Existence of 2-Carboxyphenyldiphenylarsine Oxide as a Novel Resonance Hybrid Structure with Strong Intermolecular Hydrogen Bonding Dissociating to the First Example of a Monocyclic Acyloxyhydroxyarsorane in Chloroform

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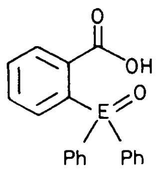
The solid state spectral and *X*-ray structural investigation of the title arsine oxide shows it to exist as a novel resonance structure (**1e**) having a short hydrogen bond; i.r. (CHCl$_3$) and ^{1}H n.m.r. (CDCl$_3$) data for dilute solutions indicate the 1-hydroxy-1,1-diphenyl-2,1λ^5-benzoxarsol-3-one structure (**1d**), providing the first example of a stable monocyclic acyloxyhydroxyarsorane.

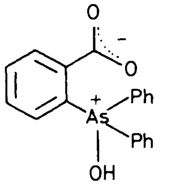
The four known stable cyclic hydroxyphosphoranes/arsoranes,[1—3] like other hypervalent molecules, are stabilized primarily by their spirocyclic nature[4] and no monocyclic acyloxyhydroxyphosphorane or arsorane has been reported so far. We now provide spectral and *X*-ray evidence to prove that the oxide 2-Ph$_2$As(O)C$_6$H$_4$CO$_2$H[5] exists as the monocyclic acyloxyhydroxyarsorane (**1d**) in dilute solution in CHCl$_3$ and as the novel resonance hybrid structure (**1e**) in the solid state; these structures contrast with those previously reported: (**1b**)[5] or (**1c**).[6]

The molecular structure† (Figure 1) shows the arsenic(v) atom to be in a trigonal bipyramidal environment with equatorial aryl groups (C–As–C angles 116.5, 118.8, and 119.4°) and apical oxygen atoms (O–As–O angle 174.9°) as expected on the basis of 'apicophilicity.' The ring As–O distance of 2.238 Å is much longer than the single bond distance (~1.93 Å).[7] On the other hand, the As–O(H) distance of 1.769 Å is much shorter than the single bond distance but is slightly longer than that in strongly hydrogen bonded compounds Ph$_3$As=O · · · HX [X = Cl, 1.702(14), 1.697(14) Å; X = Br, 1.712(12) Å; X = OH, 1.644(7) Å].[8] The O–H distance of 0.977 Å in the AsOH group is much shorter than that in COH group (1.659 Å). The O–O distance of 2.635 Å is also shorter than in Ph$_3$As=O · · · H$_2$O[8] (2.78 and 2.81 Å) and in ice (2.76 Å)[9] indicating the presence of a stronger hydrogen bond. The C(7)–O(7) and C(7)–O(8) distances of 1.235 and 1.273 Å suggest the presence of the carboxylate ion and not of carboxylic acid (**1f**) or lactone (**1g**) structures. All these bond lengths can be explained only in terms of the novel structure (**1e**), a resonance hybrid of (**1f**) and (**1g**), rather than the reported structures (**1b**)[5] or (**1c**).[6]

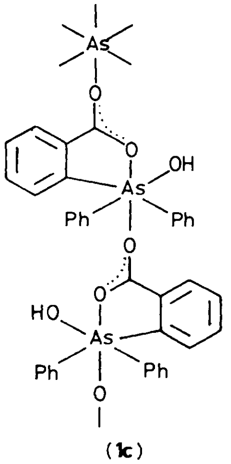
The structure (**1e**) is also consistent with the reported absence of ν(C=O) and ν(As=O) bands and the presence of ν(As–OH) (2360 cm^{-1}), ν$_{asym}$ (CO$_2$) (1620 cm^{-1}), and ν$_{sym}$ CO$_2$ (1378 cm^{-1}) bands in its solid state i.r spectrum. However, the i.r. spectrum in CHCl$_3$ shows the main ν(C=O) (1668 cm^{-1}), ν(C–O) (1342 cm^{-1}), and ν(As–OH) (3600 cm^{-1}) bands associated with shoulders at 1620, 1378, and 2360 cm^{-1} due to (**1e**) which disappear even on moderate dilution leaving only the main bands. This observation suggests the cleavage of the hydrogen bond of (**1e**) to yield (**1d**) in solution. Further support for structure (**1d**) in solution stems from its



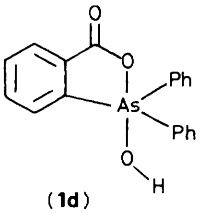
(**1a**)



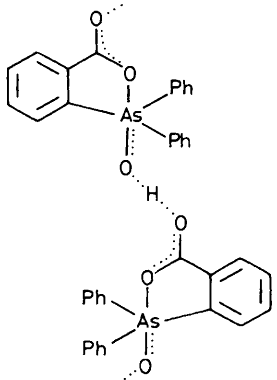
(**1b**)



