

Some Chemical and Structural Consequences of Non-bonded Interactions

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Unusual geometries at first row atoms, and maximum coordination numbers of first and second row atoms are discussed in terms of non-bonded interactions. Structures of closed shell molecules are divided into three categories in which respectively inter-electron repulsions dominate, electronic and nuclear terms are in balance, and inter-nuclear repulsions dominate.

Introduction

Atoms in molecules are non-spherical: van der Waals' radii exceed¹ covalent radii by factors between 1.5 and 2.2. Seeking to define further the shape of such atoms, Bartell introduced² a set of radii which describe and define the minimum distance of approach of two atoms X and Y in a fragment XMY. Just as the covalent radius of X in XMY refers to the direction towards M, and the van der Waals' radius refers to the direction away from M, so the "one-angle" radius refers to the atom's radius in the direction of Y: this is always a radius of that half of the atom which is closer to M, so that its value lies between the covalent radius and the conventional van der Waals' radius.

Adopting one angle radii for C, N, O, F and Cl of 1.25 Å, 1.14 Å, 1.13 Å, 1.08 Å and 1.44 Å respectively, and assuming that molecular geometry is determined in detail by contacts between close, non-bonded atoms whereby the X···Y distance in a fragment XMY is the principal determinant of the lower limit of the angle XMY, Bartell was able² to rationalise the detailed geometry of a large number of molecules, with discrepancies between the observed and calculated values of the shortest non-bonded distances of only a few hundredths of an Ångström.

Hitherto, the geometries of molecules containing only closed-shell atoms have been rationalised primarily in terms of valence-shell electron pair repulsions (VSEPR). The VSEPR method, which has had remarkable success, approaches molecular geometry solely in terms of inter-electron repulsions, ignoring inter-nuclear repulsions, and is therefore forced to interpret unexpectedly large interbond angles by means of such

expedients as intramolecular π -bonding, involving *d*-orbitals, even in molecules containing only *p*-block acceptor elements of low electronegativity such as aluminium and silicon, in which *d*-orbital participation might be expected, from energetic considerations, to be of limited importance. A further objection to this interpretation is founded on the observation that whenever a nitrogen or oxygen atom which exhibits unusually large inter-bond angles in a particular compound is replaced by the less electronegative phosphorus or sulphur, the bond angles in the heavy atom analogue revert to the expected value, rather than becoming more markedly aberrant.

This paper explores a number of structural and chemical observations in terms of the repulsions between non-bonded atoms. These observations fall naturally into two types: a) consideration of the geometry about the first row atoms C, N, O and F; in particular, deviations of the inter-bond angles from the values predicted by the VSEPR method. In general, if in a molecular fragment XMY (M = C, N, O or F), the distance X···Y is approximately equal to, or is less than, the sum of the one-angle radii of the atoms X and Y, and the angle XMY is significantly larger than the value predicted by the VSEPR method, then these two observations are to be construed as cause and effect; b) consideration of the maximum coordination numbers observed about elements both of the first (Li–Ne) row and of subsequent rows of the periodic table. If in a compound MX_p (p = 3, 4 or 6) the X···X distance is close to the close contact limit of two X atoms, then an increase in the coordination number of M will require an appreciable stretching of the MX bonds. The energetic requirement for this may prevent both permanent increases in coordination number – making p the highest attainable coordination number when M is surrounded by X, and temporary increases in coordination number – making MX_p inert to attack by nucleophilic reagents.

In the applications section below a representative selection of examples is discussed: this selection is not intended to be exhaustive, but simply to be sufficient to demonstrate the validity of the approach. A fairly complete set of radii is derived.

Results

Assignment of Radii

The one-angle radii for H, C, N, O, F and Cl employed by Bartell² are adopted without change: that for carbon was derived from isobutene³, those for hydrogen, fluorine and chlorine from compounds of the form H_2CCX_2 ($X = H, F,$ or Cl)^{4,5,6}, and those for nitrogen and oxygen from urea⁷ and formic acid⁸ respectively.

Radii for other atoms are mostly assigned by making the assumption that when in a fragment XMY of a non-cyclic compound, the angle at M exceeds the tetrahedral value if M is 2-connected oxygen, 3-connected nitrogen or 4-connected carbon, or if the angle XMY exceeds 120° when M is 2-connected nitrogen or 3-connected carbon, then the minimum $X \cdots Y$ distance experimentally observed in such a fragment represents the close-contact limit and is the sum of the one-angle radii of the atoms X and Y. This is subject to the proviso that if a derivative of 2-connected oxygen XOY is strictly linear at O, or a derivative of 3-connected nitrogen NXYZ is strictly planar at N, then the distances between, X, Y and Z may be slightly shorter than the close contact limits, with appreciable compressive strain present in the molecule.

