

## THE IR AND UV SPECTRA OF ALKYLTRIPHENYLARSONIUM COMPOUNDS

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The IR and UV spectra of the methyl, ethyl, n-propyl and n-butyl-triphenyl- and tetraphenyl, arsonium compounds have been recorded. The neighbouring group effect is noted from the variation in the intensity of the 1430 and 1000 band with the alkyl chain. The UV studies support the findings of the IR spectra and indicate dissymmetry in the molecules.

In a recent study on the phenylselenium<sup>1</sup> and phenyl- and *p*-tolylphosphonium compounds<sup>2</sup> it was observed that a correlation of the structure of the compounds with the intensity of the various absorptions is possible. It was found that the lack of conjugation among the rings could also be deduced from the intensity of the bands in the 1600-1300 and 1300-950  $\text{cm}^{-1}$  and the splitting of the bands due to the C-H out-of-plane deformation in the 800-700  $\text{cm}^{-1}$  region. It is found that the shapes and the intensity of the bands in these regions have a characteristic pattern so that the previous generalizations regarding the orientation of the rings can safely be extended to the arsonium compounds. For the present study we have prepared a series of phenylarsonium iodides. It may be mentioned here that the spectra of the phenylarsonium compounds have appeared during recent years.<sup>3,4</sup> Our results are in close agreement with the reported frequencies.

### Experimental

The methyl- and ethyl-triphenyl and tetraphenylarsonium iodides are already known. n-Propyl- and n-butyl-triphenyl arsonium iodide are new compounds. The arsonium compounds were prepared by conventional methods. The analysis and melting point of the compounds are reported in Table 1. The higher alkyl compounds are unstable and decompose easily on standing. The analytical results are therefore slightly in error.

The spectra were recorded on freshly prepared compounds and the technique was the same as described earlier. The IR spectra were run on chloroform solutions as well as KBr pellets and nujol mulls. The bands in the 1600 to 1300  $\text{cm}^{-1}$  and 1300 to 950  $\text{cm}^{-1}$  region were recorded with chloroform solutions while those in the 900 to 650  $\text{cm}^{-1}$  region were recorded with KBr pellets and nujol mulls, and these are presented in Table 2 and depicted in Figs. 1-6. The UV spectra were recorded as reported earlier and are presented in Table 3.

### Discussion

It is noted that the spectra of the triphenylarsonic compounds are characteristic of the mono-substituted benzene and the absorptions due to the alkyl group in the arsonium compounds can be easily sorted out. The difference in the absorption pattern is seen to be in the intensity of the various bands, which has been shown to represent a change in the charge distribution in the ring.

*The 1600-1300  $\text{cm}^{-1}$  Region.*—The pattern of absorption in the triphenylarsine is quite similar to the isoelectronic triphenylselenonium chloride which suggests a similarity in the distribution of rings. The *k* and *l* modes in the case of triphenylarsine as well as the alkyltriphenylarsonium compounds are not resolved in the pellet or mull spectra but they do so in the solution. These bands are quite weak which suggests that the sub-

TABLE I.—ANALYSIS OF THE ALKYLTRIARYLARSONIUM COMPOUNDS.

Compound	M.p.	Carbon %		Hydrogen %	
		Calc.	Found	Calc.	Found
$\text{Ph}_3\text{MeAs}^+\text{I}^-$	167	50.89	50.86	4.03	4.17
$\text{Ph}_3\text{EtAs}^+\text{I}^-$	148	51.95	51.43	4.33	4.37
$\text{Ph}_3\text{nPrAs}^+\text{I}^-$	135	52.94	53.42	4.62	5.45
$\text{Ph}_3\text{n-BuAs}^+\text{I}^-$	100	53.87	53.45	4.89	4.81



