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Intramolecular Non-bonded Atomic Radii: New Data and Revised Radii for Heavy *p* Elements

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New structural data are employed to confirm the values of intramolecular non-bonded atomic radii previously derived for certain p *elements and to revise earlier values for elements in the 5*p *series: the revised values include Sn, 1.82 Å; Te, 1.75 Å; I, 1.75 Å; Xe, 1.65 Å. The radius appropriate for antimony is uncertain.*

Introduction

The hypothesis that in molecular fragments MXM′, in which X is a first-row element such as carbon, nitrogen, oxygen or fluorine, the lower limit of the angle <MXM′ is set by the limiting non-bonded M...M′ distance has been applied both to molecular [1, 2] and to continuous species [3]. Secure intramolecular 'one-angle' radii are available for the majority of the lighter elements, but those which were earlier suggested [2] for the heavier elements are in some cases based on few data. Since the radii for the heavier elements were suggested, a substantial number of new structural data have been reported: consideration of these data leads to revision of a number of the earlier radii, which are in several cases felt to be more secure than previously. However no rejection of the underlying hypothesis has been indicated: for the majority of elements, the new data confirm most satisfactorily the values of the radii earlier deduced.

Results and Discussion

It is convenient to consider the elements in order of increasing atomic number

Germanium

Data for germanium compounds are set out in Table I: the polymorph of GeO$_2$ is a 4:2 polymorph analogous to low quartz (P3$_1$21 and P3$_2$21) rather than the usual 6:3 polymorph of rutile structure (P4/*m n m*): the mean value for the radius of germanium is 1.58$_4$ Å.

Arsenic

No new data for this element are available: the previously suggested [2] radius is 1.61 Å.

TABLE I. Data for Germanium Compounds.

Compound	X	M	<GeXM (/°)	d(Ge...M) (/Å)	r(Ge) (/Å)	Ref.
O(GeH$_3$)$_2$	O	Ge	126.5	3.156	1.578	25
O(GePh$_3$)$_2$	O	Ge	135.2	3.268	1.634	26
GeO$_2$	O	Ge	130.1	3.154	1.577	27
Er$_2$[Ge$_2$O$_7$]	O	Ge	136.0	3.256	1.628	28
(Ph$_2$CN)$_4$Ge	N	C	123.8	2.800	1.550	29
			130.1	2.837	1.587	
Cl$_3$GeNPMe$_3$	N	P	128.9	2.986	1.536	30
Mn[GeO$_3$]	O	Ge	123.4	3.175	1.586	31
			129.7	3.242	1.621	
Co[GeO$_3$]	O	Ge	119.4	3.096	1.548	32
Ph$_3$GeNCO	N	C	150.7	2.831	1.581	33

TABLE II. Data for Selenium Compounds.

Compound	<SeOSe (/°)	d(Se...Se) (/A)	r(Se) (/A)	Ref.
$VOSe_2O_5$	119.6	3.103	1.552	34
$ZnSe_2O_5$	121.6	3.195	1.598	35
$PrH_3(SeO_3)_2Se_2O_5$	123.8	3.248	1.624	36
$CuSe_2O_5$	122.4	3.209	1.605	37
$MnSe_2O_5$	121.6	3.197	1.599	38
$MnHSeO_3(Se_2O_5)$	126.4	3.199	1.600	39
SeO_2	125	3.16	1.58	4
$O(SeF_5)_2$	142.4	3.213	1.607	5

Selenium

A large number of new data for this element have been reported, particularly a number of derivatives containing the $[Se_2O_5]^{-2}$ ion: the data are set out in Table II. The mean value of d(Se...Se) is 3.191 Å, or, if the less precise value for SeO_2 [4] is excluded, 3.195 Å. The radius implied for selenium is 1.60 Å. It is noteworthy that in $O(SeF_5)_2$ [5], the angle <SeOSe is 142.4°, whereas in the ion $[Se_2O_5]^{-2}$ it generally falls in the range 120–124°; however, despite this wide angle the Se...Se distance in $O(SeF_5)_2$, 3.213 Å, is very close to the mean distance in six compounds containing $[Se_2O_5]^{-2}$, 3,192 Å: the angle <SeOSe in $O(SeF_5)_2$ is some 20° larger than in $[Se_2O_5]^{-2}$, but the Se...Se distances are virtually identical (within 1%). The strongly electron withdrawing SeF_5 groups shorten the Se–O bonds (1.697 Å compared with an average of 1.820 Å in the $[Se_2O_5]^{-2}$ species): this shorter bonded distance, when associated with the fixed Se...Se distance, gives rise to the much bigger angle at oxygen.