Beryllium

In beryllium bisacetylacetonate the BeOC angle is⁹ 127° , with a corresponding $Be \cdots C$ distance of 2.64 \AA : if this is taken as the close contact limit, a radius for beryllium of 1.39 \AA results.

Boron

In tetra-B-isothiocyanatotetra-N-t-butylborazocine, $(Me_3CNBNCs)_4$ the exocyclic BNC angle is 176.4° with the $B \cdots C$ distance 2.60_2 \AA ¹⁰: 6-isothiocyanatodecaborane-14, $6-B_{10}H_{13}NCS$ has a BNC angle of 171.0° with a $B \cdots C$ distance of 2.57_6 \AA ¹¹. If this latter value is regarded as the close-contact limit between boron and carbon, a radius for boron of 1.33 \AA results.

Aluminium

Both $[(CH_3)_3Si)_2N)_3Al^{12}$ and $K[(CH_3)_3AlN_3Al(CH_3)_3]^{13}$ contain planar nitrogen atoms, but there is evidence of steric compression in each (see Applications section, below). The shortest distance observed between non-sterically compressed aluminium atoms bonded to the same bridging atom is the 3.69_1 \AA observed¹⁴ in $Te_4^{+2}(Al_2Cl_7^-)_2$ where the AlClAl angle is 110.8° : this angle might, by analogy with typical angles at 2-connected sulphur, be expected to be less than 100° . Taking 3.69_1 \AA as the close-contact limit, a radius for aluminium of 1.85 \AA is obtained.

Silicon

In the compounds $(H_3Si)_2X$, for $X = CH_2, NH$ or O , the SiXSi angles are $114.4^\circ, 127.7^\circ$ and 144.1°

respectively, with $Si \cdots Si$ distances of 3.149 \AA ¹⁵, 3.097 \AA ¹⁶ and 3.107 \AA ¹⁷ respectively. In $(F_3Si)_2O$, the SiOSi angle is¹⁸ 155.7° , while the $Si \cdots Si$ distance is 3.081 \AA . If the mean of these four $Si \cdots Si$ distances is taken as the close-contact limit, the radius for silicon is found to be 1.55 \AA .

Germanium

Taking the $Ge \cdots Ge$ distance observed¹⁹ in $(H_3Ge)_2O$, 3.154 \AA , as the close contact limit, the radius for germanium is 1.58 \AA : the GeOGe angle in this compound is 126.5° .

Tin

In tetrachloro-1,4-bis(triethylstannyloxy)benzene, $1,4-[(C_2H_5)_3SnO]_2C_6H_4$, the SnOC angle is²⁰ 127° and the $Sn \cdots C$ distance 3.05 \AA , while in tris-cyclohexyltin acetate, $(C_6H_{11})_3SnOCOCH_3$, the SnOC angle is²¹ 124.8° and the $Sn \cdots C$ distance is 3.13 \AA . The latter distance, although larger, is preferred for derivation of a radius for tin: the structure determination of the acetate derivative used three-dimensional data, whereas that of the benzene derivative employed only two-dimensional data. The limits of error on the geometrical parameters derived for the benzene compound are correspondingly greater than those for the acetate. The tin radius so derived is 1.88 \AA .

Phosphorus

$(PF_2)_2O$ has²² a POP angle of 145° and a $P \cdots P$ distance of 2.92_4 \AA : adoption of this as the close contact limit gives a phosphorus radius of 1.46 \AA .

Antimony

$SbCl_5$ forms 1:1 adducts both with $POCl_3$ and with $POMe_3$. In the $POCl_3$ derivative the SbOP angle is²³ 145° with an $Sb \cdots P$ distance of 3.48 \AA : the $POMe_3$ compound has²³ an SbOP angle of 144.9° with an $Sb \cdots P$ distance of 3.34 \AA . This latter value places an upper limit of 1.88 \AA on the radius of antimony.

Sulphur

The disulphate ion in $K_2S_2O_7$ has²⁴ an SOS angle of 124.2° with an $S \cdots S$ distance of 2.90_8 \AA , while the trisulphate ion in $(NO_2)_2S_3O_{10}$ has²⁵ SOS angles of 122° with corresponding $S \cdots S$ distances of 2.89_7 \AA . The mean of these two values yields a radius for sulphur of 1.45 \AA .

Selenium

In selenium dioxide, which crystallises with an infinite chain structure, the SeOSE angle within the chain is²⁶ 125° with the $Se \cdots Se$ distance 3.16 \AA ; this indicates an upper limit to the radius of selenium of 1.58 \AA .

Tellurium

In $\alpha\text{-TeO}_2$, tellurium is four-fold coordinated by oxygen and oxygen is two-fold coordinated by tellu-

rium²⁷: the TeOTe angle is 139.5° with a Te···Te distance of 3.74 Å. This indicates a one angle radius for tellurium of 1.87 Å.

