SECONDARY BONDING TO NONMETALLIC ELEMENTS

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I. Introduction

A. THESIS

A number of recent crystal structure determinations on compounds of the nonmetals have discovered intramolecular distances that are much longer than normal bonds and intermolecular distances that are much shorter than van der Waals distances. In this chapter, these interactions are examined and a qualitative explanation attempted. It will become clear that in most of them an approximately linear arrangement is found,

Y–A---X

where Y–A is a normal bond and A---X is a short intermolecular distance.* It is with these approximately linear interactions that we are particularly concerned, and it will be our contention that they are the result of directed forces and that their behavior is sufficiently regular and understandable for the name *secondary bond* to be appropriate.†

B. EVIDENCE

The only conclusive method of establishing the presence of secondary interactions is by crystal structure determinations. An intermolecular interaction can be recognized as being significant by being shorter than the expected intermolecular (van der Waals) distance, but if it is the result of directed forces, i.e., bonds, rather than electrostatic or nondirectional van der Waals forces, then it must satisfy one or both of the following criteria: (*a*) the interacting neighbor(s) are not in the most favorable positions for nondirected forces, and/or (*b*) the interacting neighbor(s) are in stereochemically significant positions. These are, of course, the same criteria that distinguish covalent from electrostatic primary bonding. For virtually all the short interactions that have been found in compounds of the nonmetallic elements, criterion (*b*) is satisfied, with the stereochemically significant arrangement being a linear one.

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* Throughout the review, a single dash is used for normal bonds and triple dashes for short secondary interactions.

† The principal sources have been searched to July 1971, but in many structure determinations the existence of secondary interactions is only mentioned in passing, if at all, and this means that some earlier examples have probably been missed. Additional information to May 1972 is in the Appendix.

The physical evidence of melting points and boiling points can indicate association, but it cannot demonstrate the presence of directed interactions. The most it can do is to suggest that one compound shows similar intermolecular interactions to those in some similar compound whose structure is known. Infrared spectra can occasionally go further than this when the interaction is strong enough for either the secondary A---X bond to produce identifiable absorptions, or for other molecular frequencies to be shifted because of the interaction.

C. VAN DER WAALS DISTANCES

Before an intermolecular distance can be considered short, there must be some idea of the van der Waals distance that would be expected. If such distances are to be obtained as the sum of atomic van der Waals radii, with each element having a standard radius, then these radii must not be affected substantially by the atomic environment. This has not been proved, and what evidence there is shows that van der Waals radii are much more variable than, say, covalent bond radii. However, tables of van der Waals radii have been presented by Pauling (*129*, p. 260) and Bondi (*21*). Those of Pauling are simply the ionic radii of the atoms as anions; the equating of these to van der Waals radii is only tested for one or two elements. Those of Bondi are derived for the purpose of calculating molecular volumes and may not be valid for determining contact distances. He also gives compilations of intermolecular distances from which the following radii (in Å) are deduced: N, 1.55; O, 1.50; S, 1.83; F, 1.50; Cl, 1.78; Br, 1.85; and I, 2.00. These values differ systematically by up to 0.15 Å from those of Pauling, being larger for N, O, and F and smaller for Br and I; the use of ionic radii is therefore not a good approximation. However, they do correspond, to within 0.03 Å, with the mean van der Waals radii for volume calculations of Bondi. These will, therefore, be taken as the best available standard values of van der Waals radii, and are given in Table I. For four elements, Ge, Sn, Sb, and Si, values have been estimated by extrapolation, and for Xe, the figure has been revised as noted below.

Because of the problems concerning the constancy of van der Waals radii, comparison of a particular intermolecular distance with the standard value may still be unreliable, and estimation of the relative strengths of interactions between different pairs of atoms from such comparisons will be even more doubtful. An alternative approach stems from Pauling's observation (*129*, p. 263) that van der Waals radii are all approximately 0.8 Å longer than the corresponding covalent radii. Bondi (*21*) gives figures that support this, but that show that the best value of the increment varies slightly from period to period. For the elements N to F, the van der Waals radii are approximately 0.85 Å larger than the covalent radii, for Si to Cl and Ge to As, the differences are about 0.75 Å, and for Te and I, about 0.70 Å.* Therefore, a comparison of a secondary bond length with the standard single bond length may give a useful estimate of the strength of the secondary bond, and these comparisons are included in Tables II–V.

TABLE I

VAN DER WAALS AND SINGLE BOND RADII[a]

		N	O	F	
r_w		1.55	1.52	1.47	
r_c		0.70	0.66	0.64	
	Si	P	S	Cl	
r_w	2.10	1.80	1.80	1.75	
r_c	1.17	1.10	1.04	0.99	
	Ge	As	Se	Br	
r_w	1.95	1.85	1.90	1.85	
r_c	1.22	1.18	1.14	1.11	
	Sn	Sb	Te	I	Xe
r_w	2.10	2.05	2.06	1.98	2.00
r_c	1.40	1.36	1.32	1.28	1.29
		Bi			
r_w		2.15			
r_c		1.55			

[a] r_w = van der Waals radius in Å, after Bondi (*21*); See text p. 3. r_c = covalent single bond radius in Å, derived by subtracting 0.76 Å from the r_b figures of Bondi (*21*, Table I); bismuth from Bi–Bi in the element.

