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Intramolecular Non-bonded Atomic Radii: Application to the Heavier *p* Elements

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Intramolecular non-bonded atomic radii are derived for the 4p, 5p and 6p series of elements and applied to the stereochemistries of their compounds with carbon, nitrogen and oxygen. The values derived are (/Å): Ga, 1.72; Ge, 1.58; As, 1.61; Se, 1.58; Br, 1.59; In, 1.95; Sn, 1.88; Sb, 1.88; Te, 1.87; I, 1.86; Xe, 1.79; Hg, 1.76; Bi, 1.96. The values of the non-bonded radii are compared with covalent radii for elements of the 2p, 3p, 4p, 5p and 6p series.

Introduction

In an earlier paper [1], intramolecular non-bonded radii for a number of elements were deduced, and applied to problems of chemical and structural behaviour: a subsequent analysis [2] of the structures adopted by phosphorus compounds indicated the importance of non-bonded interactions in cyclopolyphosphazenes, imido-phosphoranes, and phosphorus-containing heterocumulenes. In the earlier work [1], only a few radii for elements of the 4*p* (Ga–Br) and subsequent series were obtained: in view of the recent upsurge of interest in the structural chemistry of the heavier *p* elements, this paper undertakes to derive radii for the elements of the 4*p* and heavier series, and to discuss these values in terms of effective atomic shape.

As before, if it is found that in a molecular fragment XMY the angle at M significantly exceeds the tetrahedal value when M is two-connected oxygen, three-connected nitrogen or four-connected carbon, or this angle substantially exceeds 120° when M is two-connected nitrogen or three-connected carbon, then the distance between X and Y is taken as a major determinant of <XMY: from the minimum observed distances subject to these conditions, hard-atom intramolecular non-bonded radii can be deduced.

Results

Group IIB

In tri(chloromercuri)oxonium chloride, $(ClHg)_3O^+Cl^-$, the cation contains planar OHg_3 groups [3] having an Hg···Hg distance of 3.53 Å. Similar groups are found [4] in the basic mercury perchlorate, $Hg_2O(OH)ClO_4$, in which the mean HgOHg angle is 117.6° with the inter-metallic distance 3.49 Å. Very similar mercury–mercury distances are observed in the oxide chloride $Hg_3O_2Cl_2$, 3.52 Å [5], and in the basic mercury sulphate $Hg(OH)_2\cdot 2HgSO_4\cdot H_2O$, 3.53 Å [6]. Taking the mean of these four data yields a value for the intramolecular radius of mercury of 1.76 Å.

Group IIIB

The trimer of aziridinylgallane $(C_2H_4NGaH_2)_3$ consists of a six-membered $(GaN)_3$ ring [7] in which the GaNGa angle at four-connected nitrogen is 121°, associated with a Ga···Ga distance of 3.43 Å. An electron-diffraction study [8] of gallium(I) oxide, Ga_2O, vapour revealed an angle at oxygen of 140 ± 10° [8], with a preferred Ga···Ga distance of 3.46 Å: the range on this distance implied by the angle is 3.34–3.53 Å. Few other structures are known of gallium compounds, and no other in which gallium subtends on unusually large angle at a central atom. The two data quoted above yield a gallium radius of 1.72 Å.

A similar study of indium(I) oxide revealed an angle at oxygen of 150 ± 10° [8]: the preferred In···In distance is 3.90 Å, although the range implied by the published uncertainties is 3.80–3.98 Å. The radius of indium is taken as 1.95 Å, although it must be recognised that this figure merely represents an upper bound.

No compounds of thallium which might yield an intramolecular radius have been structurally characterised: this may reflect the predominantly metallic and ionic character of thallium.

The radius for gallium deduced above suggests that the radius deduced previously, 1.85 Å, for aluminium is too large: certainly this value is quite out of line with the radii of the rest of the 3*p* series, which vary from 1.55 Å for silicon, *via* 1.45 Å for both phosphorus [2] and sulphur, to 1.44 Å for chlorine. In the tetrakis(trimethylsilyloxy)aluminate ion, $(Me_3SiO)_4Al^-$, the SiOAl angle is 147.2°, [9] and the Al···Si distance is 3.21 Å: if this distance is taken to be the hard-atom close-contact limit, this implies a radius for aluminium of 1.66 Å, consistent with the radii of both gallium, 1.72 Å and silicon, 1.55 Å.

