SPECTROSCOPIC STUDIES OF ORGANOPHOSPHORUS COMPOUNDS—II

INFRARED AND ULTRAVIOLET SPECTRA OF PHOSPHONIUM COMPOUNDS AND THEIR STRUCTURES

M. Arshad A. Beg and Samiuzzaman

Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi-32, Pakistan

Abstract—The IR spectra of the *p*-tolylphosphonium compounds have been described and assignments made. The intensities of the various bands have also been discussed in terms of the substituents in the benzene ring. The doublets observed for the C–H out-of-plane bending mode are suggested to be due to an unsymmetrical structure of the compounds having different orientations of the rings. The UV spectra have also been recorded and the fine structure in the 265–275 mμ region has been assigned to the lack of conjugative interaction between the rings.

INTRODUCTION

The IR spectra reported for a number of phosphonium compounds[1,2] include the Ph and alkyl groups. Although spectral assignments in the various regions have been made, the 700–800 cm^{-1} region where the P–C stretching, the C–H out-plane deformation, the CH_2 rocking and the X-sensitive vibrations all absorb, further elaboration regarding their assignment is desirable. An attempt has been made here to sort out the various absorptions in this region by studying the *p*-tolyphosphonium compounds since the *para* substituted compounds have a single sharp band at 800 cm^{-1} unlike the phenylphosphonium compounds which absorb strongly at 750 and 700 cm^{-1}.

The study of these compounds by Witschard and Griffin[2] lists the common features of the absorption and no assignment for the various bands have been made. Deacon *et al.*[1] on the other hand have made definite assignment of the bands. The solution spectra recorded by us compare very well with the latter work and hence in the assignment of the bands in the 1600–1300 cm^{-1} region a close parallel has been sought.

The UV spectra for the phosphonium compounds have also been recorded to obtain information regarding the nature of transitions among the aromatic rings and if possible to indicate the manner in which these are oriented in the molecule.

DISCUSSION

IR spectra

The IR spectra of the phosphonium compounds and of the phosphine are recorded in Tables 2 and 3 which also include tentative assignment of the bands. A common feature of all these phosphonium compounds as also pointed out by Witschard and

TABLE 1. IR ABSORPTION IN THE REGION 1600–1300 cm^{-1}

Compound	Methyl symmetric bending cm^{-1}	ε^a	C—C skeletal mode o cm^{-1}	ε^a	Me symmetric bending cm^{-1}	ε^a	Me symmetric bending cm^{-1}	ε^a	C—C skeletal mode n cm^{-1}	ε^a	C—H antisymmetric bending cm^{-1}	ε^a	C—C skeletal mode m cm^{-1}	ε^a	C—C skeletal mode l cm^{-1}	ε^a	C—C skeletal mode k cm^{-1}	ε^a
(4-MeC$_6$H$_4$)$_3$P	1310	7·43			1356	1·8	1380	5·8	1400	13·2	1450	8·8	1540; 1498	0·8; 30·8	1560	1·2	1600	19·1
(4-MeC$_6$H$_4$)$_3$—MePI			1323	25·0	1350	4·5	1384	9·0	1402	42·3	1450	12·5	1502	21·1	1562	v.w.	1600	103·8
(4-MeC$_6$H$_4$)$_3$—Et—PI			1320	14·2			1382	11·2	1400	39·3	1450	18·6	1540; 1500	2·7; 26·2	1560	3·5	1600	100·8
(4-MeC$_6$H$_4$)$_3$—n-PrPI			1318	11·8			1382	10·1	1400	37·3	1450	18·0	1522; 1500	1·7; 22·8	1560	2·0	1600	105·6
(4-MeC$_6$H$_4$)$_3$—n-BuPI			1318	12·8	1367; 1350	3·6; 0·9	1380	12·8	1400	43·3	1460; 1456	20·9; 18·7	1540; 1500	1·2; 23·9	1560	2·3	1600	111·6
(4-MeC$_6$H$_4$)$_3$—n-HexPI			1320	14·9			1384	13·1	1400	38·6	1470; 1456	17·1; 19·4	1545; 1500; 1496	11·6; 21·4; 6·2	1570	2·8	1600	94·4

ε^a is the apparent molecular extinction coefficient.

