

## SPECTROSCOPIC STUDIES OF ORGANOPHOSPHORUS COMPOUNDS

Part VIII. IR Spectra of Tri-*m*-tolylphosphine and Alkyltri-*m*-tolylphosphonium Iodides\*

M. ARSHAD A. BEG and SAMIUZZAMAN

PCSIR Laboratories, Karachi 39

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**Abstract.** The spectra of tri-*m*-tolylphosphine and alkyltri-*m*-tolylphosphonium iodides, where the alkyl group is methyl, ethyl, *n*-propyl and *n*-butyl have been reported and assignments have been made for the 1600–250  $\text{cm}^{-1}$  region.

Integrated intensity measurement of a number of bands shows that the same is related to the length of the alkyl chain and/or quaternization. The intensity of the *m*-tolyl phosphorus compounds is on the whole lower than the phenyl and *p*-tolyl compounds which is explained in terms of induced polarization of the formal positive charge. The intensity variation of quite a few modes and particularly those in the 1600–1400  $\text{cm}^{-1}$  region has also been interpreted similarly. The high intensity of mode *n* here again suggests that this is due to steric overcrowding. Splitting of the  $\nu(\text{C—H})$  modes is the characteristic feature of *m*-tolylphosphonium compounds also. The  $\nu_{\text{as}} \text{P—C}_{\text{aliphatic}}$  is noted at 790  $\text{cm}^{-1}$ .

The IR spectra of the triphenylphosphine and phosphonium compounds has been reported in an earlier paper where we have interpreted the spectra and mode assignments on the basis of integrated intensity of the bands.<sup>1</sup> Here we present an extension of the work to the *m*-tolylphosphonium compounds. Mooney<sup>2</sup> has recorded the spectra of *m*-halogeno-toluenes and Green<sup>3</sup> has studied fifteen *m*-disubstituted benzenes and has given complete assignments of the fundamental frequencies. Deacon and Jones<sup>4</sup> have reported the absorption frequencies of tri-*m*-tolylphosphine and methyltri-*m*-tolylphosphonium iodide. Present assignments correspond to those of Green and have been numbered according to his, as well as Whiffens notations.<sup>5</sup> Compared with the frequencies given by Deacon and Jones slight differences have been noted here in certain band positions.

### Experimental

The phosphine and phosphonium compounds were prepared as described earlier. The analysis and m.p. are listed in Table 1. The spectra were recorded on a Beckman IR-10 spectrophotometer at the University of Western Ontario under the CIDA-NRC associateship programme.

The spectral bands, their intensity and assignments are listed in Table 2.

### Results and Discussion

The spectra of tri-*m*-tolylphosphine and alkyltri-*m*-tolylphosphonium compounds are similar to those of unsymmetrical *m*-disubstituted benzenes having  $C_s$  symmetry. The spectral intensities of these compounds, as a class, are lower than the corresponding *p*-tolyl compounds. It is possible to explain the reduction in intensity in terms of the effect of formal

positive charge or the delocalization of the positive charge under induced polarization. A reduction in intensity would occur if donor acceptor groups are present in the *meta*-positions. This places the phosphorus cation as an acceptor. It can also be said that the phosphorus cation has a deactivating influence in the *meta*-position. Since there are three *meta*-substituted rings it implies that the deactivation is induced over the entire ring system.

The intensities of absorption of the methyltri-*m*-tolylphosphonium compound are either of the same order or are lower than for the phosphine for quite a few modes excepting the X-sensitive ones. This shows that the steric interaction of methyl groups is of the same order as the lone-pair in the phosphine. Perhaps the lone-pair-bond-pair repulsions and the repulsions due to the methyl group cause the same amount of stereospecific overcrowding on the central atom so that there is no change in the transition dipole.

In his study of *meta*-disubstituted benzenes Katritzky<sup>6</sup> has noted that the bands between 1600 and 1400  $\text{cm}^{-1}$  due to  $\nu(\text{C—C})$  modes are found at higher frequencies if the substituents are strongly electron attracting and the position is gradually lowered with decreasing electron withdrawing ability. It has been observed during this study that for *k* and *l* modes the positions are higher suggesting again that the phosphorus cation acts as an electron attracting substituent in the *meta*-position. Similarly the *m* mode occurs in tri-*m*-tolylphosphine at a higher wavelength than in the onium compounds and these positions in turn are higher compared with the unsymmetrical *m*-substituted benzenes. However, the *n* mode absorbs at a lower frequency. Katritzky has suggested this band to be obscured in *m*-disubstituted compounds. In the present case a very high intensity of this band has been recorded.