These radii, together with those of Bartell² are summarised in Table I. It will be noted that the radii do not increase smoothly on descending a group, but that the 4*p* elements germanium and selenium have radii rather smaller than interpolation might suggest. This trend is found¹ also in the covalent radii and in the conventional van der Waals radii, and may be ascribed to the increase in effective nuclear charge in the 4*p* elements occasioned by the interpolation of the 3*d* series between the 3*p* and 4*p* elements.

On the basis of the assigned radii in Table I, reasonable tentative estimates may be given for arsenic, 1.58 Å, bromine, 1.56 Å, and iodine, 1.85 Å.

Applications

Structures of compounds containing 4-connected carbon

This section includes, in addition to those compounds having 4 groups attached to a single carbon atom, free radicals R₃C· and carbanions R₃C⁻ which might be expected to have interbond angles at carbon close to 110°.

Disilylmethane¹⁵ was discussed earlier when the radius for silicon was assigned. Triphenylmethane has²⁸ a PhCPh bond angle of 112° with a C₁···C₁ distance of 2.54 Å (C₁ refers here to that carbon atom of the aromatic ring which is attached to the unique carbon), while the triphenylmethyl radical has²⁹ a PhCPh angle of about 116–118° and a C₁···C₁ distance of 2.53 Å.

It is suggested that the difference in interbond angle at the unique carbon stems from the change in Ph–C_{unique} distance while the C₁···C₁ distance remains unchanged. The tri-*p*-nitrophenylmethyl radical is³⁰ planar at the unique carbon atom, and has a mean C₁···C₁ distance of 2.54 Å.

The tricyanomethanide anion, C(CN)₃⁻, is planar in its ammonium³¹, sodium³² and copper(II)³³ salts: the

C···C distances in these compounds are 2.42 Å, 2.44 Å and 2.44 Å, somewhat lower than the 2.50 Å expected.

It is suggested that the principal cause of the unusual geometry in these species is the non-bonded interactions between the groups bonded to carbon: the inter-nuclear repulsions are sufficient to overcome the stereochemical effects of the valence shell electrons.

Structures of compounds containing 3-connected nitrogen

(a) *Derivatives containing only CH₃, SiH₃ or GeH₃ groups.* Unlike trimethylamine³⁴, trisilylamine has³⁵ a planar heavy-atom skeleton: the Si···Si distance is 2.99 Å, somewhat shorter than the 3.10 Å expected for the minimum close contact distance between uncompressed silicon atoms. N-methyldisilylamine also has³⁶ a planar skeleton with Si···Si and Si···C distances of 3.07 Å and 2.73 Å respectively (expected 3.10 Å and 2.80 Å respectively).

In N-silyldimethylamine³⁷ the sum of the interbond angles at nitrogen is 351.1°, substantially greater than in trimethylamine; the Si···C and C···C distances are 2.75 Å and 2.41 Å respectively. N-trichlorosilyldimethylamine Cl₃SiN(CH₃)₂ on the other hand has³⁸ a planar heavy-atom skeleton with Si···C 2.73 Å and C···C 2.41 Å. N-trifluorosilyldimethylamine also has a planar skeleton although the individual angles at nitrogen are not well determined.³⁸

Tetrasilylhydrazine, [(SiH₃)₂N]₂ has planar nitrogen atoms, with an overall molecular symmetry approximating D_{2d}²⁹: the Si···Si and Si···N distances are 3.13 Å and 2.70 Å (expected 3.10 Å and 2.69 Å respectively).

In the planar trigermylamine⁴⁰, the Ge···Ge distance is 3.18 Å, very close to the 3.16 Å expected.

In each of these molecules containing SiH₃- or GeH₃-groups, the non-bonded distances between the atoms bonded to nitrogen either are equal to or are smaller than the sum of the one-angle radii. The feeble basicity of these compounds also can be understood in terms of non-bonded interactions: if the nitrogen atom acts as an electron donor to a Lewis acid, its coordination number increases from three to four, thereby increasing any steric compression. If steric compression has caused the nitrogen to adopt a planar or near-planar configuration, an increase in its coordination number is wholly unfavourable.

(b) *Compounds containing CF₃ groups.* Tris(trifluoromethyl)amine, (CF₃)₃N, has been the subject of a structural investigation by the visual method of electron diffraction⁴¹: the C···C distance was rather poorly determined as 2.40 Å, giving a CNC angle of 114°. At the close contact limit of 2.50 Å, the CNC angle would be 120°, implying a planar C₃N skeleton. A further investigation of this compound using modern techniques would be of value. In the very crowded tetrakis(trifluoromethyl)hydrazine [(CF₃)₂N]₂, the sum

TABLE I. Radii Appropriate to the X···Y Contact in XMY Fragments (Å).