TABLE 2. IR ABSORPTION BANDS IN THE REGION 1300–1000 cm⁻¹

Compounds	In plane C—H deformation mode b	Me Rock	C—C antisymmetric stretching	In plane C—H deformation mode d and X-sensitive mode q	In plane C—H deformation mode a	Skeletal
$(4\text{-MeC}_6\text{H}_4)_3\text{P}$	1018 s	1035 m		1088 s	1193 s 1184 s	1210 m 1270 w 1278 w 1306 m
$(4\text{-MeC}_6\text{H}_4)_3\text{MePI}$	1020 w	1038 w		1110 vs	1190 m	1220 m 1228 w 1275 w
$(4\text{-MeC}_6\text{H}_4)_3\text{EtPI}$	1018 m	1035 m	1046 m	1106 vs	1192 m	1207 w 1213 w 1238 w
$(4\text{-MeC}_6\text{H}_4)_3\text{n-PrPI}$	1017 m	1035 ms	1071 m	1100 vs	1192 m	1232 m 1247 w 1253 w
$(4\text{-MeC}_6\text{H}_4)_3\text{n-BuPI}$	1016 m	1035 ms	1065 m	1110 vs	1190 s	1214 vw 1218 vw 1225 vw
$(4\text{-MeC}_6\text{H}_4)_3\text{n-HexPI}$	1020 m	1032 ms	1070 m	1113 m	1198 s	1212 sh 1245 sh

s = strong; m = medium; w = weak; ms = medium sharp; vs = very strong; vw = very weak; sh = shoulder.

G

TABLE 3. IR ABSORPTION BANDS IN THE REGION 900–700 cm⁻¹

Compound	X-Sensitive mode r	C–C symmetric stretching	P–C antisymmetric stretching	C–H out of plane deformation mode f	Me rock
(4-MeC$_6$H$_4$)$_3$P	709 m			808 vs	843 m
					847 m
					950 w
					970 w
(4-MeC$_6$H$_4$)$_3$MePI	706 m		770 s	808 s	908 s
				815 m	
(4-MeC$_6$H$_4$)$_3$EtPI	707 m——	724 s	772 s	807 s	830 w
				814 s	835 w
					845 w
					858 w
					903 m
(4-MeC$_6$H$_4$)$_3$n-PrPI	707 m	735 m	769 m	805 s	835 w
				810 sh	846 m
				813 sh	851 sh
					897 w
(4-MeC$_6$H$_4$)$_3$n-BuPI	705 m	720 s	768 m	803 vs	835 vw
				818 m	840 vw
					847 vw
					850 vw
					852 vw
(4-MeC$_6$H$_4$)$_3$n-HexPI	710 s	724 m	776 m	808 s	834 wsh
				816 s	868 ws
					894 vw

m = medium; sh = shoulder; wsh = weak shoulder; vw = very weak; s = strong; w = weak; ws = weak sharp.

TABLE. 4. ABSORPTION MAXIMA AND MOLAR EXTINCTION COEFFICIENTS IN UV REGION

Compound	λ_{max} (mμ)	$\log_{10} \varepsilon$	λ_{max} (mμ)	$\log_{10} \varepsilon$	λ_{max} (mμ)	$\log_{10} \varepsilon$
(4-MeC$_6$H$_4$)$_3$MePI	275	2·7	264	3·2	233	4·6
(4-MeC$_6$H$_4$)$_3$EtPI	274	3·2	263	3·3	233	4·4
(4-MeC$_6$H$_4$)$_3$PrPI	276	3·5	263	3·7	233	4·5
(4-MeC$_6$H$_4$)$_3$n-BuPI	276	3·3	264	3·5	234	4·8
(4-MeC$_6$H$_4$)$_3$n-HexPI	277	3·4	264	3·5	233	4·6

Griffin[2] is the occurrence of medium intensity bands in the 1600–1300 cm⁻¹ and 1250–1000 cm⁻¹ regions, weak bands in the 950–850 cm⁻¹ and a series of intense bands in the 800–700 cm⁻¹ regions.

