The Molecular Structures of Triphenylarsine "Hydroxychloride" and "Hydroxybromide". Examples of "Very Short" O · · · H · · · Hal Intramolecular Hydrogen Bonding

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ON mild hydrolysis triphenylarsine dichloride and dibromide yield products of formula $Ph_3As(OH)Hal$.[1] The i.r. spectrum of $Ph_3As{=}O{\cdot}H_2O$ contains a strong band at 888 cm.$^{-1}$ (As=O stretch); the "hydroxyhalides" are transparent in this region but show strong composite absorption in the region 2750—2000 cm.$^{-1}$, which has been assigned to OH group vibration under conditions of strong hydrogen bonding.[2] Harris and Inglis found low molar conductance values for the "hydroxyhalides" in methyl cyanide indicating that, like the dihalides, the "hydroxyhalides" are weak electrolytes, and they inferred that the solid consists of molecular $Ph_3As(OH)Hal$ units which ionise partially under the influence of the solvent.[3] However, failure to locate an absorption in the i.r. spectra of the hydroxyhalides which could be attributed to an arsenic–halogen stretching frequency cast grave doubts on the validity of a trigonal bipyramidal structure for $Ph_3As(OH)Hal$.[4]

In order to obtain conclusive details of the structures of these compounds we obtained from Dr. Harris crystals of both the "hydroxychloride" and "hydroxybromide." Crystal data are as follows: $Ph_3AsOHCl$, M 358·7, monoclinic, $a = 17{\cdot}38 \pm 0{\cdot}03$, $b = 11{\cdot}44 \pm 0{\cdot}02$, $c = 17{\cdot}21 \pm 0{\cdot}03$ Å, $\beta = 100{\cdot}5 \pm 0{\cdot}5$, $U = 3365$ Å^3, $D_m = 1{\cdot}44$, $Z = 8$, $D_c = 1{\cdot}42$. Space group $P2_1/c$ (C_{2h}^5, No. 14) from systematic absences. There are two independent molecules in the asymmetric unit.

$Ph_3AsOHBr$, $M = 403{\cdot}1$, monoclinic, $a = 10{\cdot}39 \pm 0{\cdot}02$, $b = 11{\cdot}86 \pm 0{\cdot}02$, $c = 17{\cdot}48 \pm 0{\cdot}03$ Å, $\beta = 127{\cdot}4 \pm 0{\cdot}5°$, $U = 1711$ Å^3, $D_m = 1{\cdot}58$, $Z = 4$, $D_c = 1{\cdot}56$. Space group $P2_1/c$ (C^5_{2h}, No. 14) from systematic absences.

For $Ph_3AsOHCl$, 2420 independent reflexions were collected with a Hilger and Watts Linear Diffractometer[5] using Mo-radiation and balanced ZrO_2–SrO filters. For $Ph_3AsOHBr$, 2425 independent reflexions were obtained by visual estimation from Weissenberg films (taken with Cu-K_α radiation) of the $h0$–$10l$ reciprocal lattice nets. Both structures were solved by the heavy-atom method and refined extensively by least-squares calculations. The R-factors are 0·103 and 0·098 for the chloride and bromide respectively.

Our results establish that the As atoms in triphenylarsine "hydroxyhalides" are tetrahedrally co-ordinated to three phenyl rings and to an oxygen atom which is in turn strongly hydrogen bonded to a halogen by a "very short" hydrogen bond. The Figure gives a view of a molecule of $Ph_3AsOHBr$; in the $Ph_3AsOHCl$ structure there are two crystallographically independent molecules which differ from this and from each other in the orientations of the phenyl rings. In no case is a halogen atom directly bonded to arsenic. A tetrahedral structure for $Ph_3AsOHCl$ was predicted by Jensen[6] who explained its very high dipole moment of 9·2 D by means of a resonance hybrid formulation (I) ⟷ (II).

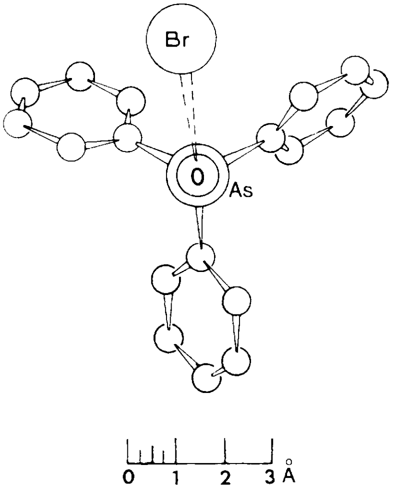


FIGURE. *A view along the oxygen–arsenic bond of a* $Ph_3AsOHBr$ *molecule; hydrogen atoms are omitted. The* As–O–Br *angle is* 108·2 ± 0·5°; *the corresponding angles in the two independent* $Ph_3AsOHCl$ *molecules are* 109·5 *and* 109·2 ± 0·6°.

$$\mathbf{Ph_3\overset{+}{As}\text{–}\overset{-}{O}}\cdots H\text{–}Hal \qquad \mathbf{Ph_3\overset{+}{As}\text{–}O\text{–}H}\cdots Hal^{-}$$