					H ^a
Be	B	C ^a	N ^a	O ^a	F ^a
1.39	1.33	1.25	1.14	1.13	1.08
	Al	Si	P	S	Cl ^a
	1.85	1.55	1.46	1.45	1.44
		Ge		Se	
		1.58		1.58	
		Sn	Sb	Te	
		1.88	1.88	1.87	

^a Ref. 2.

of the interbond angles at nitrogen is⁴² 359.2°: the CNC angle is 121.2° and the C···C distance 2.49₇ Å (expected 2.50 Å), while the CNN angle is 119.0° with the C···N distance 2.44 Å. This C···N distance is somewhat longer than the 2.39 Å expected, but the authors felt that the structural relationship between the two (CF₃)₂N-groups was governed principally by long distance F···F interactions.

In the free radical bis(trifluoromethyl)nitroxyl, (CF₃)₂NO, the sum of interbond angles at nitrogen is⁴³ 355.3°. The CNC and CNO angles are 120.9° and 117.2° respectively, and the C···C and C···O distances are 2.50₇ Å and 2.31 Å respectively (expected 2.50 Å and 2.38 Å). In the corresponding hydroxylamine, (CF₃)₂NOH, in which the NO bond is longer than in the nitroxyl, the sum of angles at nitrogen is⁴⁴ 343.2°: as expected the geometry of the (CF₃)₂N-fragment is unchanged, having a CNC angle of 120.6° and C···C distance of 2.49₃ Å. The CNO angle is reduced to 111.3 with a C···O distance of 2.34 Å, since the NO distance is 1.40 Å compared with only 1.26 Å in the nitroxyl⁴³. Again the difference in geometry at nitrogen is ascribed to different non-bonded contacts.

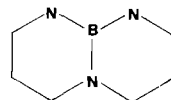
(c) *Compounds containing SO₃⁻² groups.* The nitrosodisulphonate anion, ON(SO₃)₂⁻², found⁴⁵ in the triclinic modification of Fremy's salt, K₂[ON(SO₃)₂], has a sum of interbond angles at nitrogen of 358°. The observed S···S distance is 2.85 Å (expected 2.90 Å), and the observed mean S···O distance 2.55 Å (expected 2.58 Å). The anion in potassium nitrilotrisulphonate dihydrate K₃[N(SO₃)₃]·2H₂O is likewise found⁴⁶ to be planar at nitrogen with a mean S···S distance of 2.96 Å. In the HN(SO₃)₂⁻² anion⁴⁷ the SNS angle is 125.5° and the S···S distance is 2.95 Å. The geometry at nitrogen in these three anions is to be ascribed to the repulsive interactions between the sulphur atoms.

(d) *Compounds containing boron.* N-dimethylboryl-dimethylamine, (CH₃)₂NB(CH₃)₂, crystallises⁴⁸ with two crystallographically independent molecules in the unit cell, in which the sums of interbond angles are 356° and 359° respectively, giving approximate pla-

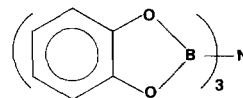
nararity at nitrogen in each case. In one molecule the C···C distance in the (CH₃)₂N-group is 2.43 Å and the C···B distances are 2.58 Å and 2.45 Å (expected 2.58 Å), and in the other the appropriate C···C distance is 2.46 Å and the C···B distances are 2.44 Å and 2.46 Å.

In the related compound (SiH₃)₂NBF₂⁴⁹ (both (CH₃)₂NBF₂⁵⁰ and (CH₃)₂NBCl₂⁵¹ are dimeric with B₂N₂ rings), the nitrogen atom is again planar with an SiSi angle of 123.9° and an Si···Si distance of 3.07 Å (expected 3.10 Å). The SiNB angle is 118° and the Si···B distance 2.78 Å (expected 2.88 Å).

The unique nitrogen atom in 1,8,10,9-triazaboradecalin is



planar⁵², and the non-bonded distances between its nearest neighbours are C···C 2.47 Å and C···B 2.51 Å (expected 2.50 Å and 2.58 Å respectively). Tri-(1,3,2-benzodioxaborol-2-yl)amine has⁵³ approximately



D_{3h} symmetry: the sum of interbond angles at nitrogen is 359.8° and the B···B distance is 2.49 Å (expected 2.66 Å).

(e) *Compounds containing phosphorus ligands.* An X-ray study of (CH₃)₂NPF₂ has shown⁵⁴ that the bonds to nitrogen in this compound are co-planar. The C···C and mean C···P distances are 2.49 Å and 2.71 Å respectively (expected 2.50 Å and 2.71 Å). Similarly in the adduct (CH₃)₂NPF₂B₄H₈ in which phosphorus is the donor atom toward the tetraborane fragment, the nitrogen is planar⁵⁵ and the C···C and mean C···P distances are 2.49 Å and 2.69 Å. In an electron diffraction study of (CH₃)₂NPF₂, it was found⁵⁶ that the nitrogen atom was pyramidal: however there was

TABLE II. Selected Geometrical Data for Some [(CH₃)₃Si]₂N- Compounds.