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

$\text{Ph}_3\text{As}$	$\text{Ph}_3\text{MeAs}^+\text{I}^-$	$\text{Ph}_3\text{EtAs}^+\text{I}^-$	$\text{Ph}_3\text{n-PrAs}^+\text{I}^-$	$\text{Ph}_3\text{n-BuAs}^+\text{I}^-$	$\text{Ph}_4\text{As}^+\text{I}^-$	Assignment
1578 (5.8)	1600 (3.0)	1590 (2.4)	1592 (4.5)	1582 (2.8)	1585 (8.4)	C—C skeletal mode <i>k</i>
1565 (4.0)	1576 (2.7)	1576 (2.0)	1565 (4.0)	1566 (3.8)	1562 (10.2)	C—C skeletal mode <i>l</i>
1488 (12.0)	1484 (11.0)	1490 (11.0)	1490 (13.0)	1490 (12.0)	1490 (22.0)	C—C skeletal mode <i>m</i>
1478 (11.0)	—	—	—	—	—	—
—	1470 (6.0)	1455 (7.1)	1460 (8.8)	1470 (11.6)	—	CH <sub>3</sub> antisymmetric deformation
—	1465 (4.8)	—	—	1462 (11.6)	—	—
1437 (15.7)	1445 (32.4)	1440 (29.8)	1444 (31.6)	1443 (14.4)	1443 (44.0)	C—C skeletal mode <i>n</i>
—	—	1415 (5.0)	1420 (7.8)	1430 (12.5)	1423 (16.4)	CH <sub>3</sub> deformation
—	—	—	—	1425 (10.3)	—	—
—	1410 (7.0)	1400 (4.9)	1405 (5.8)	1400 (7.2)	—	CH <sub>3</sub> symmetric deformation
—	1400 (8.0)	1390 (4.9)	—	1390 (7.2)	—	—
—	1340 m	1340 w	1340 m	1358 w	1345 m	combination
—	—	—	—	1340 w	—	—
1308 m	1317 m	1315 m	1315 m	1310 w	1315 m	C—C skeletal mode <i>o</i>
1270 vw	—	—	—	—	—	mode <i>e</i>
1210 w	1230 mbr	1222 mbr	1190 sh	—	1200 sbr	mode <i>a</i>
1175 w	1210 mbr	1210 mbr	—	—	1190 sh	—
1152 m	—	—	1165 w	—	1165 m	mode <i>c</i>
1075 (17.8)	1087 (34.3)	1084 (27.0)	1083 (33.8)	1083 (34.4)	1090 (69.7 )	mode <i>q</i>
—	—	1080 (4.7)	—	—	1080 (37.0 )	—
—	—	—	1070 (7.4)	—	1075 (32.2 )	—
1065 (3.9)	—	1065 (4.8)	1067 (5.7)	1065 (7.7)	1065 (28.0 )	C—C— skeletal mode <i>q</i>
1023 (5.8)	1027 (3.9)	1023 (4.9)	1024 (6.7)	1025 (5.0)	1025 (28.4 )	mode <i>b</i>
—	1018 (3.0)	—	—	—	—	—
1000 (12.0)	1000 (17.7)	996 (22.4)	1000 (24.7)	1000 (28.4)	1000 (51.4 )	Ring breathing
—	925 } w	—	912 } vw	—	—	CH <sub>3</sub> rocking
—	912 }	—	900 }	—	—	—
—	900 } s	—	—	—	—	—
—	870 }	—	—	—	—	—
—	855 w	—	—	—	—	C—H out of plane deformation mode <i>f</i>
742 sh	755 }	758 }	750 }	755 }	755 wsh	C—C symmetric stretching
738 } vs	747 } vs	750 } s	746 } vs	745 } s	745 }	—
732 }	740 }	740 }	740 }	741 }	740 } vs	—
—	—	730 m	735 sh	735 sh	735 }	—
—	—	—	725 m	725 m	—	—
690 vs	690 s	690 s	690 s	690 s	690 s	out of plane ring deformation
668 w	684 m	684 m	685 s	685 m	685 sh	X-sensitive mode <i>r</i>

Intensities recorded in the solid phase are marked by letters, s=strong, m=medium, w=weak, v=very, sh=shoulder, br=broad. Figures in the brackets are the apparent extinction coefficients.

TABLE 3.—ABSORPTION MAXIMA AND MOLAR EXTINCTION COEFFICIENTS IN UV REGION.

