound 10 gave a cleanly resolved eight line AB pattern in $CDCl_3$, only five lines were observed in DMSO because of extensive overlapping of the A and B portions of the spectrum. A similar effect was noted for 11 in $CDCl_3$. Of all the compounds examined, only tris-(*p*-chlorophenyl)-phosphine oxide (14) failed to show the AB characteristics; in the spectrum of this compound in DMSO, only two peaks (453 and 459 c/s) were observed. An extension of the internal shift comparisons cited above would indicate a near equivalence for ω_A and ω_B for this compound and the observed spectrum probably corresponds to one of the deceptively simple ABX cases discussed by Abraham and Bernstein.[14] In the limiting case [$\delta_{AB} = 0$ and $1/2(J_{AX} - J_{BX})$ small as compared to J_{AB}] the eight line AB pattern collapses to a two line pattern with the separation equal to $1/2(J_{AX} + J_{BX})$. The observed line separation for 14 is 6·9 c/s the average $1/2(J_{AX} + J_{BX})$ from Table 1 is 6·8 c/s, indicating that this interpretation of the two line AB pattern for 14 may be valid.

[11] H. H. Jaffe, L. D. Freedman, and G. O. Doak, *J. Amer. Chem. Soc.* **75**, 2209 (1953); C. E. Griffin and R. A. Polsky, *J. Org. Chem.* **26**, 4772 (1961); L. D. Quin and M. R. Dysart, *Ibid.* **27**, 1012 (1962); D. J. Martin and C. E. Griffin, *J. Organometallic Chem.* **1**, 292 (1964).

[12] G. W. Smith, *J. Mol. Spec.* **12**, 146 (1964).

[13] W. G. Paterson and N. R. Tipman, *Canad. J. Chem.* **40**, 2122 (1962).

[14] R. J. Abraham and H. J. Bernstein, *Canad. J. Chem.* **39**, 216 (1961).

The observed coupling constants are consistent with expectation. The J_{HH} values lie in the range 8·0–8·9 c/s; the range 8·1–9·4 c/s has been reported by Smith in a study of some sixty *para*-substituted benzenes.[12] The magnitude of J_{PH} values is of the order anticipated from comparisons with those observed in aliphatic organophosphorus compounds;[1] the attenuation of the coupling from *ortho* to *meta* positions is much greater than that observed for the analogous spin systems of *para*-substituted fluorobenzenes.[12]

A number of workers have observed that both proton chemical shifts and J_{PH} in alkyl-phosphorus compounds can be correlated with the hybridization state of the phosphorus atom.[1,4,15] These correlations have been interpreted by Hendrickson *et al.*[1] on the basis of sigma-electron contact contributions and the effects of substituent electronegativity on the hybridization of the phosphorus atom. Thus, the changes from neutral trivalent to positively charged tetravalent phosphorus in a series of methyl compounds (15–17) gives the progression of chemical shifts and coupling constants cited in Table 2. Since the same effects of hybridization on δ_H and J should also be operative in the aryl-phosphorus compounds, this study has been extended in the *para*-methoxy series to the analogous phosphine (18) and phosphonium salt (19); the observed parameters for these compounds and for the phosphine oxide (7) are listed in Table 2. Although the magnitude of changes are not as great for the aryl as for the alkyl derivatives, the same general progression is evident indicating a similarity in hybridization effects on δ_H and J_{PH} in both the alkyl and aryl series. The PMR spectra of 18 and 19 showed fully resolved A_2B_2X patterns similar to that of 7.

Further studies of the PMR spectra of aromatic organophosphorus compounds including tris-heteroarylphosphine oxides and the analysis of the A_2B_2XY system, tris-(*p*-fluorophenyl)phosphine oxide, are in progress.

TABLE 2. PMR PARAMETERS FOR ALKYL AND ARYL PHOSPHINES, PHOSPHINE OXIDES, AND PHOSPHONIUM SALTS[a]

		ω_A	ω_B	J_{PH_A}	J_{PH_B}	J_{HH}	Solvent
15.	$(CH_3)_3P$	53	—	2·7	—	—	Neat[b]
16.	$(CH_3)_3PO$	116	—	13·4	—	—	D_2O[b]
17.	$(CH_3)_4P^+ I^-$	148	—	14·4	—	—	$CDCl_3$[b]
18.	$(p\text{-}CH_3OC_6H_4)_3P$	433	409	7·1	1·1	8·9	$CDCl_3$[c]
7.	$(p\text{-}CH_3OC_6H_4)_3PO$	452	412	11·2	2·1	8·8	$CDCl_3$[c]
19.	$[(p\text{-}CH_3OC_6H_4)_3PCH_3]^+ I^-$	460	432	12·2	2·7	9·0	$CDCl_3$[c]

[a] All values are in c/s and frequencies are relative to TMS.

[b] Ref 1.

[c] This work.

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[15] G. Martin and G. Mavel, *C.R. Acad. Sci., Paris* **252**, 110 (1961).