Group IV

In digermyl ether, $(H_3Ge)_2O$, the Ge•••Ge distance is 3.15 Å [10] subtending an angle of 126.5° at the oxygen atom, while in germanium(IV) tetrakis(diphenylketimine),$(Ph_2NC)_4Ge$, the GeNC angle is 127° [11] with a Ge•••C distance of 2.82 Å. These data, taken together imply a germanium radius of 1.58 Å. An intramolecular radius for tin of 1.88 Å was derived previously [1]. No structural data appear to have been published on compouds of lead from which such a radius might be obtained. As with thallium this may reflect the metallic nature of this element.

Group V

In a series of salts of the μ-oxo-decafluorodiarsenate ion $[F_5AsOAsF_5]^-$, the configuration was found to be independent of the cation [12, 13]; the angles at oxygen in the potassium, rubidium, and caesium salts are 136.9°, 136.1°, and 138.8°, respectively, associated with As•••As distances of 3.233 Å, 3.214 Å and 3.225 Å, whose mean is 3.233 Å. For tetraarsenic hexoxide As_4O_6, two independent structure determinations have been carried out by electron diffraction: one study found <AsOAs = 126° [14], with an As•••As distance of 3.21 Å, while the other found <AsOAs = 128° [15], with an As•••As distance of 3.20 Å. On the basis of these five data, a radius for arsenic is assigned as 1.61 Å.

The structures of several oxo-bridged antimony species of the form $(R_3SbX)_2O$ have recently been determined. When R = phenyl and X = perchlorate, the SbOSb angle is 139.8° [16], and the Sb•••Sb distance is 3.729 Å. Three structures have been determined having R = methyl [17]: when X = perchlorate, <SbOSb = 128°, and the Sb•••Sb distance is 3.724 Å; when X = chloride, the angle at oxygen is 129° and the Sb•••Sb distance is 3.814 Å; and when X = azide, the Sb•••Sb distance of 3.744 Å subtends an angle of 126° at oxygen. The mean value of these four Sb•••Sb distances is 3.753, implying an intramolecular non-bonding radius for antimony of 1.88 Å, precisely that earlier suggested from the structure of the adduct $Me_3PO{\cdot}SbCl_5$ [1].

A single bismuth analogue has been studied having R = phenyl and X = perchlorate, $(Ph_3BiOClO_3)_2O$ [18]: in this compound the angle at the bridging oxygen is 142.4° and the bismuth•••bismuth distance is 3.919 Å, implying an intramolecular radius for bismuth of 1.96 Å.

Group VI

In *trans*-ethaneseleninic anhydride, the Se•••Se distance is 3.199 Å [19], subtending on angle of 123° at the two-coordinate anhydride oxygen, while in selenium(IV) oxide [20], which crystallises in long •••Se(O)OSe(O)O••• chains, the SeOSe angle is 125° and the Se•••Se distance is 3.16 Å. In the vanadium(IV) selenium(IV) oxide, VSe_2O_6, which according to the authors [21] could be regarded either as $VO^{+2}\,Se_2O_5^{-2}$ or as $Se_2O^{+6}\,VO_5^{-6}$ (*sic*), the angle at oxygen in the SeOSe fragment, however this is described, is 119.6°, and the interselenium distance is 3.103 Å. In the zinc species $ZnSe_2O_5$, which presumably must be $Zn^{+2}Se_2O_5^{-2}$, the SeOSe angle is found to be 121.6° [22], and the Se•••Se distance to be 3.195 Å. Selenium(VI) oxide exists in the vapour phase as a mixture of monomeric SeO_3 and tetrameric Se_4O_{12} rings of S_4 symmetry [23]: within the rings the SeOSe angle is 119.5° and the Se•••Se distance is 3.13 Å. These five structures all contain remarkably similar SeOSe fragments: the mean Se•••Se distance is 3.157 Å implying a radius for selenium of 1.58 Å.

A radius for tellurium of 1.87 Å was determined previously from the structure of tellurium(IV) oxide [1].