Compound	$\lambda_{\text{max}}$ m $\mu$	Iog $\epsilon$	$\lambda_{\text{max}}$ m $\mu$	Iog $\epsilon$	$\lambda_{\text{max}}$ m $\mu$	Iog $\epsilon$	$\lambda_{\text{max}}$ m $\mu$	Iog $\epsilon$	$\lambda_{\text{max}}$ m $\mu$	Iog $\epsilon$	$\lambda_{\text{max}}$ m $\mu$	Iog $\epsilon$
$\text{Ph}_3\text{As}$	—	—	271.5	3.2	264	3.4	259	3.6	247	3.7	—	—
$\text{Ph}_3\text{MeAs}^+\text{I}^-$	—	—	270	3.4	264	3.5	258	3.4	252	3.2	228	4.3
$\text{Ph}_3\text{EtAs}^+\text{I}^-$	—	—	270	3.5	263.5	3.6	258	3.5	252	3.4	225.5	4.4
$\text{Ph}_3\text{n-PrAs}^+\text{I}^-$	290	3.5	270	3.5	264	3.5	258	3.4	252	3.2	229	4.4
$\text{Ph}_3\text{n-BuAs}^+\text{I}^-$	290	3.6	270.5	3.4	263.5	3.4	258	3.3	252	3.2	229.5	4.3
$\text{Ph}_4\text{As}^+\text{I}^-$	—	—	271	3.4	264	3.4	258.5	3.3	253	3.2	229.5	4.4

stituent interacts only weakly with the  $\pi$  electronic cloud.<sup>5</sup> In these cases the *n* mode absorbs strongly and the intensity is higher than for any other C—C skeletal mode. As suggested for the selenonium and the phosphonium compounds, the higher intensity of this band might be due to the rings being twisted in the same sense, thus result-

ing in a propeller-shaped structure. The intensity of the *m* mode is almost as high as of mode *n*. In the presence of the electron donor substituents this mode is expected to absorb strongly. In the present case this indicates interaction with the  $\pi$  electrons of the aromatic nucleus. The intensity is high for the triphenylarsine, falls slightly



