Letters

A disagreement on the explanation of short and long As–O bonds of the $(As–O)_4$ ring in $As_4(CF_3)_6O_6(OH)_2$ in terms of As^{III}–O and As^V–O bonds

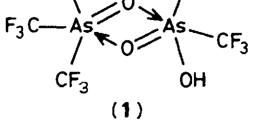
Bohra *et al.*[1] have prepared the compounds $[As(CF_3)_2O(OH)]_2$ (**1**), $[As(CF_3)O(OH)Cl]_2$ (**2**), and $As_4(CF_3)_6O_6(OH)_2$ (**3**), and determined their molecular structures using single-crystal *X*-ray studies. The four-membered $(As–O)_2$ ring contains an asymmetric As–O–As bridge in (**1**) and (**2**) and a symmetric one in (**3**) while an $(As–O)_4$ ring present in (**3**) also contains an asymmetric As–O–As bridge. The stoicheiometries of all the three compounds suggest the presence of As^V alone but the short and long As–O bonds of the $(As–O)_4$ ring have been attributed to As^{III}–O and As^V–O bonds respectively. On the other hand, the asymmetric bridge in the $(As–O)_2$ ring present in (**1**) and (**2**) has been explained in terms of the 'contribution from an extreme resonance structure in which the short ring As–O bond is replaced by As=O and the long ring As–O bond deleted'.[1] I now attempt to rationalise the variation of As–O bond length in terms of the As^V–O bond order.

All the long ring As–O bonds, except that in compound (**1**), are equal to the As–O(H) bonds (Table) while the short ring As–O bonds are close to those reported for $Ph_3As{=}O \cdots H_2O$ (164.4 ± 7 pm) and $Ph_3As{=}O \rightarrow HgCl_2$(166 ± 2 pm).[2] This observation suggests the short ring As–O bond order to be between one and two and that of the long ring As–O/As–O(H) bond to be one. The average of all the seven long As–O/As–O(H) bonds is 192.8 pm and those of the four short bonds, 170.3 pm. The arithmetic mean (181.6 pm) of the average long As–O and average short As–O bonds is very close to the observed As–O bond lengths of 183.1 and 183.3 pm in the symmetric $(As–O)_2$ ring of (**3**). These data can be fully understood if the bonding in compounds (**1**)—(**3**) is presented as shown. The presence of the four-co-ordinate arsenic as arsonate anion in (**3**) is consistent with the appearance of $\nu_{asym}(AsO_2)$ and $\nu_{sym}(AsO_2)$ at 828m and 819s cm^{-1} respectively[3,4] which are missing in the spectra of (**1**) and (**2**).

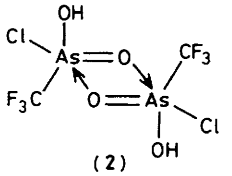
The presence of the asymmetric $As{=}O \rightarrow As$ bridge in the $(As–O)_2$ ring of (**1**) and (**2**) may be explained in terms of the property of a doubly bonded oxygen which despite the high electronegativity seeks *s*-rich orbitals, because of the shortness and better overlap of the double bond, and occupies an equatorial position in a trigonal-bipyramidal structure.[5] The apical position in (**1**) and (**2**) is occupied by the oxygen which is doubly bonded to the adjacent As^V in an equatorial position. The resonance of the type assumed to take place between As=O and As–O which is responsible for the symmetry in the $(As–O)_2$ ring in (**3**) is not possible in (**1**) and (**2**) since the doubly bonded oxygen cannot occupy an apical position, while in (**3**) both the oxygens lie in the same plane perpendicular to the O–As–O axis of the $(As–O)_4$ ring.

Table. Different types of As–O bond lengths (pm) in (**1**), (**2**), and (**3**)

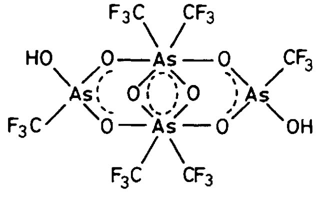
Bond type	(1)	(2)	(3)	Average
As–O(H)	190.6	193.1	191.4	192.8
Long As–O	200.3	193.7	190.1 190.5	
Short As–O	171.3	171.8	169.3 168.6	170.3
Symmetric ring As–O	—	—	183.1 183.3	183.2



(**1**)



(**2**)



(**3**)

Finally, the reported[6] description of the polymeric structure of AsO_2 in terms of As^V and As^{III} would seem plausible due to the apparent presence of As^{IV} and it cannot be considered as a case similar to (**3**).

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