The 1600–1300 cm⁻¹ *region.* The spectra of some triphenylphosphonium compounds show that in this region the bands assigned[1] to the k, l, m, and n modes (Whiffen's notations) vary in intensity depending on the nature of substituents in the benzene ring. In conjugated ring systems, these are usually of equal intensity. In

systems with slightly different orientation of the rings as in the triphenylmethyl cation[7] the intensity of the n mode is higher than in other Ph substituted compounds. In triphenylphosphine and in the alkyl-triphenylphosphonium compounds there is a considerable enhancement in the intensity of this vibration. The absorption due to mode n is usually of weak to medium intensity and is known to be independent of the nature of the substituents on the benzene ring.[6] The higher intensity may be due to the orientation of the rings. The triphenylmethyl cation has been suggested to have a propellor shaped structure[7] and the crystal structure studies on triphenylphosphine reveal that one of the rings is rotated out-of-plane with the others.[8] Since the n mode corresponds to a certain amount of tilting motion, it is possible that such vibrations would lead to greater dipole changes and hence the higher intensity of this band. From the intensity of this band in the alkyl triphenylphosphonium compounds an unsymmetrical distribution of the rings is indicated. The other absorptions corresponding to modes k, l and m are of weak to medium intensity as expected for a monosubstituted benzene ring.

Compared with the k and l modes, the m mode absorbs strongly in tri-*p*-tolyl-phosphine indicating charge disturbance possibly due to the lone pair electrons. In the alkyl-*p*-tolylphosphonium compounds, however, the absorption corresponding to mode k is very intense implying considerable charge disturbance. In tri-*p*-tolyl-phosphine oxide and sulphide the intensity of this band is also high. The expansion of the valence shell of phosphorus results in the charge transfer from the lone pairs on oxygen or sulphur to the 3d orbitals[9] and similar charge transfer is apparent in the case of the phosphonium cation. The charge disturbance as indicated by the higher intensity of the $1600 \, cm^{-1}$ band must be due to the alteration in charge symmetry of the ring amplified by the weak conjugative forces in the quadruply connected phosphorus compounds. The difference in the triphenylphosphonium compounds is apparently due to *p*-substitution.

Unlike the triphenylphosphonium compounds, the l mode is clearly resolved in the *p*-tolyl compounds and occurs at $1560 \, cm^{-1}$. The o mode is also quite predominant and occurs at $1320 \pm 2 \, cm^{-1}$ as a medium intensity band. The n mode absorbs strongly and if the analogy with the triphenylmethyl cation is correct, at least one of the rings in these compounds is also turned out of plane with the others.

The $1250-1000 \, cm^{-1}$ *region.* In this region the triphenylphosphonium compounds have an intense band at $1100 \, cm^{-1}$ due to the X-sensitive vibration and a series of weak bands at 1180, 1160, 1070 and $1030 \, cm^{-1}$. These are due to the a, d, c and b modes respectively.[1] In triphenylphosphine the absorptions due to the d and b modes are more intense than the remaining two. It is suggested that under the symmetry restrictions of this molecule, the more favoured vibration is the in-plane deformation of the C–H band towards the phosphorus atom. This is also found to be the case in conjugated ring systems as in diphenylsulphide and diphenylselenide. In weakly conjugated systems like those of the phosphonium compounds it is found that these absorptions are usually of medium intensity. However, the ring breathing mode absorbing at $1000 \, cm^{-1}$ is more intense in these cases. This may be attributed to weak conjugative forces under which the vibrations are localized to the ring.

In *para* substituted benzenes mode c is not expected. Mode d is not clearly resolved in the *p*-tolylphosphonium compounds. This is possibly coupled with the X-sensitive vibration q occurring at $1110 \, cm^{-1}$ as a strong band. The absorptions occurring as

sharp bands at 1195 and 1015 cm^{-1} are assigned to the a and b modes. The absorption at 1035 ± 3 cm^{-1} is assigned to the Me rocking and so are the weak to medium intensity bands at 960 and 980 cm^{-1}.

