

THE INFRARED SPECTRA OF ALKYLTRI-*p*-TOLYL ARSONIUM COMPOUNDS

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The IR spectra of *p*-tolyl arsonium compounds have been recorded and assignments of the bands in 1600-700  $\text{cm}^{-1}$  region have been made. The intensity of the 1600  $\text{cm}^{-1}$  and 1490  $\text{cm}^{-1}$  bands are found to depend on lone pair interaction since the former is weak and the latter is strong in tri-*p*-tolyl arsine while it is the reverse in the *p*-tolyl arsonium compounds. The splittings in the 800  $\text{cm}^{-1}$  band are noted in the arsonium compounds and this together with the higher intensity of the 1410  $\text{cm}^{-1}$  band is suggested to imply an unsymmetrical orientation of the rings.

In our earlier studies on the selenium and phosphorus phenyls<sup>1,2</sup> and the phosphorus *p*-tolyls the shape and the intensity of the absorption bands were correlated with their structure. The variation in intensity of the IR bands in the 1600-1300 and 1200-1000  $\text{cm}^{-1}$  region for the tri-*p*-tolyl arsine and alkyltri-*p*-tolyl arsonium compounds can also be interpreted in terms of lone pair interaction with the  $\pi$  electrons of the rings. Similarly, the splitting in the 800-700  $\text{cm}^{-1}$  region as observed in earlier cases is a characteristic feature of the arsonium compounds also. It appears from the literature that although the IR of some *p*-tolyl arsonium compounds have been reported,<sup>3</sup> their assignments have not so far been made and hence this paper provides the same for the various absorptions.

## Experimental

*n*-Propyl- and *n*-butyltri-*p*-tolyl arsonium iodides are new compounds. The arsines were prepared by the Grignard method and were purified by recrystallization with an ether-benzene mixture. The arsonium compounds were prepared by refluxing an ethereal solution of the arsine with the respective alkyl halide. The arsonium compounds being insoluble were precipitated on cooling. The lower alkyls were obtained in about  $\frac{1}{2}$  hr while the higher alkyls or aryls required 2-3 hr refluxing. After washing them with ether they were subjected to further purification by dissolving in water. The crystals obtained from

the slow evaporation of the aqueous solution were heated to 110°C. They were further dried in a drying pistol. The higher alkyl members reacted with water giving an acid, and deposited a solid which was possibly due to hydrolysis. Their purification by this method was hence quite difficult. They also decomposed on standing. The analytical results (in Table 1) are therefore slightly in error. The m. ps are all uncorrected.

The spectra were run on freshly prepared samples. The IR was run on chloroform solution and intensity measurements were reported on this basis. Where overlapping bands occurred (e.g. in the 1200 and the 900-650  $\text{cm}^{-1}$  region) the same was obtained from KBr pellets and/or nujol mulls. The 1600-1300  $\text{cm}^{-1}$  region is not well resolved in solution and hence the spectra have been obtained using KBr pellets. These spectra are reported in Table 2. Since we find that the shape of the bands is equally important the spectra are given in Figs. 1-5.

## Discussion

In the tri-*p*-tolyl arsine the *k* and *l* modes (Whiffen's notation) are resolved and both have a weak intensity which shows that the substituent is weakly interacting. The *m* mode occurring at 1495  $\text{cm}^{-1}$  is very prominent and absorbs strongly, indicating a large dipole change accompanying this vibration. A high intensity for this mode has also been observed in the case of tri-*p*-tolyl

TABLE 1.—ANALYSIS OF THE ALKYL TRI-*p*-TOLYL ARSONIUM COMPOUNDS.