Group VII

Rather few molecular species exist which are suitable for the determination of non-bonded radii for the halogens. In tetrabromoethylene [24], C_2Br_4, the C•••Br distance is 2.854 Å and the geminal Br••• Br distance is 3.176 Å, which together suggest a mean bromine radius of 1.59 Å. In benzoyl triphenylphosphoranylidenemethyl iodide $Ph_3PC(COPh)I$, the non-bonded distances of interest about the central carbon atom are P•••I, 3.32 Å and C•••I, 3.10 Å [25], which together suggest a radius for iodine of 1.86 Å.

Group VIII

A tentative radius for xenon may be derived from the structure of xenon(II) fluoride fluorosulphonate, $FXeOSO_2F$ [26] in which the XeOS angle is 123.7° and the Xe•••S distance is 3.238 Å, indicating a hard-atom radius for xenon of 1.79 Å.

Applications

The principal application to be discussed of the radii deduced above for the heavier *p*-elements is to anomalous bond angles at light atoms such as carbon, nitrogen and oxygen. The question of maximum coordination numbers has been discussed earlier [1] in terms of non-bonded interactions, and needs no rehearsal here.

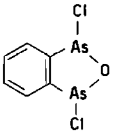
In accord with the essentially metallic character of the heavier group III elements, very few structures are currently known of molecular species: aside from those used for assignment of radii, none as yet is known which shows anomalous geometry. Of the lighter elements, the scandium compound tris(bis(trimethylsilyl)amino)scandium(III), $[(Me_3Si)_2N]_3Sc$, contains planar Si_2NSc fragments having an SiNSc angle of 119.7° [27], larger than tetrahedal, with an Si•••Sc distance of 3.27 Å: this implies a lower limit to the scandium radius of 1.72 Å.

In view of the revision above of the radius of aluminium to 1.66 Å, the stereochemistry found in certain compounds of this element requires reconsideration. In the silylamino derivative $[Me_3Si)_2N]_3Al$, the nitrogen atoms are planar [28], with an Si•••Si distance of 3.00 Å, (expected 3.10 Å), and Si•••Al distance of 3.07 Å, shorter than the 3.21 Å expected: consequently the planarity at nitrogen is ascribed to interatomic repulsion. In μ-oxo-bis(bis(2-methyl-8-quinolinato)aluminium), the AlOAl bridge is linear [29], and the Al•••Al distance is 3.35 Å (expected 3.32 Å): potassium μ-fluoro-bis(triethylaluminate), $K(Et_3AlFAlEt_3)$, has a linear AlFAl bridge with Al–F distances of 1.80 Å [30], so that the Al•••Al distance is somewhat longer than the minimum contact distance. Highly ionic metal oxides such as Li_2O are linear at oxygen [31], and it is possible that in both Li_2O and this μ-fluoro di-aluminium species intercore repulsion completely dominates the interelectronic repulsion which tends to bend the system. At any rate, it seems implausible to suppose that the contraction of the 3*d* orbitals in an element of such low electronegativity as aluminium is structurally significant.

The wide angles at oxygen and nitrogen in $(H_3Ge)_2O$ and $(Ph_2NC)_4Ge$, 126.5° and 127°, were mentioned when the radius of germanium was assigned. The structures of $(H_3Ge)_3N$, H_3GeNCO and $(H_3GeN)_2C$ in which the angles at nitrogen are all wider than expected have been discussed previously [1]. In bis(trimethylgermyl)ether, the angle at oxygen is 141° and the Ge•••Ge distance is 3.34 Å, indicating same steric compression [32]. Similarly, in bis(trimethyltin)oxide, $(Me_3Sn)_2O$, the angle at oxygen is 141° [32], with an Sn•••Sn distance of 3.66 Å. A number of polymeric species have SnOM angles in excess of 130°, *viz.*, Me_3SnOMe [33], $Me_3SnOCOR$ ($R = CH_3, CF_3$) [34], $(Me_3Sn)_3OHCrO_4$ [35], $Me_3SnNCO{\cdot}Me_3SnOH$ [36] : as with the pseudohalides of elements such as tin [37], it is very difficult when polymeric species are found to assess the relative importance of intermolecular and intramolecular interactions.

