

# Physical Sciences Section

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## SPECTROSCOPIC STUDIES OF ORGANOPHOSPHORUS COMPOUNDS

### Part IX. IR Spectra of Tri-*o*-tolylphosphine and Alkyltri-*o*-tolylphosphonium Iodides\*

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**Abstract.** The IR spectra of tri-*o*-tolylphosphine and alkyl-tri-*o*-tolylphosphonium iodides where the alkyl group is methyl, ethyl, *n*-propyl or *n*-butyl group have been reported and assignments in the 1600–250  $\text{cm}^{-1}$  region made on the basis of band position and integrated intensity measurements. The intensity of the spectral bands of these compounds is comparable with *m*-tolyl and lower than the phenyl and *p*-tolyl compounds. This is suggested to be a result of steric-overcrowding. This phenomenon is found to decrease as the chain length is ascended as shown by the intensity of various modes in general and mode *n* in particular. The bands at 745, 540 and 504  $\text{cm}^{-1}$  are split into doublets or triplets with a separation of 10–40  $\text{cm}^{-1}$ . The splitting is discussed in terms of quaternization. The  $\nu_{\text{as}}$  P—C<sub>aliphatic</sub> absorbs weakly and occurs at  $780 \pm 10 \text{ cm}^{-1}$ .

The IR spectra of the tri-*m*-tolylphosphine and phosphonium iodides have been presented earlier<sup>1,2</sup> and bands in the 1600–250  $\text{cm}^{-1}$  have been assigned. We now present the spectra of the tri-*o*-tolylphosphine and phosphonium compounds in the same region. The vibration spectra of *o*-disubstituted benzenes have been studied by various workers and assignment of the bands has been made mainly by Green.<sup>3</sup> Deacon and Jones<sup>4</sup> have reported the X-sensitive and inplane C—H deformation modes of tri-*o*-tolylphosphine and methyltri-*o*-tolylphosphonium iodide.

The spectra of the *o*-disubstituted phosphonium compounds would be interesting since in our earlier papers we have hinted at the stereospecific overcrowding on the central phosphorus atom. On changing from the phosphine to the phosphonium compounds a change in the bond angles is expected and also a certain amount of relief in the hindrance to free rotation of the ring. The previous interpretations have been based on a propeller-shaped model for the compounds with hindrances in free rotation so that some of the modes which are observed in the phosphonium compounds are degenerate in the phosphine. A case in example is reported with regard to the (*k*) and (*l*) modes in the triphenylphosphine and modes (*h*) and (*g*) in *m*-tolylphosphine. In the latter compound a strong band occurs at 780  $\text{cm}^{-1}$  overlapping the X-sensitive modes in this region. On the other hand the expected bands are noted in the phosphonium compounds. It is indeed noted that like the *m*-tolyl phosphorus compounds the intensity of the methyltri-*o*-tolylphosphonium iodide is approximately the same as for the phosphine. Such an effect has not been noted in either the triphenyl or tri-*p*-tolyl com-

pounds. The intensity of the other alkylphosphonium compounds increases gradually with chain length suggesting that in the compounds other than the methyl analogue the steric-overcrowding has been relieved to a certain extent.

### Experimental

Tri-*o*-tolylphosphine was obtained from Eastman Kodak through the grant under the CIDA-NRC Associateship programme. The compound had m.p. 122–4° (reported<sup>4</sup> 125–126°). The phosphonium compounds were prepared by methods already described.<sup>1</sup> The reaction had to be carried out by refluxing for a longer time (1–3 hr). The yields were, however, poor specially for longer chain alkyls (Table 1).

The spectral bands were recorded as described earlier<sup>1</sup> on Beckman IR-10 spectrophotometer and are listed in Table 2.

TABLE 1. CHARACTERIZATION OF ALKYLTRI-*o*-TOLYLPHOSPHONIUM COMPOUNDS.