Compounds	M. ps		% C		% H	
	Found	Reported	Calc.	Found	Calc.	Found
( <i>p</i> -tolyl) <sub>3</sub> Me As <sup>+</sup> I <sup>-</sup>	167	179 176	53.87	53.60	4.89	4.90
( <i>p</i> -tolyl) <sub>3</sub> Et As <sup>+</sup> I <sup>-</sup>	150	158	54.76	54.41	5.15	5.14
( <i>p</i> -tolyl) <sub>3</sub> <i>n</i> -Pr As <sup>+</sup> I <sup>-</sup>	147	—	55.59	54.88	5.40	5.22
( <i>p</i> -tolyl) <sub>3</sub> <i>n</i> -Bu As <sup>+</sup> I <sup>-</sup>	60	—	56.39	54.02	5.64	5.37

TABLE 2.—IR ABSORPTION IN THE REGION 1600–670  $\text{cm}^{-1}$ .

$(4\text{-MeC}_6\text{H}_4)_3\text{As}$		$(4\text{-MeC}_6\text{H}_4)_3\text{-MeAs}^+ 1^-$		$(4\text{-MeC}_6\text{H}_4)_3\text{-EtAs}^+ 1^-$		$(4\text{-MeC}_6\text{H}_4)_3\text{-n-PrAs}^+ 1^-$		$(4\text{-MeC}_6\text{H}_4)_3\text{-n-BuAs}^+ 1^-$		$(4\text{-MeC}_6\text{H}_4)_4\text{-As} 1^-$		Assignment
1500	(4)	1600 1585	(22) (16)	1600	(19)	1600	(17)	1600 1596	(38) (7)	1603	(36)	C—C skeletal mode <i>k</i>
1565	(3)	1565 1530	(8) (6)	1565	(6)	1568 1548 1530	(7) (7) (7)	1570 1545	(9) (7)	1568 1550 1545	(10) (10) (9)	C—C- skeletal mode <i>l</i>
1495	(17)	1498	(14)	1496	(18)	1498	(11)	1495	(26)	1496 1480	(28) (15)	$\nu(\text{CC})$ ( $a_1$ ) C—C skeletal mode <i>m</i>
1435	(8)	1440 1430	(8) (7)sh	1456 1442	(14) (13)	1450 1442	(10) (10)	1440 1430	(20) (17)	1458 1445	(29) (16)	$\text{CH}_3$ anti-symmetric deformation
1395	(8)	1402	(21)	1400	(17)	1400	(16)	1400	(21)	1404	(26)	$\nu(\text{CC})$ ( $b_2$ ) C—C skeletal mode <i>n</i>
—	—	1390 1370	(7)sh (7)sh	1390 1370	(14) (11)	1390 1370	(11) (5)sh	1390 1370	(20) (12)	1390 1385	(20)sh (20)sh	$\text{CH}_3$ symmetrical deformation
1310	(5)	1320	(9)	1318	(7)	1335 1315	(12) (6)	1335 1315	(7) (12)	—	(20)	$\nu(\text{CC})$ ( $b_2$ ) C—C skeletal mode <i>o</i>
1270	(2)	1275	(5)	1280 1275	(5) (5)	1280 1270	(5) (5)	1280 —	(6) —	1280 —	(9) —	$\beta(\text{C—H})$ ( $b_2$ ) mode <i>e</i>
—	—	—	—	1235	(16)	1235	(12)	1235	(30)	—	—	$\text{CH}_2$ wagging
—	—	1193	(29)	1193	(17)	1192 1180	(17) (5)	1190	(28)	1195 1180	(40) (13)	$\beta(\text{C—H})$ ( $a_1$ ) mode <i>a</i>
—	—	1125	(18)	1152 1145 1125	(17) (13) (4)	1152 1130	(14) (4)	1125	(9)	—	—	$\beta(\text{C—H})$ ( $b_2$ ) mode <i>d</i>
—	—	1085	(79)	1085	(39)	1080	(40)	1080	(65)	1085	(79)	(X-sensitive) mode <i>q</i>
—	—	1040	(6)	1040	(12)	1038	(7)	1040	(12)	1045	(25)	$\text{CH}_3$ rocking
—	—	1018	(11)	1018	(11)	1018	(12)	1015	(24)	1020	(23)	$\beta(\text{C—H})$ ( $a_1$ ) mode <i>b</i>
945	w	—	—	975	w	—	—	972	w	—	—	$\gamma(\text{C—H})$ ( $b_1$ )
845	m	905 890 880	m m m	—	—	845	w	892	w	898	w	$\text{CH}_3$ rocking
805	vs	810 805 800	sh vs vs	818 803	s vs	810 802	vs vs	812 805 792	s vs s	810 800	s vs	$\gamma(\text{C—H})$ ( $b_1$ ) C—H out of plane deformation mode <i>f</i>
—	—	—	—	760	vs	728 720	s s	—	—	—	—	C—C symmetric stretching.
705	s	703	m	700	w	698	w	698	w	695	w	$\varphi(\text{CC})$ ( $b_1$ ) X-sensitive mode <i>r</i>