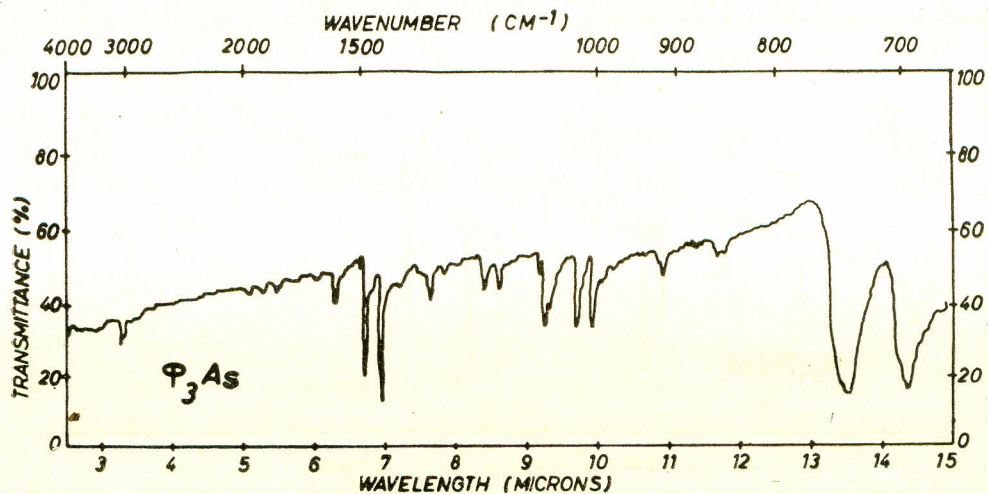


Fig. 1.—Triphenylarsine

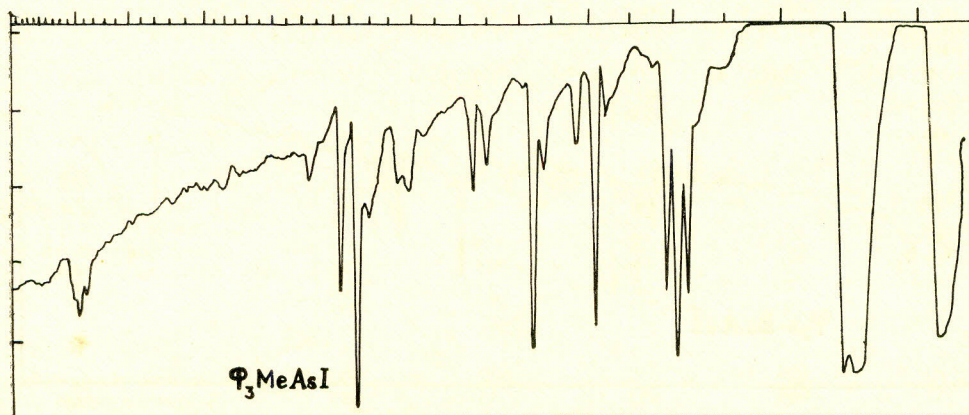


Fig. 2.—Methyltriphenylarsonium iodide.

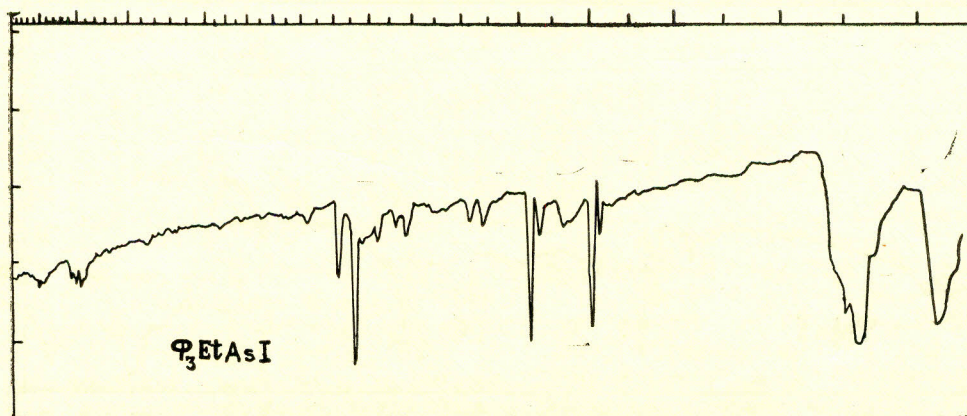


Fig. 3.—Ethyltriphenylarsonium iodide.



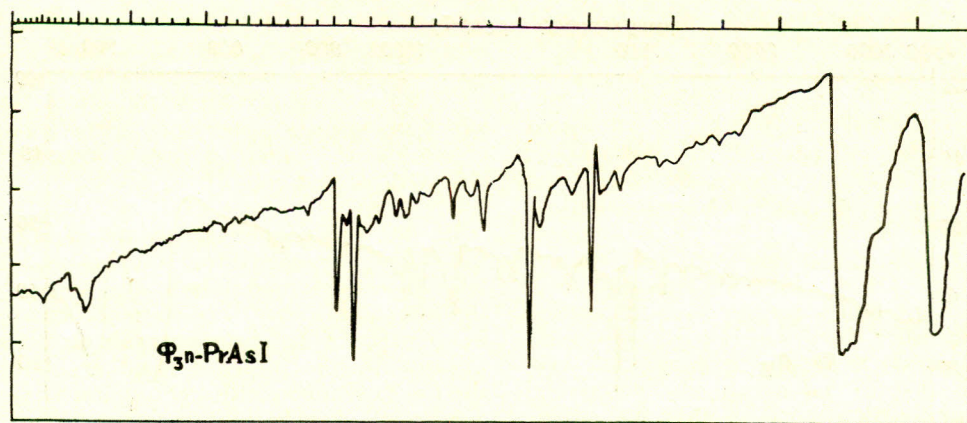


Fig. 4.—n-Propyltriphenylarsonium iodide.