Compounds	M.p. (°C)	Carbon		Hydrogen	
		Calc	Found	Calc	Found
Me( <i>o</i> -tolyl) <sub>3</sub> PI	210	59.01	58.95	5.40	5.35
	reported <sup>4</sup> 234.5				
Et( <i>o</i> -tolyl) <sub>3</sub> PI	243	60.00	59.90	5.60	5.32
<i>n</i> -Pr( <i>o</i> -tolyl) <sub>3</sub> PI	238	60.70	60.67	5.91	6.21
<i>n</i> -Bu( <i>o</i> -tolyl) <sub>3</sub> PI	208	61.43	61.01	6.14	6.30

\*Part of the Ph. D. thesis submitted by Samiuzzaman to the University of Karachi, Karachi.

TABLE 2. IR ABSORPTIONS AND APPARENT INTEGRATED INTENSITIES OF TRI-*o*-TOLYLPHOSPHINE AND ALKYLTRI-*o*-TOLYLPHOSPHONIUM IODIDES.

<i>o</i> -T <sub>3</sub> P		Me- <i>o</i> -T <sub>3</sub> PI		Et- <i>o</i> -T <sub>3</sub> PI		n-Pr- <i>o</i> -T <sub>3</sub> PI		<i>n</i> -Bu- <i>o</i> -T <sub>3</sub> PI		Assignments
cm <sup>-1</sup>	A	cm <sup>-1</sup>	A	cm <sup>-1</sup>	A	cm <sup>-1</sup>	A	cm <sup>-1</sup>	A	
1585	812	1587	644	1585	1377	1587	1491	1585	1467	$\nu(\text{C—C})$ mode ( <i>k</i> )
1565	539	1560	657	1558	1169	1562	1976	1562	1792	$\nu(\text{C—C})$ mode ( <i>l</i> )
1465	2633	1468	3460	1465	3831	1470	sh	1460	sh	$\nu(\text{C—C})$ mode ( <i>n</i> )
1445	2997	1445	2877	1445	3199	1440	3503	1440	5984	$\nu(\text{C—C})$ mode ( <i>m</i> )
1420	sh	1525	sh	1418	sh	1420	sh	1420	sh	$\delta_{\text{as}}\text{CH}_3$
		1400	320	1405	sh					
1375	769	1378	624	1375	1027	1394	2635	1390	2695	
						1375	sh	1380	2195	
1280	sh	1280	sh	1278	2789	1270	3049	1280	4138	$\nu(\text{C—C})$ mode ( <i>o</i> )
1265	1630	1278	1805							
								1220	863	X-sensitive
1195	822	1195	1468	1190	1863	1190	1317	1195	2355	$\beta(\text{C—H})$ mode ( <i>a</i> )
				1168	1027	1170	983	1160	941	
				1155	1058	1155 <sub>m</sub>	818			
1125	1246	1130	1287	1130	3109	1130	6310	1130	2818	X-sens. mode ( <i>q</i> )
		1065	1677	1072	1049	1010				CH <sub>3</sub> rocking + X-sensitive
1025	1414	1537	1025	2987	1030	2065	1030	1035	2396	$\beta(\text{C—H})$ mode ( <i>b</i> )
975	903	985	538	995	913	800	990	990	1549	$\gamma(\text{C—H})$ mode ( <i>j</i> )
940	386	960	224							$\gamma(\text{C—H})$ mode ( <i>h</i> )
		890	sh	885	1022			900	1628	CH <sub>3</sub> rocking
		885	4428							
860	482			865	962			860	895	$\gamma(\text{C—H})$ mode ( <i>i</i> )
795	282	789	1135	798	2725	800	1787	800	2451	X-sensitive
760	sh	778	1590	768	3728	765	2557	765	3607	$\nu_{\text{as}}\text{P—C}$ aliphatic
750	900	755	1958	760				760	3057	$\nu(\text{C—H})$ mode ( <i>g</i> )
740	6521	745	2892	75	5870	745	3690	750	4032	
718	149			715	2598	715	1228	718	2287	
		703	6543	705	1224	705	959	708	1948	$\varphi(\text{C—C})$ mode ( <i>v</i> )
				695	812					
		675	8026	685	620	680	1023	680	698	X-sens. mode ( <i>r</i> )
				670	271					
555	451			555	1493	555	1406	557	1368	
542	804	542	8561	544	1536	545	1032	545	788	X-sens. mode ( <i>t</i> )
						532	443	535	680	
504	627	510	1442	515	1500	520	1623	523	1486	$\varphi(\text{C—C})$ mode ( <i>w</i> )
		497	2038	494	888	500	1239	500	1308	
		470	1080	475	1571	475	1619	478	1081	Combination
		455	1144	460	1279	463	1698	465	1538	$\varphi(\text{C—C})$ mode ( <i>x</i> )
445	2647			445	1272	450	1789	455	2139	
420	643	430	989	420	493	440		420	817	X-sens. mode ( <i>y</i> )
370	839	385	904	370	475	370	664	370	526	X-sens. mode
		365	209			360	852	340	938	
265	478									
250	320							260	666	X-sens. mode ( <i>u</i> )