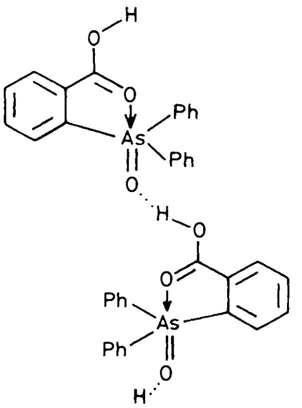
(**1c**)



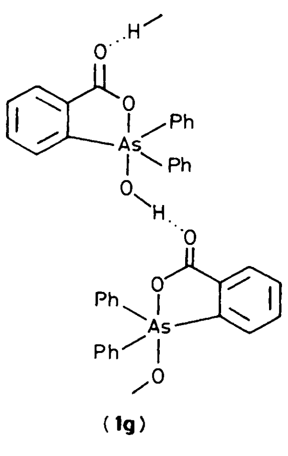
(**1d**)



(**1e**)



(**1f**)



(**1g**)

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† *Crystal Data:* C$_{19}$H$_{15}$O$_3$As, M = 366.2, orthorhombic, a = 11.919(3), b = 15.255(3), c = 17.466(4) Å, U = 3176 Å^3, space group *Pccn*, Z = 8, D_c = 1.53 g cm^{-3}, μ(Cu-K_α) = 30 cm^{-1}. Data were measured on a Nicolet R3m diffractometer with Cu-K_α radiation (graphite monochromator) using ω-scans. The structure was solved by the heavy atom method and refined anisotropically to give R = 0.028, R_w = 0.032 for 2074 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $\theta \leq 58°$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

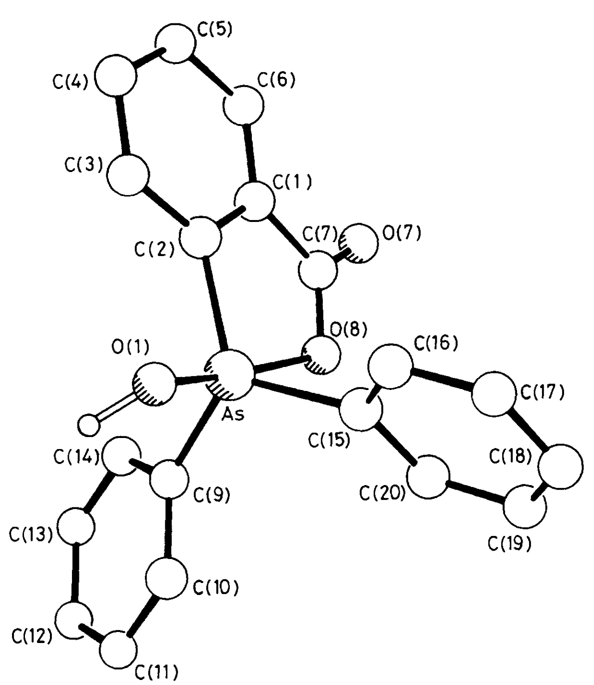

Figure 1. The *X*-ray structure of 2-$Ph_2As(O)C_6H_4CO_2H$. Selected bond angles (°): C(2)–As–O(8) 79.0; C(9)–As–C(15) 116.5; C(7)–O(8)–As 112.4; C(2)–As–C(9) 118.8; C(1)–C(7)–O(8) 114.2; C(2)–As–C(15) 119.4; C(2)–C(1)–C(7) 117.1; O(1)–As–O(8) 174.9; H(1)–O(1)–As 119.0; O(1)–H(1)–O(7′) 176.8. Selected bond lengths (Å): H(1)–O(1) 0.977; O(8)–As 2.23; H(1)–O(7′) 1.659; O(7)–C(7) 1.235; O(1)–As 1.769; O(8)–C(7) 1.273.

typical ^1H n.m.r. ($CDCl_3$) low-field multiplet at δ 8.16 due to the two aromatic protons *ortho* to arsenic and the carbonyl group. These protons appear at δ 7.35 and 8.20 respectively in the parent arsine.[10] The compound (**1d**) is thus the first example of a monocyclic acyloxyhydroxyarsorane.

In contrast to these five-co-ordinate structures (**1d**) and (**1e**) for 2-$Ph_2As(O)C_6H_4CO_2H$, the phosphorus analogue has been assigned a four-co-ordinae structure (**1a**; E = P) in the solid state as well as in $CHCl_3$.[11] This structural difference, however, seems to be consistent with the tendency of the large arsenic(v) atom to acquire a higher co-ordination number and the large energy difference between the P=O (544 kJ mol^{-1}) and P–O (335 kJ mol^{-1}) bonds relative to that for As=O (389 kJ mol^{-1}) and As–O (301 kJ mol^{-1}) bonds. In view of these findings, the oxidation product of 2-$Ph_2AsCH_2CH_2CO_2H$ assumed[12] to exist as the zwitterion 2-$Ph_2As^+(OH)$-$CH_2CH_2CO_2^-$ similar to (**1b**) should also possess the structure analogous to (**1d**)–(**1e**).

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