The Crystal Structure of Methylphenylarsinic Acid: A Contaminant of Rice Plants and Groundwater

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Methylphenylarsinic acid, MePhAsO•OH, a contaminant of rice plants and of groundwater, has been the subject of a single crystal X-ray study. In the crystal lattice the molecules form hydrogen-bonded chains linking O···HO entities; As–O, OH are 1.654(1), 1.719(1) Å.

Methylphenylarsinic acid has been found as a contaminant of groundwater and of rice plants at two locations in eastern Japan; Kamisu City in Ibaraki Prefecture and Hiratsuka City in Kanagawa Prefecture. Its presence is likely to result from the inappropriate disposal of warfare agents or the materials for their preparation, or from the dumping of industrial wastes.[1,2] Possibly methylphenylarsinic acid has been synthesized in the soil by the microbial methylation of discarded phenylarsonic acid.[3]

Chiral arsenic, resulting in separable enantiomers, has been reported[4] for arsines in which the trivalent arsenic atom is tetrahedrally configured with the lone pair occupying the fourth coordination position around the arsenic atom.[5] The pentavalent arsenic atom in arsinic acids is also tetrahedrally configured.[6] However, the arsenic atom in methylphenylarsinic acid will not be chiral in aqueous solution because rapid migration of the proton between the two oxygens will render them equivalent. We have synthesised[7] and recrystallised methylphenylarsinic acid from methanol/acetone to serve as an analytical standard and to facilitate toxicity testing, and this has provided an opportunity to examine the crystal structure of the compound and to explore the proton distribution in the solid state.

A full sphere of CCD area-detector diffractometer data was measured (ω-scans, $2\theta_{\max} = 75°$, monochromatic Mo Kα radiation, $\lambda = 0.71073$ Å; $T =$ ca. 300 K) yielding 32201 total reflections, these merging to 4232 unique ($R_{\mathrm{int}} = 0.064$) after "empirical"/multiscan absorption correction (proprietary software, "T"$_{\mathrm{min/max}} = 0.73$), 2761 with $F > 4\sigma(F)$ being considered "observed" and used in the full-matrix least-squares refinement on F^2 (reflection weights: $(\sigma^2(F^2) + (0.0392P)^2 + 0.2594P)^{-1}$ ($P = (F_o{}^2 + 2F_c{}^2)/3$);[8] $(x, y, z, U_{\mathrm{iso}})_{\mathrm{H}}$ were constrained at estimates except for the hydroxy-H for which they were refined. At convergence R_1, wR_2 were 0.029, 0.067, values for all data being 0.062, 0.067.[8] Neutral atom complex scattering factors were employed. Pertinent results are given below and in the Figures, the latter showing 50% probability amplitude displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms where shown having arbitrary radii of 0.1 Å.

Crystallographic Data:[9] $C_7H_9AsO_2$, $M_r = 200.1$. Orthorhombic, space group $Pbca$ (D_{2h}^{14}, No. 60), $a = 12.5846(6)$, $b = 7.9151(4)$, $c = 16.1254(7)$ Å, $V = 1606$ Å^3. D_{calcd} ($Z = 8$) $= 1.661$ g cm^{-3}. $\mu_{\mathrm{Mo}} = 4.2$ mm^{-1}; specimen: $0.20 \times 0.15 \times 0.07$ mm.

The results of the room-temperature single crystal X-ray structure determination are consistent in terms of stoichiometry and connectivity with the expected formulation MePhAsO•OH, a single molecule devoid of crystallographic symmetry comprising the asymmetric unit of the structure, in a centrosymmetric (racemic) space group. The phenyl geometries are unremarkable, as also the As–C distances, consistent with As$^{\mathrm{V}}$, no substantial difference being evident between As–C(Me,Ph). There are

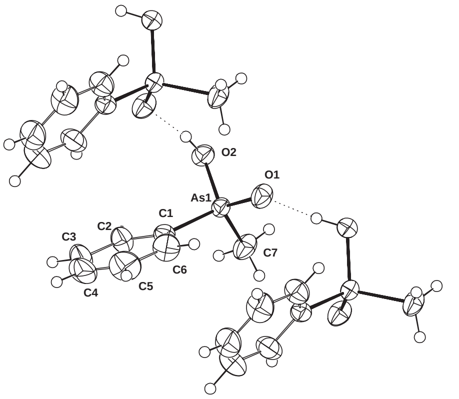

Figure 1. Projection of a single molecule, with its hydrogen-bonded neighbours.

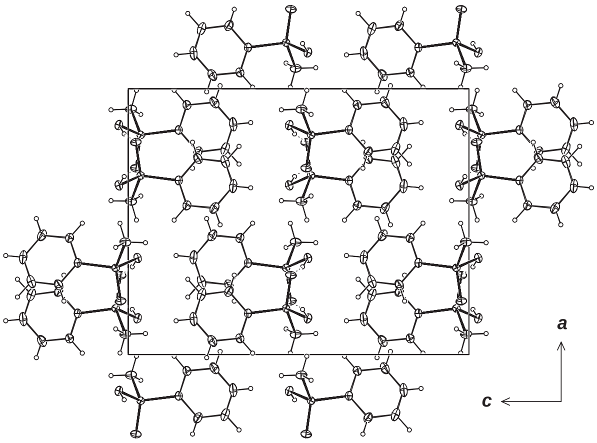

Figure 2. Unit cell contents projected down *b*.

substantial significant differences in the two As–O distances, however, and their associated angles, O(1)–As–C(Ph,Me) being 109.24(7), 112.87(7) and O(2)–As–C(Ph,Me) 107.16(6), 103.29(7), with O–As–O 111.68(7)°, consistent with the relativities in As–O(1,2), these being 1.654(1), 1.719(1) Å, the latter oxygen O(2) being associated with a protonic hydrogen atom (O(2)–H(2A) 0.90(2) Å; As–O(2)–H(2A) 110(1)°). The latter hydrogen bond to O(1) of adjacent molecules (O(2), H(2A)···O(1)($3/2 - x$, $1/2 + y$, z) 2.514(2), 1.63(2) Å), forms an infinite string parallel to *b* (Figures 1 and 2).

References and Notes

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9 Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-603843. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).