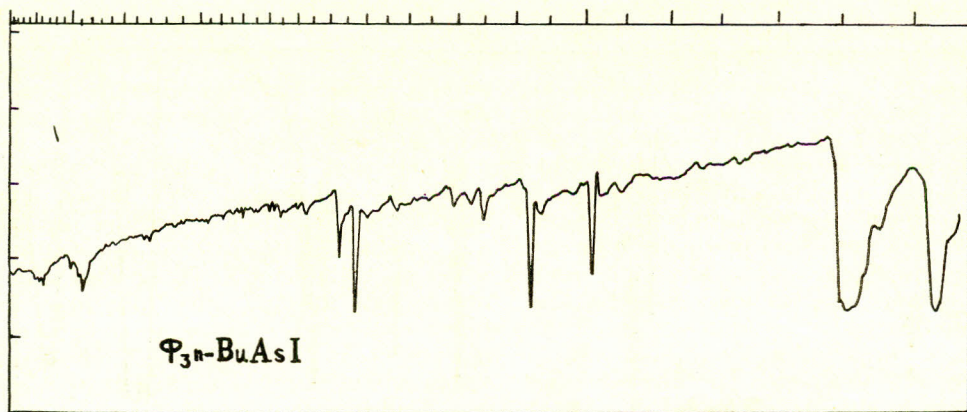


Fig. 5.—n-Butyltriphenylarsonium iodide.

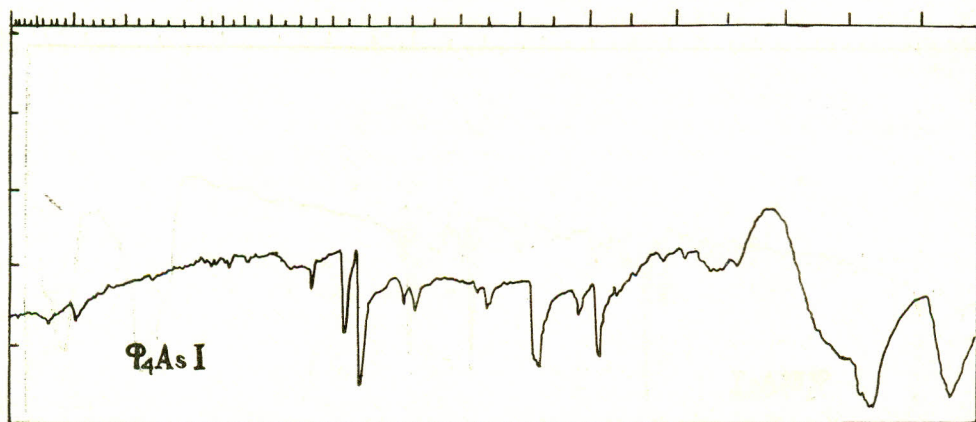


Fig. 6.—Tetraphenylarsonium iodide.



in the case of the methyl- and ethyl-triphenylarsonium compounds and rises again for the *n*-propyl-, *n*-butyl-triphenyl- and the tetraphenylarsonium compounds. It may therefore be concluded that the alkyl C—H bending vibrations contribute to the intensity of this absorption. It is also possible that this is due to the interaction of a bulky group in the neighbourhood. This is supported by the fact that  $\epsilon^a$  for the tetraphenylarsonium iodide is of the same order as that of triphenylarsine. For a reasonable interaction it is necessary that the fourth ring occupies a position similar to the other three, i.e. the rings are symmetrically inclined towards the molecular axis. This suggests that in the tetraphenyl compound the distribution of the rings is also like that of the propeller blades.

*The 1300–950 cm<sup>-1</sup> Region.*—For a monosubstituted ring there are 5 medium intensity bands in this region which are due to the in-plane C—H deformation modes as assigned in Table 2. Among the arsines mode *b* absorbs strongly and, as suggested earlier,<sup>1</sup> it shows conjugation of the rings. In the arsonium compounds this mode absorbs weakly and if the analogy with the phosphonium compounds is correct, this must be due to lack of conjugation. In all the compounds the ring breathing mode absorbs strongly. The intensity of this mode increases gradually from the triphenylarsine to the tetraphenylarsonium compounds. This shows that there is a neighbouring group contribution to the electron density of the ring which is in line with our conclusions regarding the intensity of mode *m*. The intensity rises with the length of the alkyl chain. Since alkyl groups are electron donors the variation of intensity must be due to their positive inductive effect. The *q* mode is also intense and must be due to charge disturbance. A shift of this absorption to higher frequency due to a change in hybridization may be noted in the arsonium compounds.