The adducts of tin(IV) chloride with oxygen donors such as phosphoryl chloride [38], dimethyl sulphoxide [38] and selenyl chloride [39] exhibit angles at two-connected oxygen substantially greater than tetrahedral, but varying very widely: the lowest angles observed [38] both in these adducts and in those of antimony(V) chloride (see below) are essentially the same as the values predicted by the hard-atom model. It seems probable that in these adducts, the stereo-chemistry at oxygen is dominated by intermolecular forces, subject to a lower limit imposed upon the bond angle at oxygen <MOX by the distances M•••X (M = Sn, Sb; X = P, As, S, Se).

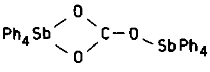
In *o*-phenylenediarsine oxychloride (I), the angle at oxygen is 151° [40], remarkably large for an angle in a five-membered ring:



(I)

the As•••As distance however is 3.27 Å, little more than the hard-atom contact distance 3.22 Å. In the acyclic bis(diphenylarsenic)oxide, $(Ph_2As)_2O$, the angle at oxygen is 137° [41], associated with as As•••As distance of 3.11 Å: in this example, the angle AsOAs is much larger than that expected from VSEPR considerations and the As•••As distance shorter than expected, indicating substantial steric compression.

Tetraphenylantimony methoxide, Ph_4SbOCH_3, has an SbOC angle of 120.8° [42], and triphenylantimony dimethoxide, $Ph_3Sb(OCH_3)_2$, has SbOC angles of 122.5° and 120.7° [42], all wider than expected for two-coordinate oxygen. The associated Sb•••C distances are all a little shorter than the close contact distance, being 3.022, 3.054 and 3.008 Å respectively (mean 3.026 Å). In μ-carbonato-bis(tetraphenyl)antimony, (II) [43]



(II)

the exocyclic SbOC angle is 124.3°, and the Sb•••C distance is 3.15 Å (expected 3.13 Å).

The orthorhombic phase of antimony(III) oxide consists of chains joined by SbOSb bridges in which <SbOSb = 130.8° [44] : the steric rather than electronic origin of this wide angle is revealed by the Sb•••Sb distance, 3.68 Å, somewhat shorter than the expected 3.76 Å.

In the 1:1 adducts of antimony(V) chloride with oxygen donors such as phosphoryl chloride [45], trimethylphosphine oxide [45], diphenylsulphoxide [38], dimethylsulphone [38], selenyl chloride [46] and dimethylformamide [47], the angles SbOM (M = P, S, Se, C) are found to vary over a wide range (although always greater than the VSEPR prediction) from 117° in the diphenylsulphoxide adduct [38] to 145° in that of phosphoryl chloride [45]. As with the analogous adducts of tin(IV) chloride, the Sb••• M distance varies widely also, subject to a lower limit at the hard-atom contact distance, which in turn imposes a lower limit on <SbOM.

Antimony(V) fluoride is tetrameric [48], consisting of *cis*-linked octahedra: there are two types of SbFSb bridge, one having <SbFSb = 141°, associated

TABLE. Covalent and Intramolecular Non-Bonded Radii for the Typical Elements.

Element	Covalent radius (/Å)	Non-bonded radius (/Å)	Ratio
Be	0.941[a]	1.39	0.677
B	0.817[b]	1.33	0.614
C	0.767[c]	1.25	0.614
N	0.726[d]	1.14	0.637
O	0.745[e]	1.13	0.659
F	0.709[f]	1.08	0.656
Al	1.202[g]	1.66	0.724
Si	1.169[h]	1.55	0.754
P	1.103[i]	1.45	0.761
S	1.020[j]	1.45	0.703
Cl	0.994[k]	1.44	0.690
Ga	1.26[l]	1.72	0.750
Ge	1.202[m]	1.58	0.761
As	1.218[n]	1.61	0.757
Se	1.163[o]	1.58	0.736
Br	1.142[p]	1.59	0.718
In	1.47[q]	1.95	0.754
Sn	1.386[r]	1.88	0.737
Sb	1.336[s]	1.88	0.727
Te	1.356[t]	1.87	0.725
I	1.340[u]	1.86	0.720
Xe		1.79	
Hg	1.33[v]	1.76	0.756
Tl	1.45[w]		
Pb	1.42[x]		
Bi	1.43[y]	1.96	0.730