### Results and Discussion

The vibrations of the *o*-tolylphosphorus compounds are expected to be similar to those of the unsymmetrical *o*-disubstituted benzenes having *C<sub>s</sub>* symmetry.

Katritzky and Jones<sup>5</sup> have discussed the spectra in terms of the intensity and have classified them as donors, acceptors, halogens and weakly interacting substituents. Such a classification is helpful as would be apparent from the following discussion. Contrary

to expectations the formal positive charge on the phosphorus atom in the phosphonium compounds does not bring about any significant enhancement in the intensity on quaternization in contrast with the triphenyl and tri-*p*-tolyl analogues. This is similar to the *m*-tolyl compounds.<sup>2</sup>

**1600–1200 cm<sup>-1</sup> Region.** This region is characteristic of C—C skeletal vibration modes, (*k, l, m* and *n*), two CH<sub>3</sub> asymmetric deformation modes and a ring CH<sub>3</sub> symmetric deformation. Deacon and Jones have

reported only two bands in this region for the phosphine at 1587 and 1560 and three for methyltri-*o*-tolyl phosphonium iodide at 1587, 1562 and 1540  $\text{cm}^{-1}$ . This study has noted nearly all the expected bands in the region. Mode (*k*) absorbs at  $1575 \pm 5 \text{ cm}^{-1}$  while (*l*) occurs at  $1560 \pm 2 \text{ cm}^{-1}$ . Thus unlike the phenyl compounds these two modes are clearly resolved. Both the bands are of moderate intensity, although in methyltri-*o*-tolylphosphonium iodide, where a doublet has been observed, these absorptions are weaker than in the phosphine. The intensity is, however, higher in the case of ethyl, *n*-propyl and *n*-butyltri-*o*-tolylphosphonium iodides. These two bands occur at 1590 and 1562  $\text{cm}^{-1}$  in *o*-iodotoluene and at 1592 and 1565 in *o*-bromotoluene,<sup>3,6</sup> so that it is reasonable to assign these two bands to the *k* and *l* modes. As regards the intensity it is found that the same increases with chain length. If the donor-acceptor criteria of Katritzky is correct then this could be taken as an evidence that the available orbitals of the quaternary phosphorus atom behave as an acceptor of the  $\pi$ -character from the *o*-substituted tolyl group. The dependence of intensity on the chain length also indicates that the inductive effect of the alkyl group is transmitted to the ring through the positive central atom.

A very strong band found at  $1465 \pm 5 \text{ cm}^{-1}$  in the spectrum of the phosphine as well as in the methyl and ethylphosphonium compounds and as a shoulder in the *n*-propyl and *n*-butyl compounds is assigned to mode (*n*), in accord with the positions suggested by Katritzky. In our earlier papers<sup>1,2</sup>, this mode has been described as a tilting vibration. Unlike the phenyl and *p*-tolyl compound the substituent positions are also involved in stretching the ring leading to its out-of-plane rotation. A large dipole change is, therefore, expected for the bilateral contraction and expansion of the ring with one of the *ortho* substituents as the central atom and another one interacting stereospecifically. A high intensity of this band is, therefore, a result of steric-overcrowding by the ring methyl group and the alkyl group on phosphorus and that is why an increase in chain length increases the intensity of an otherwise insensitive mode.