**1600–1300  $\text{cm}^{-1}$  Region.** For a *meta*-substituted toluene four skeletal modes *k*, *l*, *m* and *n*, one methyl symmetric and one asymmetric bending vibrations

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TABLE 1. CHARACTERIZATION OF TRI-*m*-TOLYLPHOSPHINE AND ALKYLTRI-*m*-TOLYLPHOSPHONIUM IODIDES.

Compound	M.p. (°C)	C (%)		H (%)	
		Cal	Found	Cal	Found
( <i>m</i> -Tolyl) <sub>3</sub> P	85 (reported; 100)	82.85	82.39	6.90	6.89
Me( <i>m</i> -Tolyl) <sub>3</sub> PI	165 (reported; 167.68)	59.01	59.40	5.40	5.34
Et( <i>m</i> -Tolyl) <sub>3</sub> PI	160	60.00	59.83	5.60	5.62
<i>n</i> -Pt( <i>m</i> -Tolyl) <sub>3</sub> PI	164	60.70	59.28	5.91	5.95
<i>n</i> -But( <i>m</i> -Tolyl) <sub>3</sub> PI	150	61.43	61.40	6.14	6.04

TABLE 2. IR ABSORPTION AND INTEGRATED INTENSITIES OF TRI-*m*-TOLYLPHOSPHINE AND ALKYLTRI-*m*-TOLYLPHOSPHONIUM IODIDES.

<i>m</i> -T <sub>3</sub> P		Me- <i>m</i> -T <sub>3</sub> PI		Et- <i>m</i> -T <sub>3</sub> PI		<i>n</i> -Pr- <i>m</i> -T <sub>3</sub> PI		<i>n</i> -But- <i>m</i> -T <sub>3</sub> PI		Assignment	
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		
1590	712	1595	82	1595	759	1592	45	1595	606	ν(C—C) mode k	ν <sub>5</sub>
1580	sh	1580	60	1580	315	1585	405	1575	457	ν(C—C) mode l	ν <sub>6</sub>
1470	928	1490	320	1485	954	1480	996	1475	1220	ν(C—C) mode m	ν <sub>7</sub>
1450	618	1470	294	1450	865	1450	950	1450	1443	δ <sub>as</sub> CH <sub>3</sub>	
1400	410	1410	798	1410	773	1405	941	1405	555	ν(C—C) mode n	ν <sub>8</sub>
1380	sh			1385	548	1380	548			δ <sub>s</sub> CH <sub>3</sub>	
1320	194	1330	128	1328	366	1314	243	1315	945	Combination or β(C—H) mode e	ν <sub>9</sub>
1270	247					1272	546			ν(C—C) mode o	ν <sub>10</sub>
1222	233	1225	59	1225	366	1228	136	1225	485	X-sens mode	ν <sub>11</sub>
1208	241										
1172	241			1182	107	1175	295	1180	131	Combination or β(C—H) mode c	ν <sub>12</sub>
1105	929	1120	1296	1120	1750	1118	2618	1115	3034	X-sens mode q	ν <sub>13</sub>
1040	329	1045	24	1045	495	1082	522	1045	664	CH <sub>3</sub> rocking and β(C—H) mode b	ν <sub>14</sub>
1000	287	1000	83	995	666	995	728	998	960	Ring breath mode p	ν <sub>15</sub>
910	83	910	86	920	153	993	194	965	528	γ(C—H) mode j or X-sens	ν <sub>22</sub> ν <sub>16</sub>
890	215	885	sh	895	161	875	637	885	2126	γ(C—H) mode h	ν <sub>23</sub>
				878	651	854	375	870	1391	γ(C—H) mode g	ν <sub>24</sub>
		800	sh	800	1426	800	2178	800	800		
		790	566	788	559	785	831	782	3445	ν <sub>as</sub> P—C (alkyl) stretching	
780	1523	775	764	775	1098	774	1023	760	sh	γ(C—H) mode i	ν <sub>25</sub>
				740	1180	730	907	735	1154		
700	2708			700	1577	695	1397	695	3116	φ(C—C) mode v	ν <sub>26</sub>
650	171	645	2390	270	164					X-sens mode r	ν <sub>17</sub>
				650	51						
572	77										
560	174			560	558	560	413	560	682		
556	86	550	240	550	163	550	163	545	404	φ(C—C) mode w	ν <sub>27</sub>
545	86										
540											
520	119	525	80	522	146	535	15	535	393		
						525	17	525	476	X-sens mode t	ν <sub>18</sub>
488	130	270	1224	465	1170	475	1351	480	900	X-sens mode y	ν <sub>19</sub>
								465	255		
448	640	445	234	448	259	455	369	450	2013	φ(C—C) mode x	ν <sub>28</sub>
375	69			390	2					Combination	ν <sub>30</sub>
				355	29						
270	89	265	34	265	26			265	197	X-sens mode u	ν <sub>20</sub>