[a] r(CH_3–Be) 1.708 Å in $CH_3BeC_5H_5$: D. A. Drew and A. Haaland, *Acta Chem. Scand.*, *26*, 3079 (1972). [b] r(CH_3–B) 1.578 Å in $B(CH_3)_3$: L. S. Bartell and B. L. Carroll, *J. Chem. Phys.*, *42*, 3076 (1965); 1.590 Å in $[(CH_3)_2BH]_2$: B. L. Carroll and L. S. Bartell, *Inorg. Chem.*, *7*, 219 (1968).

[c] r(C–C) 1.534 Å in C_2H_6: L. S. Bartell and H. K. Higginbotham, *J. Chem. Phys.*, *42*, 851 (1965). [d] r(N–N) 1.453 Å in N_2H_4: A. Yamaguchi, I. Ichishima, T. Shimanouchi and S. I. Mizushima, *J. Chem. Phys.*, *31*, 843 (1959).

[e] r(O–O) 1.49 Å in H_2O_2: S. C. Abrahams, R. L. Collin and W. N. Lipscomb, *Acta Cryst.*, *4*, 15 (1951); O. Bain and P. A. Giguere, *Can. J. Chem.*, *33*, 527 (1955). [f] r(F–F) 1.418 Å in F_2: D. Andrychuk, *Can. J. Chem.*, *29*, 151 (1951).

[g] r(CH_3–Al) 1.989 Å in $(CH_3)_3AlN(CH_3)_3$: G. A. Anderson, F. R. Forgaard and A. Haaland, *Acta Chem. Scand.*, *26*, 1947 (1972); 1.949 Å in $[(CH_3)_2AlH]_2$: A. Almenningen, G. A. Anderson, F. R. Forgaard and A. Haaland, *Acta Chem. Scand.*, *26*, 2315 (1972). [h] r(Si–Si) 2.332 Å in Si_2H_6: B. Beagley, A. R. Conrad, J. M. Freeman, J. J. Monaghan, B. G. Norton and G. C. Holywell, *J. Mol. Struct.*, *11*, 371 (1972); 2.342 Å in $Si_2(CH_3)_6$: B. Beagley, J. J. Monaghan, and T. G. Hewitt, *J. Mol. Struct.*, *8*, 401 (1971). [i] r(P–P) 2.219 Å in P_2H_4: as for Si_2H_6; 2.192 Å in $P_2(CH_3)_4$: A. McAdam, B. Beagley and T. G. Hewitt, *Trans. Faraday Soc.*, *66*, 2732 (1970). [j] r(S–S) 2.057 Å in H_2S_2: M. Winnewisser and J. Haase, *Z. Naturforsch.*, *23B*, 56 (1968); 2.023 Å in $(CH_3)_2S_2$: B. Beagley and K. T. McAloon, *Trans. Faraday Soc.*, *67*, 3216 (1971); 2.037 Å in S_8: S. C. Abrahams, *Acta Cryst.*, *8*, 661 (1955). [k] r(Cl–Cl) 1.988 Å in Cl_2: G. Herzberg, "Molecular Spectra and Molecular Structure: Spectra of Diatomic Molecules", D. Van Nostrand, New York (1945). [l] r(Ga–N) 1.97 Å in $[(CH_2)_2NGaH_2]_3$: ref. 7. [m] r(Ge–Ge) 2.404 Å in Ge_2H_6: B. Beagley and J. J. Monaghan,, *Trans. Faraday Soc.*, *66*, 2745 (1970). [n] r(As–As) 2.435 Å in As_4: Y. Morino, T. Ukaji and T. Ito, *Bull. Chem. Soc. Japan*, *39*, 64 (1966). [o] r(Se–Se) 2.326 Å in $(CH_3)_2Se_2$: P. D'Antonio, G. George, A. H. Lowrey and J. Karle, *J. Chem. Phys.*, *55*, 1071 (1971). [p] r(Br–Br) 2.284 Å in Br_2: as for Cl_2. [q] r(CH_3–In) 2.24 Å in $KIn(CH_3)_4$; 2.26 Å in $CsIn(CH_3)_4$: K. Hoffmann and E. Weiss, *J. Organometal. Chem.*, *50*, 17 (1973). [r] r(Sn–Sn) 2.772 Å in $Sn_2(CH_3)_6$: K. T. McAloon, *Ph. D. Thesis*, UMIST, (1970); 2.770 Å in Sn_2Ph_6: H. Preut, H. J. Haupt and F. Huber, *Z. Anorg. Chem.*, *396*, 81 (1973) [s] r(Ph_{eq}–Sb) 2.115 Å in $SbPh_5$: A. L. Beauchamp, M. J. Bennet and F. A. Cotton, *J. Am. Chem. Soc.*, *90*, 6675 (1968); 2.119 Å in both Ph_4SbOCH_3 and $Ph_3Sb(OCH_3)_2$: ref 42; 2.131 Å in Ph_4SbOH: A. L. Beauchamp, M. J. Bennett and F. A. Cotton, *J. Am. Chem. Soc.*, *91*, 297 (1969). r(Ph–Ph) 1.510 Å in biphenyls: O. Bastiansen and A. Skancke, *Acta Chem. Scand.*, *21*, 587 (1967). [t] r(Te–Te) 2.712 Å in Ph_2Te_2: G. Uabres, O. Dideberg and L. Dupont, *Acta Cryst.*, *B28*, 2438 (1972). [u] r(I–I) 2.679 Å in I_2: T. Ukaji and K. Kuchitsu, *Bull Chem. Soc. Japan*, *39*, 2153 (1966). [v] r(CH_3–Hg) 2.083 Å in $Hg(CH_3)_2$: K. Kashiwabara, S. Konaka, T. Iijima, and M. Kimura, *Bull. Chem. Soc. Japan*, *46*, 407 (1973); r(Ph–Hg) 2.093 Å in $HgPh_2$: L. V. Vilkov, M. G. Anashkin and G. I. Mamaeva, *Zhur. Strukt. Khim.*, *9*, 372 (1968). [w] r(CH_3–Tl) 2.218 Å in $Tl(CH_3)_3$: A. G. Robiette and G. M. Sheldrick, personal communication. [x] r(Pb–Pb) 2.83 Å in Pb_2Ph_6: H. Preut, H. J. Haupt and F. Huber, *Z. Anorg. Chem.*, *388*, 165 (1972). [y] r(Ph–Bi) 2.19 Å in $(O_3ClOBiPh_3)_2O$: ref. 18.