Compound	<(SiSi)(°) ^a	<(SiNM)(°) ^a	r(Si···Si)(Å)	r(Si···M)(Å) ^a	Ref.
L ₂ Be ^b	129.3	115.3	3.12	2.78 ^c	62
L ₃ Al	118	121	3.00	3.07 ^d	63
L ₃ Sc	121	119.5	3.01	3.27	64
L ₃ Fe	121.2	119.4	3.02	3.15	66
L ₂ CoPPh ₃	124.5	117.7	3.02	3.13	67
LNi(PPh ₃) ₂	126	117	3.03	3.05	67
L ₃ Eu	129.4	115.3	3.04	3.34	64

^a M = Be, Al, Sc, Fe, Co, Ni or Eu. ^b L = [(CH₃)₃Si]₂N-. ^c Close contact limit 2.94 Å. ^d Close contact limit 3.40 Å.

severe correlation between the geometrical parameters, with all the non-hydrogen bonded distances lying under one peak in the radial distribution curve, and all the non-bonded distances $X \cdots Y$ in fragments XMY lying under a second, very broad peak, so that some of the parameters may not be well determined.

In N-difluorophosphinosilylamine, $\text{SiH}_3\text{NHPF}_2$, the SiNP angle is⁵⁷ 127.9° and the $\text{Si} \cdots \text{P}$ distance is 3.03 \AA ; the close contact limit is 3.01 \AA .

(f) *Compounds containing metal atoms.* The dialkyl-amido compounds, $[\text{((CH}_3)_2\text{CH)}_2\text{N}]_3\text{Cr}$ ⁵⁸, $[\text{(CH}_3)_2\text{N}]_5\text{Nb}$ ⁵⁹, $[\text{(CH}_3)_2\text{N}]_6\text{W}$ ⁶⁰ and $[\text{(CH}_3)_2\text{N}]_6\text{Mo}$ ⁶¹ all contain planar C_2NM groups. In the molybdenum and tungsten compounds the $\text{C} \cdots \text{C}$ distances are 2.43 \AA and 2.41 \AA respectively, with $\text{C} \cdots \text{Mo}$ 3.06 \AA and $\text{C} \cdots \text{W}$ 3.19 \AA . No details were recorded for the chromium or niobium compounds, but in the niobium example the authors felt⁵⁹ that the planarity at nitrogen was best ascribed to steric influences.

Metal derivatives of the $[(\text{CH}_3)_3\text{Si}]_2\text{N}$ -group have been shown to contain planar Si_2NM fragments for $\text{M} = \text{Be}$ ⁶², Al ⁶³, Sc ⁶⁴, Cr ⁶⁵, Fe ⁶⁶, Co ⁶⁷, Ni ⁶⁷, and Eu ⁶⁴. Structural data for the Si_2NM fragments are recorded in Table II. It will be noted that the $\text{Si} \cdots \text{Si}$ distance does not, in any of these compounds, exceed significantly the close-contact limit of 3.10 \AA . On traversing the $3d$ series from scandium, by way of iron and cobalt to nickel, the $\text{Si} \cdots \text{M}$ distance decreases; this would be expected as a result of the decrease in size of the metal atoms across the series. This decrease is accompanied

by a reduction of the SiNM angle with a concomitant increase in the SiNSi angle. These structural data imply lower limits for the radii of the $3d$ metals as follows: Sc , 1.72 \AA ; Fe , 1.60 \AA ; Co , 1.58 \AA ; Ni , 1.50 \AA .

(g) *Miscellaneous compounds.* Triphenylamine has⁶⁸ a CNC angle of 116° with a $\text{C} \cdots \text{C}$ distance about nitrogen of 2.41 \AA (expected 2.50 \AA). Tetrasulphur-tetraimide, $\text{S}_4(\text{NH}_4)$, has⁶⁹ a mean SNS angle of 122.5° and a mean $\text{S} \cdots \text{S}$ distance of 2.93 \AA (expected 2.90 \AA).

Compounds containing 2-connected nitrogen

(a) *Pseudohalides.* Among the isocyanates, isothiocyanates, azides and carbodiimides of carbon, silicon, germanium and phosphorus of general formula R_xMNXY (for $\text{R} = \text{H}$, CH_3 , F or Cl ; $\text{M} = \text{C}$, Si , Ge or P ; $\text{XY} = \text{CO}$, CS , N_2 or CNMR_x) the bond angles MNX range from 116.8° in methyl azide⁷⁰ to 163.8° in silyl isothiocyanate⁷¹; this latter value is a thermal average over all populated vibrational states, the ground vibrational state having a linear SiNCS skeleton⁷².