The 800–700 cm^{-1} *region.* There is a series of split bands in this region in both the phenyl and *p*-tolylphosphonium compounds. The intense band at 800 cm^{-1} is clearly C–H out-of-plane deformation mode for a *p*-substituted ring system. This band is in certain cases split but is usually observed to occur in this region in all the *p*-tolylphosphonium compounds, phosphine oxide, sulphide and the phosphine. The other two bands which are also consistent are those at 780 ± 5 and 710 ± 5 cm^{-1}. The former occurs only in the alkyl-tri-*p*-tolylphosphonium compounds and not in the phosphine, phosphine oxide or sulphide and may therefore be assigned to the P–C (aliphatic) asymmetric stretching frequency in analogy with the assignments for the other alkyl-phosphonium compounds.[10] The latter band may be assigned to the X-sensitive mode r. This band is quite clear in all the *p*-tolylphosphorus compounds, unlike the triphenyl analogues particularly in triphenylphosphine, where this vibration is overlapped by the intense band due to the C–H out-of-plane deformation. There is, however, one band of moderate intensity occurring at 730 ± 5 cm^{-1} in *p*-tolylphosphonium compounds containing an alkyl group. It is absent in the phosphine, the phosphine oxide and sulphide and in methyl-tri-*p*-tolylphosphonium iodide. In our earlier studies[10] a similar band in this region was assigned to the C–C symmetric stretching mode. It could, however, also be a CH_2 rocking mode or a mixing of these two vibrations.

The splitting of the bands and the observation of doublets in this region and particularly that due to the C–H out-of-plane deformation has been demonstrated in the case of phenylacetic acids to be a result of the difference in the electron density of the rings which then absorb at different frequencies.[11] The rotation of one of the rings with respect to the other may be one such form in which the former becomes non-equivalent with the other, thus absorbing differently. It has been observed in the case of triphenylphosphine that one of the rings is inclined to the extent of 30° more than the others towards the normal to the pyramid base of the molecule.[8] In the solid state spectra recorded by us and also by Steger and Stopperka,[12] a doublet occurs at 746 and 752 cm^{-1}. With the formation of a quadricovalent structure having no conjugative interaction among the rings a further disturbance in the angular distribution would be expected. In the alkyl-triphenylphosphonium compounds the splitting is ∼15 to 20 cm^{-1}. An unsymmetrical distribution of the rings in the onium compounds may therefore be deduced from these observations. In the *p*-tolylphosphine there is no splitting while in phosphonium compounds it is small ∼7 cm^{-1} indicating only weak intermolecular repulsions leading to not too large twisting of the rings.

UV spectra

The UV spectra of the phosphonium compounds are typical of the quadruply connected phosphorus compounds. The absorptions listed in Table 4 divide them into two regions. One is the band at 265–275 mμ and the other is a high intensity band at 233 mμ.

The 233 *mμ band.* This occurs in all the phosphonium compounds. The high intensity of the bands in this region suggests that they are due to charge transfer.

Since lengthening of carbon chains does not affect the intensity, the alkyl groups should not be responsible for these absorptions. There can be only two reasons for these bands: (1) Steric interactions and (ii) charge transfer between ion pairs. Slightly hindered arsines have been shown to have an absorption band in this region.[13] Since IR spectra also indicate the inequivalence of the rings the absorption noted here supports this conclusion. This may not be a steric hindrance in the strict sense but with a change in the symmetry of the molecule, the distribution of the aromatic rings in space may be unsymmetrical, similar to that found in triphenylphosphine.[8] Charge transfer between ion pairs may also be a possible explanation. The positive charge on the phosphorus atom on the formation of a quadricovalent structure encourages a $d\pi$–$p\pi$ bonding. Charge transfer would then occur into these orbitals from the lone pairs on the halide ion. Since charge disturbance has also been indicated by the IR study in the 1600–1300 cm^{-1} region it is likely that this band has similar origin.

The 265–275 mμ *band*. In the tri-*p*-tolylphosphine there is a structureless band at 265 mμ. The corresponding phosphonium compounds, however, record maxima at 264 and 275 mμ. There is only a slight rise in the intensity of these bands as the alkyl chain is lengthened. There is no shift in the position of the bands and hence no change in the transition energy.

Fine structure in this region has been attributed to lack of conjugative interaction between the rings and the phosphorus atom.[14, 15] Obviously the utilization of the lone pair electron and a consequent change in hybridization is responsible for this phenomenon. However, with different steric distributions of the rings also, the dissipation of the energy of the electronically activated molecule would be hindered. The trivalent compounds on the other hand have a structureless band indicating that the dissipation of energy of the activated molecule is not retarded. This shows that the distribution of the rings is conducive to conjugation and that the lone pair on the phosphorus atom can stabilize a quinonoid structure of the ring.[16] The splitting of the band in this region may then be a result of an unsymmetrical structure of the compounds in so far as the orientation of the rings is concerned. The conclusions regarding the unsymmetrical structure of the compounds deduced from IR studies is supported also by the UV spectra.