with an Sb···Sb distances of 3.81 Å (hard-atom limit 3.76 Å), and the other having <SbFSb = 170 ° and Sb···Sb = 4.04 Å. It appears that the SbFSb angle is very easily deformed by intermolecular forces in the solid state, possibly because the bonding in the bridges is highly ionic: it would be of interest to determine the geometry of species such as $(SbF_5)_4$ in the vapour phase, where the structure can reflect only intramolecular forces. A number of other fluoro-bridged structures appear to be subject to geometrical perturbation by intermolecular forces. In caesium heptafluorodiantimonate(III), $CsSb_2F_7$, the SbFSb angle is 125.3° [49], while in the analogous Sb(V) anion $Sb_2F_{11}^-$, determined as the XeF_3^+ salt, the SbFSb angle is 155.4° [50]: the Sb···Sb distances are 3.98 Å and 3.96 Å respectively. Other examples are found in $[Co(NH_3)_6^{+3}][Sb_2F_9^{-3}]$ in which <SbFSb is 142.1 ° (Sb···Sb = 4.44 Å) [51]; $Xe_2F_{11}^+AuF_6^-$ in which <XeFXe is 169.2° [52], associated with an Xe···Xe distance of 4.45 Å; $Xe_2F_3^+AsF_6^-$ where the Xe···Xe distance is 4.13 Å and <XeFXe = 150° [53]; $XeF_5^+AsF_6^-$ in which there are three independent AsFXe angles of 110°, 114°, and 158° [53], associated respectively with As···Xe distances of 3.80, 3.80 and 4.31 Å; $SbF_5 \cdot XeF_4$ in which <XeFSb is 140.8° [54], and the Xe···Sb distance is 4.15 Å; and the ion $(Et_3Al)_2F^-$ discussed above. These geometries can be rationalised neither in terms of inter-electronic repulsions (VSEPR model) nor in terms of a hard-atom model: highly ionic bridges whose angles are very easily deformed by intermolecular forces, so that a given ion may exhibit widely different geometries when associated with different counter ions, is the most plausible interpretation.