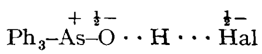
(I) (II)

The oxygen ··· chlorine distances in $Ph_3AsOHCl$, 2·854 and 2·817 ± 0·017 Å, are considerably shorter (by 0·25 Å) than the mean value (3·08 ± 0·01 Å) for an O–H ··· Cl^- bond given by Pimentel and McClellan.[7] In $Ph_3AsOHBr$ the oxygen ··· bromine separation, 3·034 ± 0·012 Å, is also 0·25 Å shorter than the mean value (3·38 ± 0·01 Å) reported for the O–H ··· Br^- hydrogen bond.[7] Of particular interest is the position of the proton involved in the hydrogen bond. Unfortunately the X-ray data did not allow a precise determination of its position. However, some insight into the problem can be gained from a consideration of the arsenic–oxygen–halogen distances and from various spectroscopic measurements.

The As–O distances (1·702 and 1·697 ± 0·014 in $Ph_3AsOHCl$ and 1·712 ± 0·012 Å in $Ph_3AsOHBr$) are significantly longer (by ~ 0·06 Å) than the As=O bond in triphenylarsine oxide monohydrate (1·644 ± 0·007 Å)[8] and are comparable with the As–O single bond length (1·69 Å) found for example in *o*-phenylenediarsine oxychloride.[9] We have also measured the n.m.r. spectra of $Ph_3As{=}O$, $Ph_3AsOHCl$ and $Ph_3AsOHBr$. The aromatic proton signal in $Ph_3As{=}O$ occurs at τ 2·40 when the spectrum is recorded in deuteriochloroform under anhydrous conditions, but introduction of a small amount of a protonating solvent, *e.g.* trifluoroacetic acid, shifts the signal to τ 2·14. Hadži and his co-workers[10] have noted that in the presence of a similar protonating agent, trichloroacetic acid, the i.r. spectra of $Ph_3As{=}O$ is of the type limited to symmetrical hydrogen bonds (*i.e.* the species R–O ··· H ··· O–R′ is present) and the downfield shift in the n.m.r. spectrum on such hydrogen bond formation can be attributed to either or both of electric field effect or $d\pi$–aromatic overlap. In a previous communication we reported an O ··· H ··· O distance of 2·40 ± 0·03 Å for a "very short", possibly symmetrical, hydrogen bond in $[Ph_3As\underset{\cdot}{-}O\cdots H\cdots O\underset{\cdot}{-}AsPh_3]^+$,[11] and as the weighted mean of "very short" symmetrical O ··· H ··· O bonds in a variety of acid salts has been reported[12] as 2·446 ± 0·003 Å it would seem not unreasonable to associate the above shift in the $Ph_3As{=}O$ n.m.r. signal from τ 2·40 to 2·14 with the arrival of a shared hydrogen atom ~1·22 Å from the arsenic oxygen atom. The aromatic proton signals of both $Ph_3AsOHCl$ and $Ph_3AsOHBr$ in deuteriochloroform also appear at the same value, τ 2·14, and are not changed by the addition of small amounts of protonating solvent. This may be interpreted as indicating that the proton involved in the hydrogen bond in these compounds is associated with the oxygen atom in a similar manner to that found in the triphenylarsine oxide–trifluoracetic acid complex.

The hydrogen bonding situation in the "hydroxyhalides" is thus extremely reminiscent of that found in acid salts with "very short" hydrogen bonds. In the latter case it is suspected that the O · · · H · · · O bond is genuinely symmetrical with O · · · H *ca.* 1·22 Å. If one accepts that the oxygen–hydrogen separation is increased from 0·957 Å in water[13] to 1·22 Å (a 28% increase) in "very short" O · · · H · · · O hydrogen bonds, it would appear entirely reasonable to expect that, if either HCl or HBr were similarly involved, their H–Hal bond lengths would also be increased by about 28% from 1·274[13] to 1·62 Å and from 1·408[13] to 1·80 Å respectively. We feel that it is more than just coincidental that the sums of these modified O · · · H and H · · · Hal distances (2·84 and 3·02 Å for O · · · H · · · Cl and O · · · H · · · Br respectively) are almost identical to our observed distances (2·84 and 3·03 Å respectively), and that in the "hydroxyhalides" we have the O · · · H · · · Hal analogue of the "very short" O · · · H · · · O systems but with the important difference that we expect the hydrogen bonded proton not to be symmetrically disposed in the bond.

The mean As–C distance in both compounds is 1·895 Å, close to that normally associated with a phenyl–arsonium bond, *e.g.* 1·897 ± 0·009 Å.[14] Within the limitations of conventional valence bond notation we suggest (III), essentially Jensen's formulation, as a plausible representation of the triphenylarsine hydroxyhalides.



$$\mathrm{Ph_3{-}}\overset{+}{\mathrm{As}}{-}\overset{\frac{1}{2}-}{\mathrm{O}}\cdot\cdot\,\mathrm{H}\cdot\cdot\cdot\overset{\frac{1}{2}-}{\mathrm{Hal}}$$

(III)

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