Bromine

No new data are available: a radius of 1.59 Å has been suggested [2].

Tin

In $(Me_3Sn)_2O$, a gas-phase electron diffraction study showed that the Sn...Sn distance is 3.655 Å, subtending an angle <SnOSn of 140.8° [6]: in $(Ph_3Sn)_2O$, an X-ray study revealed an Sn...Sn distance of 3.641 Å, subtending an angle <SnOSn of 137.1° [7]. It is noteworthy that the change of substituent appears to have very little influence upon the geometry of the SnOSn fragment. By contrast $[(PhCH_2)_3Sn]_2O$ is linear at oxygen [8], having d(Sn–O) of 1.919 Å and d(Sn...Sn) of 3.838 Å: the linearity at oxygen of certain oxo compounds has been discussed [9] in terms of the second order Jahn–Teller effect. Clearly the two tin atoms in $[(PhCH_2)_3Sn]_2O$ do not span the limiting non-bonded distance, there being in this instance no force causing the linear SnOSn skeleton to bend [9]: the remarkable similarity of the Sn...Sn distances in the vapour phase $(Me_3Sn)_2O$ and the solid phase $(Ph_3Sn)_2O$ gives as a revised radius for tin the value of 1.82 Å. This is somewhat smaller than the radius earlier suggested (1.88 Å) but is consistent with the Sn...C distance of 3.05 Å found [10] in 1,4-bis(triethylstannyloxy)-2,3,5,6-tetrachlorobenzene in which the <SnOC angle is 127°. This determination used only two-dimensional data so that the precision is not high; nevertheless the Sn...C is very close to the calculated value of 3.07 Å from which it is not significantly different.

Antimony

Considerable difficulty at present surrounds attempts to assign a one angle radius to antimony: there are few data, and these are not consistent. The data are in Table III: $(Ph_2Sb)_2O$ clearly implies a radius for antimony of 1.72 Å, much smaller than the value implied by the four species of type $(XSbR_3)_2O$, which is 1.88 Å. Neither of these values is consistent with values deduced here for tin, 1.82 Å and tellurium, 1.75 Å. The clear cut difference between the values in $(Ph_2Sb)_2O$ and $(XSbR_3)_2O$ suggests the possibility that different radii might be appropriate to three-coordinate antimony and five-coordinate antimony. However for selenium, there appears to be no significant difference between three-coordination, as in $[Se_2O_5]^{-2}$ and six-coordination, as in $O(SeF_5)_2$: similarly for tellurium (*cf.* below) there appear to be no significant differences between three-, four-, or six-coordinate tellurium, exemplified by $(Te_2O_3)SO_4$, $(SCNTePh_2)_2O$ and $O(TeF_5)_2$ respectively.

Tellurium

Recent data for tellurium compounds are listed in Table IV: these data indicate that the radius of tellurium is 1.75 Å. As with the selenium analogue, the angle at oxygen in $O(TeF_5)_2$ is much bigger than those in the other species, although d(Te...Te) is the same. In $U(OTeF_5)_6$, the U...Te distance is 3.847 Å and subtends an angle at oxygen of 170° [11].

TABLE III. Data for Antimony Compounds.

Compound	<SbOSb (/°)	d(Sb...Sb) (/Å)	Ref.
$(Ph_2Sb)_2O$	122	3.445	40
$(O_3ClOSbPh_3)_2O$	139.8	3.729	41
$(ClSbMe_3)_2O$	129	3.814	42
$(O_3ClOSbMe_3)_2O$	128	3.724	42
$(N_3SbMe_3)_2O$	126	3.744	42

TABLE IV. Data for Tellurium Compounds.