The $(NSeO_2)_3^{-3}$ anion in potassium tri(selenylimide) has a planar N_3Se_3 ring [55], in which the mean Se•••Se distance is 2.95 Å, considerably shorter than expected, and is thereby analogous to the isoelectronic planar cyclotriphosphazenes $(NPX_2)_3$. The occupied π-molecular orbitals in these D_{3h} species are of symmetry types A_2'' and E'', of which the A_2'' orbital, consisting of all the nitrogen $2p_z$ orbitals and all the selenium (or phosphorus) d_π orbitals radial to the ring combined together in-phase is strongly bonding between pairs of selenium (or phosphorus) atoms: the Se•••Se distance cannot therefore be properly thought of as being a wholly non-bonded distance.

While the number of structures to which this approach is applicable is still much smaller for the heavier elements than for the lighter nevertheless it is hoped that the non-bonded radii derived here may form some basis for the understanding of molecular structures, as more are determined.

Discussion

In the Table are collected together the limiting non-bonded radii derived here, and in previous work [1, 2, 56], together with values of covalent radii derived for the most part from compounds $[R_nX]_p$ containing homonuclear bonds X–X, and ratios of (covalent radius)/(non-bonded radius). It is apparent that this ratio is generally smaller for the Be–F row of the periodic table than for the subsequent rows: for principal quantum number n = 2 → 6, the mean values of this ratio are 0.643, 0.726, 0.744, 0.732, and 0.743 respectively, although this last figure is based on two data only.

While for n = 3 → 6, the value of this ratio appears to be essentially constant, it is significantly smaller when n = 2. For compounds in which the covalent radii are strictly additive, wider interbond angles $\sphericalangle MXM'$ would be expected, when atoms M and M′ had low ratios of (covalent radius)/(non-bonded radius) then when they had high ratios: this contrasts markedly with the observation of *smaller* angles at X when the atoms M and M′ have n = 2, with a concomitant small ratio. Similarly those elements which exhibit wider angles in fragments MXM′ are just those for which, if the covalent radii were additive, angles smaller than those predicted by the VSEPR model would be expected.

Consequently the underlying cause for the wider angles in MXM′ fragments when M and/or M′ have n ⩾ 3 must be seen in the non-additivity of the covalent radii. The difference between the observed bond length and the sum of the covalent radii appears, in the most extensive series of data available for similar species *i.e.* $(H_3M)_2O$ (M = C, Si, Ge) and $[(CH_3)_3Sn]_2O$, to be roughly proportional to the difference in electronegativity, in accord with the well-known generalisation of Schomaker and Stevenson [57] (*cf.* ref. 58 for further discussion of this electronegativity correction to bond-lengths). On going from the n = 2 row of the periodic table to the n = 3 row, the difference in electronegativity $|x_M - x_X|$ increases markedly for a common X, so that $(r_M + r_X) - d(M{-}X)$ increases: apparently this term is so great when n ⩾ 3 that it more than outweighs the effect of the larger radius ratio, so giving wider bond angles.

Turning to the individual values of the non-bonded radii, those of the *2p*, *3p*, *4p* and *5p* series are felt to be secure, except possibly for that of xenon, which is derived from a single structure. In the *6p* series, that of bismuth 1.96 Å seems entirely reasonable in view of the values for its lighter congeners: N, 1.14; P, 1.45; As, 1.61; and Sb, 1.88 Å. Both the non-bonded and covalent radii of mercury seem rather small, although the ratio of these radii, 0.756 Å, is fairly typical of the heavier elements: the lower radii may be associated with the fact that Hg(II) is formally a d^{10} species, and in none of its compounds has any *6p* electrons. The atoms of the *4p* series, Ga → Br, have both covalent and non-bonded radii *ca.* 5% smaller than expected from simple interpolation between the *3p* and *5p* series, probably due to the increase in effective nuclear charges in the *4p* elements resulting from the population of the *3d* orbitals.

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