A, integrated intensity; T, tolyl.

are expected to absorb in this region.  $\nu(\text{C—C})$  mode *k* occurs in *m*-chlorotoluene at  $1604\text{ cm}^{-1}$  while in *m*-bromo and *m*-iodotoluene it occurs at  $1599$  and  $1593\text{ cm}^{-1}$  respectively. In the spectrum of the phosphine this mode absorbs at  $1590\text{ cm}^{-1}$  and in the phosphonium compounds it is noted at  $1595\text{ cm}^{-1}$ . The order of intensity for this mode is:  $n\text{-Pr-}m\text{-T}_3\text{PI} < \text{Me-}m\text{-T}_3\text{PI} < m\text{-T}_3\text{P} < \text{Et-}m\text{-T}_3\text{PI} < n\text{-But-}m\text{-T}_3\text{PI}$ . Mode 1 absorbs in the phosphine as a shoulder at  $1580\text{ cm}^{-1}$  and in the phosphonium compounds at  $1580 \pm 5\text{ cm}^{-1}$  while the same occurs in the *m*-chloro, *m*-bromo and *m*-iodotoluenes at  $1578$ ,  $1568$  and  $1564\text{ cm}^{-1}$  respectively. The intensity increases regularly in the order  $m\text{-T}_3\text{P} < \text{Me-}m\text{-T}_3\text{PI} < \text{Et-}m\text{-T}_3\text{PI} < n\text{-Pr-}m\text{-T}_3\text{PI} < n\text{-But-}m\text{-T}_3\text{PI}$ .

An increase in intensity is noted with an increase in the chain-length of the alkyl group attached to phosphorus. The band at  $1470\text{ cm}^{-1}$  in the phosphine and at  $1475$  in the phosphonium compounds may be assigned to mode *m*. This band shifts to higher frequencies by approximately  $20\text{ cm}^{-1}$  in the methyl compound, by  $15\text{ cm}^{-1}$  in ethyl,  $10\text{ cm}^{-1}$  in propyl and  $5\text{ cm}^{-1}$  in the butyl compound. Except for the methylphosphonium compound nearly all the others have the same order of intensity for this mode. This can be explained on the basis of the electron withdrawing ability of the phosphorus cation. The positive inductive effect of the alkyl group is transmitted to the ring through the cation, i.e. the deactivation of the ring at the *meta*-position is further affected by the induced polarization of the alkyl group and the position of the band changes because the higher the inductive effect, the higher is the shift.

The band at  $1450\text{ cm}^{-1}$  is consistent in its position in all the compounds and in agreement with Green this has been assigned to the methyl asymmetric bending vibration. The band at  $1405 \pm 5\text{ cm}^{-1}$  is observed as a strong band in this region in the phosphine as also in the phosphonium compounds. Deacon and Jones have also reported this band and Green has assigned the same to the combination of  $416$  and  $1002\text{ cm}^{-1}$  fundamental vibrations which does not seem to be in order in the present case. As mentioned above this is the region for  $\nu(\text{C—C})$  mode *n*. In our earlier studies mode *n* has been found to absorb strongly and it has been suggested that this is due to the stereospecific orientation of the rings whereby the tilting or the out-of-plane stretching vibration of the ring attains a higher transition dipole and hence absorbs strongly. In the *m*-substituted toluene derivatives of phosphorus the same trend is noted for this band and hence it has been assigned to mode *n*. The phosphine absorbs at  $1380\text{ cm}^{-1}$  as a weak shoulder and this absorption is noted only in ethyl and propyl-tri-*m*-tolylphosphonium compounds where it absorbs weakly. This is assigned to methyl symmetric bending mode. The in-plane  $\beta(\text{C—H})$  mode *e* occurring in the halogenotoluenes at  $1295\text{--}1300\text{ cm}^{-1}$  is most probably masked by the band at  $1320$  which is suggested to be a combination band of fundamental X-sensitive vibrations ( $\nu_{13}$ ) and ( $\nu_{29}$ ), the latter has not been observed here. In the case of phosphine the position is  $1105 + 215 = 1320\text{ cm}^{-1}$  and for the phosphonium compounds  $1120 + 210 = 1330\text{ cm}^{-1}$ . It may be noted that mode *q* as well as this band shift