*The 800–650 cm<sup>-1</sup> Region.*—Splitting into three bands occurs in this region for the triphenylarsine. The band pattern is similar to the triphenylselonium compound except that the bands are not as much separated suggesting the existence of perturbed rings as mentioned earlier. It is possible that the rings are not quite inequivalent but are dissymmetrically oriented giving rise to three bands as required for an unsymmetric molecule having C<sub>3</sub> symmetry. The structure of triphenylphosphine shows that one ring is inclined towards the molecular axis about 30° more than the other two rings. The splitting into a doublet recorded for this phosphine is 10 cm<sup>-1</sup>. In the case of the arsine a triplet is observed. The three rings may therefore be unsymmetrically inclined.

The intensity of the *n* mode, however, suggests rotation of the rings in the same sense. The rings are therefore unsymmetrically inclined but favourably rotated to allow the interaction of the lone pair with the  $\pi$  electrons of the benzene ring giving rise to quinonoid structure and hence the observed conjugation.

In the alkyltriphenylarsonium compounds the splitting is larger than in the arsine. This will have to be attributed to lack of conjugation among the rings so that the three rings absorb at different frequencies. The spectra in this region are complicated by the presence of other bands due to the C—C symmetric stretching and CH<sub>2</sub> rocking. The bands due to these vibrations can be sorted from their absence in the arsine and tetraphenylarsonium iodide.

The splitting is into three bands with a separation of the order of 10 cm<sup>-1</sup>. It is quite likely that this is due to lattice interactions. It has been shown from the X-ray studies of tetraphenylarsonium iodide that the crystal consists of interpenetrating cations and anions, each iodine being near the edge of the phenyl group.<sup>6</sup> The splittings here may therefore be due to the different species in the crystal. The lattice interactions may be minimized by recording the spectra in *n*-ujol mulls. In this case also the splittings occur at the same frequency. The spectra in the various regions have all indicated a dissymmetrical structure for the various arsonium compounds and to have differently inclined rings. The lattice interaction is therefore not a major reason for the observed splittings.

*UV Spectra.*—The UV spectra support the conclusions of IR studies. It is clear from Table 3 that the bands occur in two regions: (i) the 230 m $\mu$  and (ii) 265 m $\mu$ . The band in the 230 m $\mu$  region have a very high intensity. The iodide anion also absorbs here but the absorptions of this ion and the arsonium cation are not additive which suggests that the intensity might be due to charge transfer into the *d* orbitals of the positively charged arsenic atom as observed in the case of the phosphonium compounds. We have seen from the IR spectra that there are three factors which contribute to the intensity of the absorption: (i) the lone pair, (ii) the alkyl chain, and (iii) the orientation of the ring. In the absence of the lone pair on the arsenic atom, i.e. on quaternization the contribution of electron density is either from the anion because of their proximity to the ring or originate from the positive inductive or the neighbouring group effects of the alkyl chain. The intensity of the charge transfer bands varies slightly with the length of the alkyl chain. There-



fore, the inductive and neighbouring group effect of the alkyls is also a factor in the enhancement of the intensity of the bands. The break in the band in this region is noted to indicate dissymmetry in the molecule.<sup>1</sup> The unsymmetrical orientation of the ring is therefore supported by the spectra in this region.

In the 265  $m\mu$  region we observe fine structure in all the arsonium compounds. In the arsine we note inflections in this region. This indicates a fair amount of disturbance in the electronic charge cloud of the ring. In the phosphine such inflections have not been observed. It can be easily suggested that the rings are differently oriented so as to cause a slight hindrance in the easy dissipation of energy of activated state which leads to the observation of inflections. There being no lone pairs in the onium compounds, fine structure would be observed in this region. In the tetraphenylarsonium compound the weak

band at 290  $m\mu$  observed in the n-propyl- and n-butyltriaryl compounds is missing. This may be tentatively assigned to the alkyl group participation in the overall electronic environment which was also deduced from the intensity of the ring-breathing frequency in the IR spectrum.

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