Mode (*m*) occurs at  $1440 \pm 5 \text{ cm}^{-1}$ . The intensity of this band has no uniform relation with the increase in chain length but it is quite high for propyl and butyl compounds. The high intensity is in line with the observation of Katritzky for the donor-acceptor type of molecules. A very weak band near 1420  $\text{cm}^{-1}$  appearing as a shoulder is assigned to  $\delta_s \text{ CH}_3$  because of its low intensity. The band near 1375  $\text{cm}^{-1}$  is found in the phosphine and methyl, ethyl and butyl compounds as a medium intensity band and as a shoulder in the propyltri-*o*-tolylphosphonium compound. This may, by virtue of its intensity and in analogy with the *m*-tolyl compounds be assigned to the symmetric  $\text{CH}_3$  bending vibrations.

**1300-900  $\text{cm}^{-1}$  Region.** For *o*-disubstituted-benzenes mode (*o*), two  $\beta(\text{C}-\text{H})$  one  $\gamma(\text{C}-\text{H})$ , two  $\text{CH}_3$  rocking and three X-sensitive modes ( $\nu_{11}$ ,  $\nu_{13}$  and  $\nu_{14}$ ) are expected to absorb in this region.

Mode (*o*) usually absorbs between 1275-1299  $\text{cm}^{-1}$  while in the spectra of the phosphonium compounds it occurs near 1280  $\text{cm}^{-1}$  and a gradual increase in its

intensity has been observed from phosphine to *n*-butylphosphonium compounds. This indicates the influence of alkyl group as well as of changes in hybridization on this vibration. A similar trend has also been noted in the phosphonium compounds reported earlier.<sup>2</sup> An X-sensitive mode is found to absorb at 1206  $\text{cm}^{-1}$  in *o*-iodotoluene and at 1233  $\text{cm}^{-1}$  in *o*-fluorotoluene.<sup>3</sup> The band at 1190  $\text{cm}^{-1}$  in the present case is not sensitive to changes in hybridization but there is a progressive rise in intensity as the chain length increases. Furthermore the intensity is enhanced several times in the phosphonium compounds. This band may, therefore, be the X-sensitive mode  $\nu_{11}$ .

The band found near 1150-60  $\text{cm}^{-1}$  which is more intense in the spectrum of the phosphine than in those of the phosphonium compounds has been assigned to the  $\beta(\text{C}-\text{H})$  vibration mode (*a*). In *o*-disubstituted-benzenes Green has also assigned it to a  $\beta(\text{C}-\text{H})$  mode (*a*). The X-sensitive mode (*q*) is found to absorb at 1125  $\text{cm}^{-1}$  in the phosphine and at 1130  $\text{cm}^{-1}$  in the phosphonium compounds. It may be noted that the intensity is quite high compared with the other phosphine or phosphonium compounds. The intensity of this mode also shows a regular increase with increase in chain length. A strong to medium intensity band is found to occur at about 1072  $\text{cm}^{-1}$  in all the alkyltri-*o*-tolylphosphonium compounds and is absent from the spectrum of the phosphine and is assigned to the X-sensitive mode  $\nu_{13}$ . This band is quite conspicuous and is diagnostic for the formation of phosphonium compounds. The  $\text{CH}_3$  rocking mode absorbs weakly near 1040 and is observed in methyl- and ethyltri-*o*-tolylphosphonium compounds. A weak methyl rocking frequency has been noted by Mooney<sup>6</sup> for *o*-halogenotoluenes. The band near 1025  $\text{cm}^{-1}$  has been assigned to  $\beta(\text{C}-\text{H})$  mode (*b*). Deacon and Jones<sup>4</sup> have also observed a weak band here and have assigned it similarly. Because of its low intensity the band near 975  $\text{cm}^{-1}$  is assigned to  $\gamma(\text{C}-\text{H})$  mode (*j*) in analogy with the halogenotoluenes where the same is noted at 970  $\text{cm}^{-1}$ .

**900-700  $\text{cm}^{-1}$  Region.** The P-C asymmetric stretching, two out-of-plane C-H deformations and one out-of-plane ring deformation modes are found to occur in this region.

Mallion, Mann, Tong and Wystrach<sup>7</sup> have studied a number of spectra of organophosphorus compounds and have assigned vibrations due to the P-methyl group. For methyltri-*o*-tolylphosphonium compounds they have observed a shoulder at 902  $\text{cm}^{-1}$  and a medium intensity band at 890  $\text{cm}^{-1}$  and have assigned it to P-methyl group frequency. In the present series of compounds we have recorded the P-Caliphatic at  $780 \pm 10 \text{ cm}^{-1}$ . The band at 765-778 in the present compounds is, therefore, assigned to this vibration. It may be noted that this absorption occurs in a very complex region but it can be sorted out from the others by its absence from the spectrum of the phosphine.