to lower frequencies as the series is ascended. There is also a progressive increase in intensity as the chain-length increases and is in the order  $\text{Me-}m\text{-T}_3\text{PI} < m\text{-T}_3\text{P} < n\text{-Pr-}m\text{-T}_3\text{PI} < \text{Et-}m\text{-T}_3\text{PI} < n\text{-But-}m\text{-T}_3\text{PI}$ . The positive inductive effect would particularly affect the X-sensitive modes and hence the assignment of this band as a combination mode of X-sensitive vibration is justified.

**1300–900  $\text{cm}^{-1}$  Region.** A *m*-disubstituted benzene has absorptions corresponding to three  $\beta(\text{C—H})$  modes *b*, *c* and *e*, three X-sensitive and two ring vibration modes *o* and *p* in this region. A weak band at about  $1270\text{ cm}^{-1}$  observed in tri-*m*-tolylphosphine and in *n*-propyl-tri-*m*-tolylphosphonium iodide has been assigned to mode *o*. The band at  $1222\text{ cm}^{-1}$  has been assigned to the X-sensitive mode  $\nu_{11}$  and the intensity variation supports this assignment. The one of low intensity occurring near  $1172\text{--}82\text{ cm}^{-1}$  in the phosphine, ethyl, *n*-propyl and *n*-butyl-tri-*m*-tolylphosphonium iodide might be a combination mode of two X-sensitive modes *r* and *t* at  $650$  and  $520\text{ cm}^{-1}$  but it is more likely the  $\beta(\text{C—H})$  mode *c* although it is a little too high for this frequency as compared with halogenotoluenes where it occurs at  $1165\text{ cm}^{-1}$ .

A very strong band at  $1105$  in phosphine and at  $1120\text{ cm}^{-1}$  in the phosphonium compounds has been assigned to the X-sensitive mode *q* because of its shift to higher frequencies on quaternization. This is also in agreement with the observations of Deacon and Jones.<sup>4</sup> Mooney<sup>2</sup> has assigned this absorption to C—X stretch. This band is characteristic of aryl phosphonium compounds. Witchard and Griffen<sup>7</sup> have also observed this band in all the compounds having at least one phenyl group attached to the phosphorus atom and have assigned it to the phenyl group perturbed by a heavy substituent atom.

A weak to medium intensity band is found in the phosphine and phosphonium compounds near  $1040\text{ cm}^{-1}$ . This may be assigned to  $\text{CH}_3$  rocking but this is also the range for the  $\beta(\text{C—H})$  mode *b* as also suggested by Deacon and Jones for the spectra of phosphine and methyltri-*m*-tolylphosphonium iodide. Ring breathing vibration mode *p* absorbs near  $1000\text{ cm}^{-1}$  with the following order of intensity:  $\text{Me-}m\text{-T}_3\text{PI} < m\text{-T}_3\text{P} < \text{Et-}m\text{-T}_3\text{PI} < n\text{-Pr-}m\text{-T}_3\text{PI} < n\text{-But-}m\text{-T}_3\text{PI}$ . The band at about  $910\text{ cm}^{-1}$  may be assigned to the X-sensitive vibration  $\nu_{16}$  occurring at  $924\text{ cm}^{-1}$  in bromotoluene but in the less electronegative halogenotoluenes, the same is noted at  $819\text{--}958\text{ cm}^{-1}$ . While the shift of this band to higher frequency on quaternization supports the assignment of X-sensitive mode, the higher position than halogenotoluenes is not justifiable. The region  $910\text{--}960\text{ cm}^{-1}$  is also the range for  $\gamma(\text{C—H})$  mode *j*. It is possible that the  $\gamma(\text{C—H})$  mode has masked the X-sensitive mode consequently it has been assigned to both the vibrations.