Compound	<TeOTe (/°)	d(Te...Te) (/Å)	Ref.
$(Te_2O_3)SO_4$	124	3.513	43
$M_2O(NO_3)_2$[a]	125.0	3.519	44
$O(TeF_5)_2$	145.5	3.499	5
$O(SCNTePh_2)_2$	121.7	3.467	45

[a] M represents diphenyltelluroxine $O(C_6H_4)_2Te$.

Iodine

In I_2O_5, the angle <IOI is 139.2°, associated with an I...I distance of 3.63 Å [12]. In HI_3O_8 (≡$HIO_3 \cdot I_2O_5$) by contrast, the I_2O_5 fragments exhibit an I...I distance of only 3.49 Å, subtending an angle <IOI of 125.8° [13]. In the $(IO)_n$ chains of $(IO)_2SO_4$, the angle <IOI is again smaller than in I_2O_5, at 127.1°, but the I–O bonds are longer, and d(I...I) is 3.54 Å [14]. It is possible that IOI fragments are subject to only weak forces resisting the deformation of the angle <IOI, *i.e.* Class 4 behaviour [15] where the bond angle can be extensively deformed with the expenditure of very little energy, subject only to the lower limiting value imposed by d(I...I). In these terms the iodine radius is assigned as 1.75 Å. Consistent with this is the structure of C_2I_4, determined by neutron diffraction at 4 K [16]: in C_2I_4 the mean C...I distance is 3.03 Å, and the mean I...I distance is 3.50 Å, supporting a radius of 1.75 Å, as deduced from HI_3O_8.

Xenon

In $Xe(OSeF_5)_2$, the angle <XeOSe is 125°, and the Xe...Se distance is 3.249 Å [17]: this suggests a xenon radius of 1.65 Å. The Xe...S distances in $FXeOSO_2F$ [18] and $[(FXeO)_2SOF]^+[AsF_6]^-$ [19] are 3.238 Å and 3.310 Å respectively, while the Xe...As distance in $FXeAsF_6$ is 3.72 Å [20]. These are probably not limiting close-contact distances.

Mercury

The mercury(II) chloride substitution product of pentan-2,4-dione, $(MeCO)_2C(HgCl))_2$ has an angle <HgCHg of only 103°, but the Hg...Hg distance is 3.412 Å [21], smaller than any d(Hg...Hg) previously recorded, and implies a mercury radius, assuming that the observed Hg...Hg distance is truly non-bonding, of 1.71 Å.

TABLE V. Revised Intramolecular Radii (/Å).

Be	B	C	N	O	F	
1.39	1.33	1.25	1.13	1.12	1.08	
	Al	Si	P	S	Cl	
	1.66	1.55	1.45	1.45	1.44	
	Ga	Ge	As	Se	Br	
	1.72	1.58	1.61	1.60	?1.59	
	In	Sn	Sb	Te	I	Xe
	?	1.82	?	1.75	1.75	?1.65
Hg	Tl	Pb	Bi			
1.71	?	?	?			

Lead

A single structure has appeared for a lead compound. In $Ph_3SiOPbPh_3$, the angle <SiOPb is 142°, and the Pb...Si distance is 3.67 Å [22] implying an upper limit to the radius of lead of 2.12 Å. However because of the partial disorder of the silicon and lead atoms, the structure is of somewhat low accuracy: the refined value of the Si–O distance, for example, is 1.87 Å, whereas Si–O bonds in this type of environment are usually in the range 1.61–1.68 Å. It is perhaps noteworthy that in the analogous tin deriva-

tive, $Ph_3SiOnPh_3$, the disorder was such that the structure could not be solved [22]. In Ph_3PbNCO [23], the molecules are associated into chains: the angle <PbNC is 148°, and the intramolecular distance Pb...C is 3.43 Å, implying a lead radius of 2.18 Å: however, as with many other Group IV pseudohalides, it is likely that the force constant opposing bending of the skeleton in the mode δ(PbNC) is very small [15], so that the observed geometry of the molecule is dominated by intermolecular, rather than intramolecular forces; similar remarks may be applied to the tin analogue [24].

The revised intramolecular radii are set out in Table V.

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