Intensities record in the solid phase are marked by letters, s strong, m medium, w weak, v very, sh shoulder. Figures in the bracket are the apparent extinction coefficients.

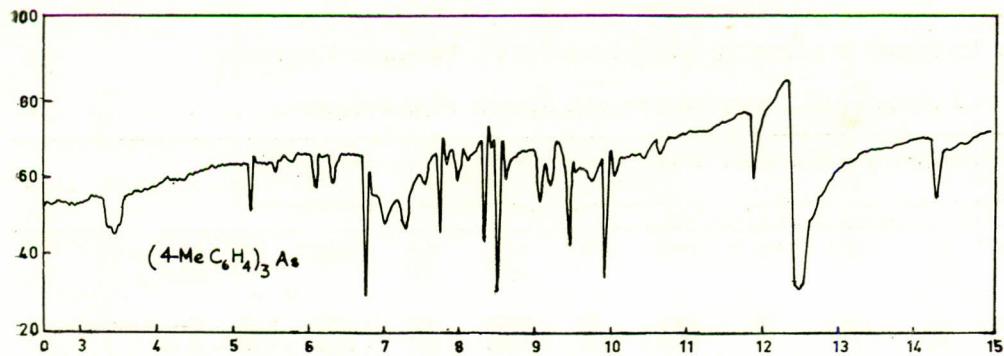


Fig. 1

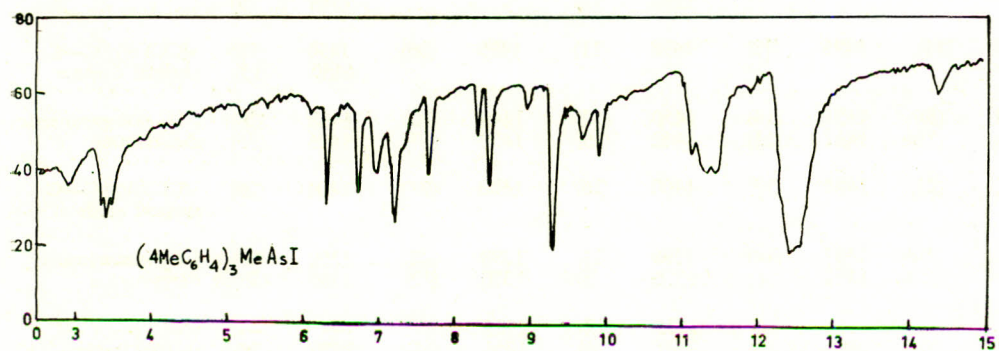


Fig. 2

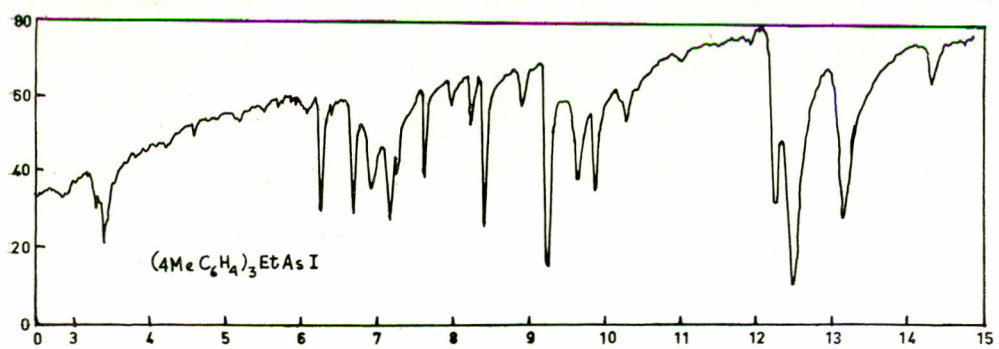


Fig. 3

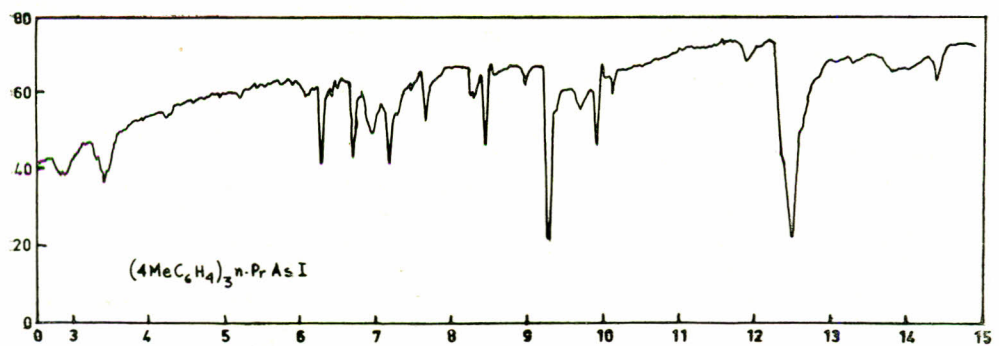


Fig. 4

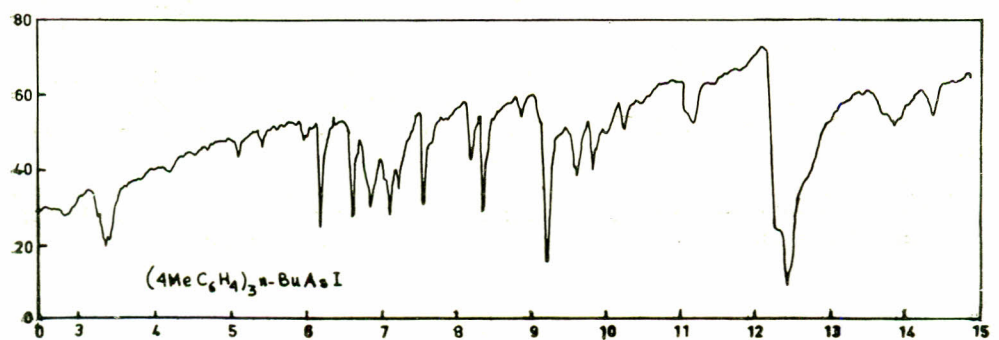


Fig. 5

phosphine<sup>2</sup>. It has been suggested by Mooney<sup>4</sup> that in the *p*-halogeno toluenes this band is due to methyl antisymmetric bending. The high intensity for this vibration is most likely due to charge disturbance in the ring as suggested by Katritzky and observed in earlier cases of the phenyls as well as the *p*-tolyls.<sup>2</sup>

Since mode *m* consists of dilation of the rings at the carbon adjacent to the substituent and contractions at the end *para* to it, it should be possible for the charge density to be easily shifted from the substituent to the other end of the ring. Consequently lone pair interaction will result in a higher transition dipole for this vibration. This might be the reason for the higher intensity of this vibration, as observed in a series of *p*-tolyl compounds having a substituent with a lone pair.<sup>6</sup> The onium compounds carrying no lone pair do not give rise to high intensity of this band. In such compounds mode *k* absorbs strongly. The latter absorption represents dilation at the *para* position and, according to Katritzky,<sup>5</sup> the intensity will be due to the algebraic difference of the interactions of the groups at the 1-4 positions. In this case the opposing effect of the methyl and the positively charged arsenic result in high intensity.