In Table III are recorded the observed MNX angles and the observed $\text{M} \cdots \text{X}$ distances, together with the values calculated for the angle MNX and the $\text{M} \cdots \text{X}$ distance by applying the present hypothesis that the interbond angles at nitrogen are determined primarily by the $\text{M} \cdots \text{X}$ interactions. All of the compounds in Table III have been investigated by electron diffraction, so that in those cases where the skeletal bending frequency, $\delta(\text{MNC})$, is low, the structure is an average

TABLE III. Observed and Calculated MNX^a Angles and $\text{M} \cdots \text{X}^a$ Distances in Some Molecular Pseudohalides.

Compound	$\langle (\text{MNX})_{\text{obs}} (^\circ) \rangle$	$r(\text{M} \cdots \text{X})_{\text{obs}} (\text{\AA})$	$r(\text{M} \cdots \text{X})_{\text{calc}} (\text{\AA})$	$\langle (\text{MNX})^{\text{calc}} (^\circ) \rangle$	$\delta (^\circ)^b$	Ref.
CH_3NCO	140.3	2.46	2.50	145.2	- 4.9	70
SiH_3NCO	151.7	2.83	2.80	146.7	+ 5.0	71
$(\text{CH}_3)_3\text{SiNCO}$	150	2.86	2.80	141.4	+ 8.6	73
SiF_3NCO	160.7	2.80	2.80	160.7	0	74
$\text{Si}(\text{NCO})_4$	146.4	2.78	2.80	149.8	- 3.4	75
GeH_3NCO	141.3	2.86	2.83	138.0	+ 3.3	76
PF_2NCO	130.6	2.67	2.71	133.9	- 3.3	77
CH_3NCS	141.6	2.53	2.50	138.5	+ 3.1	70
SiH_3NCS	163.8	2.87	2.80	149.2	+14.6	71
$(\text{CH}_3)_3\text{SiNCS}$	154	2.89	2.80	141.3	+12.7	73
PF_2NCS	140.5	2.74	2.71	137.0	+ 3.5	77
CH_3N_3	116.8	2.29	2.39	125.6	- 8.8	70
SiH_3N_3	123.8	2.67	2.69	125.1	- 1.3	78
GeH_3N_3	119	2.68	2.72	121.8	- 2.8	76
$(\text{SiH}_3\text{N})_2\text{C}$	150.6	2.81	2.80	149.1	+ 1.5	78
$(\text{GeH}_3\text{N})_2\text{C}$	138	2.81	2.83	140.7	- 2.7	76
$(\text{PF}_2\text{N})_2\text{C}$	132.8	2.68	2.71	135.7	- 2.9	79

^a $\text{M} = \text{C}$, Si , Ge or P ; $\text{X} = \text{C}$ or N . ^b $\delta = \langle (\text{MNX})_{\text{obs}} \rangle - \langle (\text{MNX})_{\text{calc}} \rangle$

over all populated states: this average is taken to be a reflection of the close-contact limit. The compounds $\text{Cl}_n\text{Si}(\text{NCO})_{4-n}$ ($n = 1, 2$ or 3)⁸⁰ were omitted from the table because there is severe correlation between some of their structural parameters, in particular the non-bonded distances, so that some interbond angles are not well determined. The root-mean-square deviation of $r(\text{M}\cdots\text{X})_{\text{obs}}$ from $r(\text{M}\cdots\text{X})_{\text{calc}}$ for the compounds in Table III is 0.05 \AA , and the r.m.s. deviation of $\langle(\text{MNX})_{\text{obs}}\rangle$ from $\langle(\text{MNX})_{\text{calc}}\rangle$ is 6.1° , indicating that the hypothesis of limiting non-bonded contacts is a remarkably good guide to the stereochemistry of such pseudohalides.

(b) *Miscellaneous compounds.* Both tetrathiazyl tetrafluoride⁸¹ and tetrathiazyl tetra-bis-(trifluoromethyl)nitroxide⁸², $[\text{NSON}(\text{CF}_3)_2]_4$ have angles at the endocyclic 2-coordinate nitrogen greater than 120° : the values are 123.9° and 123.4° respectively, associated with $\text{S}\cdots\text{S}$ distances of 2.82 \AA and 2.80 \AA respectively (expected 2.90 \AA).

Compounds containing 2-connected oxygen of fluorine

The compounds $(\text{SiH}_3)_2\text{O}^{17}$, $(\text{SiF}_3)_2\text{O}^{18}$, $(\text{GeH}_3)_2\text{O}^{19}$, $(\text{PF}_3)_2\text{O}^{22}$ and $(\text{SO}_3)_2\text{O}^{-2, 24}$ have been mentioned above in the section dealing with assignment of radii, along with $(\text{C}_6\text{H}_{11})_3\text{SnOCOCH}_3^{21}$ and $\text{SbCl}_5\text{OPR}_3$ ($\text{R} = \text{Cl}$ or CH_3)²³.