The band at 935  $\text{cm}^{-1}$  due to  $\gamma(\text{C}-\text{H})$  is insensitive to the substituent in the halogenotoluenes. This band is noted only in the phosphine and its methylphosphonium iodide. In the spectrum of the latter compound a shoulder at 890  $\text{cm}^{-1}$  and a strong band at 885  $\text{cm}^{-1}$  have been observed and assigned to  $\text{CH}_3$  rocking vibrations since these absorptions are absent

from the spectrum of the phosphine and the intensity is of decreasing order within the series. In n-propyl and n-butyl compounds the corresponding bands are observed at 885 and 900  $\text{cm}^{-1}$  respectively. The band at 860  $\text{cm}^{-1}$  is assigned to another  $\gamma(\text{C—H})$  mode (*i*) in analogy with the halogenotoluenes and similarly the one at 795–800  $\text{cm}^{-1}$  to an X-sensitive vibration  $\nu_{16}$ . It may be noted that the latter occurs towards higher frequencies in the phosphonium compounds.

Another characteristic feature which is observed in this region is the splitting of bands occurring at 743–54 assigned to  $\gamma(\text{C—H})$  mode (*g*) and at 693–704  $\text{cm}^{-1}$  to  $\phi(\text{C—C})$  mode (*v*) in *o*-halogenotoluenes. The former is split into two to three bands at 740–760  $\text{cm}^{-1}$  in the phosphine and the phosphonium compounds while the latter is observed at 703–718  $\text{cm}^{-1}$ . The splitting is consistent in all the spectra recorded here. As stated earlier for *n* mode the rings would be rotated to relieve the strain due to steric-overcrowding expected in tri-*o*-tolylphosphine and phosphonium compounds. The effect is more marked here because of the nature of these vibrations. Consequently the intense single band with a shoulder in the phosphine is now observed with clear separation as we go higher up in the series.

**650–250  $\text{cm}^{-1}$  Region.** The absorptions expected in this region are due to the X-sensitive and out-of-plane ring deformation modes. The 675  $\text{cm}^{-1}$  band is observed only in the spectra of the phosphonium compounds. It is sufficiently intense and is assigned to the X-sensitive mode. The bands at 555 and 542  $\text{cm}^{-1}$  are both a result of splitting of the main band at 538–576  $\text{cm}^{-1}$  occurring in the halogenotoluenes and is assigned to X-sensitive mode (*r*). The band at 504  $\text{cm}^{-1}$  is another ring deformation  $\phi(\text{C—C})$  mode (*w*) which is split into a doublet in the phosphonium compounds. It is also noted that the band of medium

intensity occurring in the methylphosphonium compound at 510  $\text{cm}^{-1}$  is gradually shifted to higher frequency as we pass on to the n-butyl compound. Such a movement is also noted for the  $\phi(\text{C—C})$  mode (*w*) among the halogenotoluenes. This vibration seems to be mass sensitive. The band at 470–78  $\text{cm}^{-1}$  is most likely a combination mode  $2\nu_{29}=2 \times 235$ . Shifts to higher frequency with chain length also suggest it be an X-sensitive mode possibly  $\nu_{29}$ . The splitting in this region appears to be the characteristic pattern due to the absorption corresponding to nonequivalent rings. The band occurring in the phosphine at 420  $\text{cm}^{-1}$  moves to slightly higher frequency in the phosphonium compounds at 420–40  $\text{cm}^{-1}$  and is suggested to be the X-sensitive mode (*y*)  $\nu_{19}$ . The 370  $\text{cm}^{-1}$  band is sensitive to substituents. Here also the intensity variation suggests that it could be assigned to the X-sensitive vibration  $\nu_{20}$  and similar would be the case with the 250–260  $\text{cm}^{-1}$  band which is assigned to  $\nu_{21}$  also suggested by Green for the halogenotoluenes.

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