**900–700  $\text{cm}^{-1}$  Region.** This region is a complex part of the spectrum. Three  $\gamma(\text{C—H})$  modes *h*, *g* and *i*, one  $\varphi(\text{C—C})$  mode *v*, and the P—C<sub>aliphatic</sub> stretching frequency are expected to absorb here.

As stated earlier the single band due to  $\gamma(\text{C—H})$  occurring at  $780\text{ cm}^{-1}$  in the spectrum of the phosphine is split into three to four bands in the phosphonium

compounds and so is the case with the absorption band at  $890\text{ cm}^{-1}$  due to  $\gamma(\text{C—H})$  in the phosphine which on removal of degeneracy on quaternization is split into two to three bands. This has been seen in the previous cases to be characteristic of the positive charge on the phosphorus atom. The split bands are of medium intensity. The bands at  $890$  and  $878\text{ cm}^{-1}$  are attributed to  $\gamma(\text{C—H})$  modes h and g. Two weak bands are found at  $800$  and  $790\text{ cm}^{-1}$  which are absent in the phosphine. They may be assigned to P—C (alkyl) antisymmetric stretch in agreement with our previous assignments. The absorption near  $775\text{ cm}^{-1}$  in the phosphonium compounds may be due to  $\gamma(\text{C—H})$  mode i and the one near  $700\text{ cm}^{-1}$  due to  $\varphi(\text{C—C})$  mode v.

**700–250  $\text{cm}^{-1}$  Region.** In this region the out-of-plane ring deformation modes w and x, the in-plane ring deformation modes s and t and X-sensitive modes r, t, y and u are expected to absorb.

For the *m*-iodotoluene Green has assigned a band occurring at  $657\text{ cm}^{-1}$  to the X-sensitive mode r. The band at  $650\text{ cm}^{-1}$  observed in tri-*m*-tolylphosphine and its methyl and ethylphosphonium compounds, with a very high intensity for the methyl compound has been assigned to the same mode.

Tri-*m*-tolylphosphine and phosphonium compounds show a characteristic absorption pattern in the  $556\text{--}445\text{ cm}^{-1}$  region. Tri-*m*-tolylphosphine shows a weak absorption at  $572\text{ cm}^{-1}$ . All the phosphonium compounds and the phosphine have medium to strong bands at  $560\text{ cm}^{-1}$  and  $545\text{ cm}^{-1}$ . In the propyl and butyltri-*m*-tolylphosphonium compounds the latter is split into a doublet occurring at  $545$  and  $535\text{ cm}^{-1}$ . The absorption here is due to the out-of-plane ring deformation mode w as also suggested by Deacon and Jones. The single band in the phosphine spectrum splits into three bands occurring at about  $556$ ,  $545$ ,  $540\text{ cm}^{-1}$  and absorb strongly.

A band at  $520\text{ cm}^{-1}$  of varying intensity is found in all the *m*-tolylphosphonium compounds and the

phosphine. This band has been assigned to the X-sensitive vibration  $\nu_{18}$  mode t.

The strong band near  $470 \pm 10\text{ cm}^{-1}$  is assigned to another X-sensitive vibration  $\nu_{19}$  mode y. This band absorbs strongly in the phosphine whereas in the phosphonium compounds it has the following pattern:  $m\text{-T}_3\text{P} < n\text{-But-}m\text{-T}_3\text{PI} < \text{Et-}m\text{-T}_3\text{PI} < \text{Me-}m\text{-T}_3\text{PI} < n\text{-Pr-}m\text{-T}_3\text{PI}$ . Another medium intensity band near  $450\text{ cm}^{-1}$  may be due to the out-of-plane ring deformation mode x as also assigned by Deacon and Jones.

Two weak bands near  $375$  and  $270\text{ cm}^{-1}$  have also been observed. The former is noted only in the phosphine and the ethyl phosphonium compounds. Their intensity has no relation with the alkyl group on the phosphorus atom. The latter is assigned to the X-sensitive mode u in agreement with the position in halogenotoluenes. The former is probably  $2\nu_{30} = 2 \times 187$  which is also near the position in nitrotoluene.<sup>7</sup> Thus the two unobserved X-sensitive bands  $\nu_{29}$  and  $\nu_{30}$  are estimated at  $210 \pm 5$  and  $187 \pm 5\text{ cm}^{-1}$ .

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