$(\text{SiCl}_3)_2\text{O}$ has⁸³ an SiOSi angle of 146° and an $\text{Si}\cdots\text{Si}$ distance of 3.04 \AA , while the cyclic species $(\text{SiH}_2\text{O})_4$ ⁸⁴ and $[(\text{CH}_3)_3\text{SiO}]_4$ ⁸⁵ have SiOSi angles of 148.6° and 142.5° respectively, associated with $\text{Si}\cdots\text{Si}$ distances of 3.13 \AA and 3.12 \AA , all essentially identical with the close contact limit. The compounds SiH_3OCH_3 ⁸⁶, SiF_3OCH_3 ⁸³ and $\text{SiH}_3\text{OC}_6\text{H}_5$ ⁸⁷ all have interbond angles at oxygen greater than 120° , with $\text{Si}\cdots\text{C}$ distances less than the close contact limit of 2.80 \AA . In the anion $[\text{Al}(\text{OSi}(\text{CH}_3)_3)_4]^-$, the AlOSi angle is 147.2° and the $\text{Al}\cdots\text{Si}$ distance 3.21 \AA , somewhat smaller than the 3.40 \AA expected.

The diphosphate anion in $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ has⁸⁸ a POP angle of 133.5° and a $\text{P}\cdots\text{P}$ distance of 2.95 \AA , while the $\text{P}_3\text{O}_{10}^{-5}$ anion in the sodium salt has⁸⁹ POP of 126.5° and $\text{P}\cdots\text{P}$ of 2.87 \AA . Both $\text{P}\cdots\text{P}$ distances are very close to the limiting $\text{P}\cdots\text{P}$ distance of 2.92 \AA . In chlorine heptoxide, Cl_2O_7 , the ClOCl angle is⁹⁰ 118.6° , associated with a $\text{Cl}\cdots\text{Cl}$ distance of 2.94 \AA (close contact limit 2.88 \AA).

The salt $\text{K}[(\text{C}_2\text{H}_5)_3\text{AlFAl}(\text{C}_2\text{H}_5)_3]$ contains⁹¹ a linear AlFAl unit, in which the Al-F distance is 1.80 \AA , so that $\text{Al}\cdots\text{Al}$ is 3.60 \AA . In μ -oxo-di-[bis-(2-methyl-8-quinolino)aluminium], the AlOAl bridge is linear⁹² with Al-O 1.676 \AA and $\text{Al}\cdots\text{Al}$ 3.354 \AA . In each of these compounds the $\text{Al}\cdots\text{Al}$ distance is shorter than the 3.70 \AA expected for the close contact limit, so that the linearity of the AlXAl bridges is thereby understood.

Maximum coordination numbers

Coordination numbers greater than four are rare in simple molecular species of the type MX_p where M is an element of the first (Li-Ne) row of the periodic table. The two types of lithium in $\text{LiN}_3 \cdot \text{H}_2\text{O}$ are⁹³ both 6-coordinate, one by terminal nitrogens of azide groups, the other by water molecules, and lithium in $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ is⁹⁴ also 6-coordinate, but there appears to be no authentic example of a coordination number above 4 in a simple molecular compound for beryllium or any subsequent element of the first row.

In carbon tetrafluoride⁹⁵ the $\text{F}\cdots\text{F}$ distance is 2.15 , just on the close contact limit: to maintain this limit in a trigonal bipyramidal CF_5^- species, assuming equality of axial and equatorial C-F bond lengths would require the C-F bonds to be stretched from the 1.317 \AA found in CF_4 to about 1.52 \AA , an increase of some 16%. For comparison the Si-F bonds in⁹⁶ SiF_6^{2-} are about 11% longer than in⁹⁷ SiF_4 , and those in⁹⁸ GeF_6^{2-} some 3% longer than those in⁹⁹ GeF_4 . Similarly in CCl_4 , the $\text{Cl}\cdots\text{Cl}$ distance is¹⁰⁰ 2.88 \AA , and in CBr_4 the $\text{Br}\cdots\text{Br}$ distance is¹⁰¹ 3.17 \AA , just on the close contact limits so that expansion of the carbon's coordination number would also require about a 16% increase in the C-X bond length if the $\text{X}\cdots\text{X}$ limit is maintained.