EXPERIMENTAL

Tri-*p*-tolylphosphine was prepared by the Grignard method. The phosphonium compounds R(*p*-tol)$_3$P$^+$I$^-$ were obtained by refluxing an ethereal soln of the phosphine and the corresponding alkyl iodide. Compounds having R = Me, Et, n-Pr, n-Bu and n-hexyl were prepared. Except the n-Bu and n-hexyl-tri-*p*-tolylphosphonium compounds which are being reported here for the first time, others are already known. All these compounds have been characterized by analysis. They were purified by precipitation with ether from an alcoholic soln. Since the m.ps of the reported compounds are high special care was taken to dry the samples. They were precipitated in anhydrous solvents and then dried in vacuum. For comparison a sample of the Me compound was also prepared by dehydrating the hydrate (m.p. 108°) by heating in a drying pistol. Table 5 lists the analyses and the m.ps of the compounds.

IR spectra were recorded on Beckman IR-4 and Perkin–Elmer 237 spectrophotometers using Nujol mulls, KBr discs and $CHCl_3$ solns. Slight shifts have been noted when a comparison of the pellet and soln spectra was made. The bands listed here are for the soln spectra. UV spectra were recorded on a Beckman DK2 spectrophotometer. Spectroscopic Grade MeOH was used as solvent and the concentrations were so adjusted as to obtain the optical density in the range of 0·5 to 1·0 at λ_{max}.

Table 5

Compound	%C		%H		M.p.	
	Calc	Found	Calc	Found	Reported	Found
$(4\text{-}MeC_6H_4)_3MePI$	59·19	59·00	4·40	5·54	220[3] 192–193[4]	210
$(4\text{-}MeC_6H_4)_3EtPI$	60·00	59·18	5·60	5·68	185[5]	176
$(4\text{-}MeC_6H_4)_3n\text{-}PrPI$	60·70	60·74	5·91	6·02	182[5]	172
$(4\text{-}MeC_6H_4)_3n\text{-}BuPI$	61·43	61·01	6·14	6·30		162
$(4\text{-}MeC_6H_4)_3n\text{-}HexPI$	62·78	62·26	6·59	6·60		148

REFERENCES

[1] G. B. Deacon, R. A. Jones and P. E. Rogasche, *Austral. J. Chem.*, **16**, 360 (1963).
[2] G. Witschard and C. E. Griffin, *Spectrochimica Acta* **19**, 1905 (1963).
[3] P. W. Morgan and B. C. Herr, *J. Am. Chem. Soc.* **74**, 4526 (1952).
[4] G. B. Deacon and R. A. Jones, *Austral. J. Chem.* **16**, 499 (1963).
[5] A. Michaelis, *Liebigs Ann.* **315**, 43 (1901).
[6] A. R. Katritzky, *Quart. Rev.* **13**, 353 (1959).
[7] D. W. A. Sharp and N. Sheppard, *J. Chem. Soc.* 674 (1957).
[8] J. J. Daly, *J. Chem. Soc.* 3799 (1964).
[9] J. R. Van Wazer, *Phosphorus and its Compounds* Vol. 1; pp. 18 and 42. Interscience, New York (1958).
[10] M. A. A. Beg and M. S. Siddiqui, *Canad. J. Chem.* **43**, 608 (1965).
[11] R. D. Kross, V. A. Fassel and M. Margoshes, *J. Am. Chem. Soc.* **78**, 1332 (1956).
[12] E. Steger and K. Stopperka, *Chem. Ber.* **94**, 3023 (1961).
[13] W. R. Cullen and R. M. Hochstrasser, *J. Mol. Spectroscopy* **5**, 118 (1960).
[14] H. H. Jaffe and L. D. Freedman, *J. Am. Chem. Soc.* **74**, 1069 (1952).
[15] H. H. Jaffe, *J. Chem. Phys.* **22**, 1430 (1954).
[16] K. Bowden and E. A. Braude, *J. Chem. Soc.* 1073 (1952).