The *n* mode in *p*-tolyl compounds occurs at  $1409 \pm 8$   $\text{cm}^{-1}$ . In the arsine and the arsonium compounds there is a strong absorption at  $1395$ – $1405$   $\text{cm}^{-1}$ . The intensity of the absorption is highest in tetra-*p*-tolyl compound and quite low in the arsine. In the earlier papers we have suggested that the higher intensity of this mode is due to steric interaction and disymmetrical orientation of the rings. The tri-*p*-tolyl arsine having a low intensity vibration here may, therefore, be regarded as having a more symmetrical structure than its triphenyl analogue.

The methyl of the tolyl group is seen to absorb at  $1450$   $\text{cm}^{-1}$ . This band is absent in the triphenyl analogues, while the tri-*p*-tolyl arsine and the tetra-*p*-tolyl arsonium compounds have a band in this position. The methyl group of the alkyl chain on the other hand absorbs at a lower frequency and we find a weak band or a shoulder on the main band at  $1450$   $\text{cm}^{-1}$  having approximately same intensity. Similarly, the methyl symmetric deformation frequency occurs at  $1390$   $\text{cm}^{-1}$  and this band is also split into two bands, the lower frequency band is also assigned to the methyl deformation frequency of the alkyl chain while the higher one is due to the tolyl. A weak band occurring at  $1230$ – $40$   $\text{cm}^{-1}$  is assigned to  $\text{CH}_2$  wagging vibration and the medium intensity absorption at  $1310$ – $20$   $\text{cm}^{-1}$  to mode *o*. The

assignment of these bands agrees very well with those given by Cullen, Deacon and Green.<sup>7</sup>

**1300–950  $\text{cm}^{-1}$  Region.**—Mode *e* is a weak absorption and occurs at  $1275$   $\text{cm}^{-1}$ , but is not marked in all the arsonium compounds. A strong band at  $1190 \pm 5$   $\text{cm}^{-1}$  is consistent in all the compounds and is assigned to mode *a* and so is mode *d* occurring at  $1125$   $\text{cm}^{-1}$  which is the usual range of this vibration. The strong band at  $1085$   $\text{cm}^{-1}$  can easily be assigned to the *X* sensitive mode *q*. The band at  $1040 \pm 3$   $\text{cm}^{-1}$  is the  $\text{CH}_3$  rocking mode as also observed in the alkyltriphenyl arsonium compounds.<sup>7</sup> The medium intensity band at  $1018 \pm 2$   $\text{cm}^{-1}$  is due to mode *b*.

**1000–690  $\text{cm}^{-1}$  Region.**—Here the strong bands at  $803 \pm 2$  have been assigned to the C—H out-of-plane deformation. It is observed that this band is split into a doublet or a triplet in all the arsonium compounds, while tri-*p*-tolyl arsine has a single sharp band here. In our previous study on the *p*-tolyl phosphonium compounds also, a similar feature was noted and it was suggested that this is due to the unsymmetrical orientation of the rings.

The splitting, however, is of the order of  $10$ – $15$   $\text{cm}^{-1}$  and it is quite likely that this is due to lattice interactions. It has been observed from the X-ray studies of tetraphenyl arsonium iodide,<sup>8</sup> that the lattice has interpenetrating cations and anions. Since splittings have also been recorded in the spectra from nujol mulls it may not be entirely due to lattice interactions. The other absorptions which occur in this region are due to the  $\text{CH}_3$  rocking and C—C symmetric stretching and the ring deformation, and they have duly been assigned in Table 2.

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