The hexafluorosilicate ion has⁹⁶ an Si-F distance of 1.71 \AA , and an $\text{F}\cdots\text{F}$ distance of 2.42 \AA : its isoelectronic analogues AlF_6^{3-} , PF_6^- , and SF_6 have^{102, 103, 104} M-F distances of 1.81 \AA , 1.63 \AA and 1.56 \AA respectively, with corresponding $\text{F}\cdots\text{F}$ distances of 2.56 \AA , 2.30 \AA and 2.20 \AA , very close to the close contact limit of 2.16 \AA in the SF_6 case. To expand the coordination number of Al , Si , P or S to 7 in fluoro complexes would require, assuming pentagonal bipyramidal geometry, equal axial and equatorial bond lengths and a fluorine close-contact distance of 2.16 \AA , a stretching of the M-F bonds of 1%, 7%, 12% and 17% of the distance in the hexafluoro species for $\text{M} = \text{Al}$, Si , P and S respectively. Subject only to limitations of charge the ions AlF_7^{4-} and SiF_7^{3-} might be expected to be capable of existence: if prepared, these would represent the first simple molecular compounds of the second (K-Ar) row of the periodic table having coordination numbers greater than 6.

To increase the coordination numbers of carbon tetrahalides or sulphur hexafluoride requires a considerable stretching of the C-X or S-F bonds (about 16% in each case), much greater than is required to increase the coordination numbers of silicon tetrahalides or of selenium hexafluoride¹⁰⁵ (about 7% in each case) and requiring a much greater expenditure of energy. Arguments such as this may account in large measure for the rarity of coordination numbers greater than four in the first row, and greater than six in the second.

If an atom cannot readily increase its coordination number then an attacking nucleophile cannot make a close approach. It is of interest in this context that, although thermodynamically unstable with respect to

hydrolysis, both the carbon tetrahalides and sulphur hexafluoride are kinetically wholly inert to hydrolysis (and to nucleophilic attack in general), while the silicon tetrahalides, and selenium hexafluoride are much more reactive towards nucleophiles.

Discussion

The VSEPR method considers only inter-electron repulsions, and for the majority of molecular species such a description is appropriate: this paper has exemplified a description of molecular geometry which takes account both of inter-electron and of inter-nuclear repulsions, and which for a number of molecules is more appropriate than that provided by the VSEPR approach.

There exists also a class of molecules in which inter-nuclear repulsions totally dominate electronic effects, so that non-bonded atoms move as far apart from one another as possible. It has been shown by microwave spectroscopy that SiH_3NCO ¹⁰⁶, SiH_3NCS ⁷², and $(\text{CH}_3)_3\text{SiNCO}$ ¹⁰⁷ have linear SiNCX ($\text{X} = \text{O}$ or S) chains in their vibrational ground states, and similarly $\text{Si}(\text{NCS})_4$ has¹⁰⁸ virtually linear SiNCS groups in the solid state: in each case the $\text{Si} \cdots \text{C}$ distance is rather greater than the sum of the one-angle radii. There is reason to suppose¹⁰⁹ that other isocyanates and isothiocyanates of silicon likewise possess linear ground states, but have excited vibrational states which are markedly bent, up to the limits imposed by the close contacts between non-bonded atoms. Other than these silicon pseudohalides, there appear to be few other molecules in this class: the only other elements whose pseudohalides have skeletal MNCX groups which are close to linearity are boron and tin, for whose pseudohalides structures are known only in the solid state. In the boron pseudohalides the $\text{B} \cdots \text{C}$ distances are close to the values expected^{10,11,110}, while the tin species are^{111,112,113} all associated in the solid state; this association may perturb the SnNC angles in the direction of linearity.

Those derivatives of 3-connected nitrogen which contain planar nitrogen atoms cannot be placed in this class since the analogous derivatives of 2-connected oxygen containing the same ligands are non-linear. In those aluminium derivatives of 2-connected oxygen or fluorine which contain linear AlXAl ($\text{X} = \text{O}$ or F) units^{91,92}, the $\text{Al} \cdots \text{Al}$ distances are less than the close-contact limit.

The gaseous hydroxides of potassium, rubidium and caesium have been shown to be linear at oxygen^{114,115}, with $\text{M} \cdots \text{H}$ distances of 3.15 Å, 3.27 Å and 3.37 Å respectively. These molecules are almost certainly highly ionic in character, so that dominance of inter-nuclear repulsions is expected. Lithium oxide Li_2O is¹¹⁶ likewise linear with the $\text{Li}-\text{O}$ distance about 1.59 Å, but

Cs_2O rather surprisingly is¹¹⁷ bent. An SCF calculation on Li_2O has¹¹⁸ indicated that the potential well describing the LiOLi bend is very flat: it is possible that Cs_2O is quasi linear with a double minimum bending potential function.

While a precise description of the bonding in the gaseous oxides and hydroxides of the alkali metals has yet to be given, it nevertheless seems clear that these are to be classed, along with the pseudohalides of silicon, as members of the third category of molecules, in which inter-nuclear repulsions are dominant.

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