One general statement can be made about van der Waals distances that is perhaps most valuable because it is most likely to be correct. Any element in periods 3, 4, and 5 (K to Rn) will have a van der Waals radius that in corresponding compounds is *at least as large* as that of the element of the same group in the preceding period. When the later

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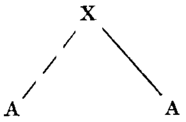
* This leads to the suggestion embodied in Table I that for Xe *in compounds*, the van der Waals radius should be 2.00 Å, rather than 2.16 Å derived from the packing of free atoms.

element forms an intermolecular contact that is *shorter* than that formed by the earlier element, then the intermolecular attraction must be stronger.

D. Bridge Bonds

The atom X forming a secondary interaction with atom A is often itself attached to another atom of type A, i.e., it forms a bridge



Such bridges occur in which the A---X interaction covers the whole range from being essentially nonexistent to being as strong as the normal X–A bond, and it can be very difficult to decide whether it should be called a primary or a secondary interaction. In principle, if the bridge is at all asymmetric, the weaker bond could be called secondary, but in practice it is better to reserve the term for cases where there is a difference of at least several tenths of an Ångström between the two bond lengths. Conversely, when the bridge is symmetrical but both bonds are much longer than normal, the atom X could be regarded as forming secondary bonds to both atoms A. This situation is less common, but the bonding in one or two molecules is more comprehensible if viewed in this way.

E. Charge Transfer Adducts

A number of structures of addition compounds have been determined that show short interactions, mainly between halogens and O, S, Se, or N of heteroatom-containing organic molecules. These interactions have been identified as charge-transfer bonds, and the subject has been reviewed (*10*, *86*). They show the structural feature of bond linearity Y–A---X, and it is almost certain that the bonding is similar to that in the compounds to be described. There is no clear dividing line, but the present chapter will concentrate on systems containing a single molecular species (or pair of ions) rather than on addition complexes.

F. Classification

In the main sections, compounds are grouped under each element A, the "central" atom of the linear arrangement. Usually, if the overall atomic arrangement is Y–A---X–Z, there is no difficulty deciding whether A or X is "central" because only the angle of Y–A---X is approximately 180° and the angle of A---X–Z is in the range 90°–120°. The only exceptions are the compounds in which X–Z is the N–C of a covalent cyanide, which often form long linear chains. Although there is good evidence that the noncyanide atom A corresponds to the "central" atom in other compounds, these cyanides have been collected separately. For secondary interactions to occur, the central atom must not already be surrounded by atoms forming primary covalent bonds; this means that the main area of chemistry involved is that of nonmetals in their lower oxidation states, when they have incomplete coordination polyhedra. In most of the compounds concerned, the primary geometries have been explained by the electron pair repulsion model (*81*).

Quantitative information about bond lengths and angles is collected in Tables II-V for the short interactions that are approximately linear. In the figures illustrating the geometries, bond distances are generally mean values, but in the tables the individual values are given. In some cases the figures only show the immediate environment of the central atom.

II. Group VIII*

XENON WITH FLUORINE

The melting points of the xenon fluorides decrease from XeF_2 (140°C) to XeF_4 (114°C) to XeF_6 (48°C), and from this it should follow that the intermolecular forces decrease in the same order. Unexpectedly, the crystal structures reveal that the Xe–F intermolecular distances actually decrease from XeF_2 to XeF_4, while XeF_6 contains no extended Xe---F intermolecular interactions. This example illustrates the danger of using melting point evidence unsupported by structure determinations. In XeF_2 (*118*) the xenon atom has eight nonbonded contacts, with Xe---F equal to 3.41 Å, directed at the corners of a cube; in XeF_4 (*34*) there are four interactions with a length of 3.23 Å, arranged approximately tetrahedrally, and in the mixed crystal $XeF_2 \cdot XeF_4$ (*35*), there are a series of contacts of lengths between 3.28 and 3.42 Å. The van der Waals distance is 3.47 Å. Presumably the melting point behavior is caused by larger numbers of weaker forces producing greater binding than smaller numbers of stronger forces.

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* Summarized in Table II.

The investigation of XeF_6 (*3*, *32*, *33*) has proved difficult and it shows at least four phases, but it seems that all contain tetramers or hexamers. The intermolecular forces are between fluorine atoms only, and this presumably accounts for the low melting point. In one phase, the tetramers can be approximately described as pyramidal XeF_5^+ units linked by F^-; some Xe–F bridges are symmetrical with Xe–F, 2.5 Å, some asymmetrical with distances of 2.23 and 2.60 Å. There are either two or three interactions with the xenon through the base face of the pyramid, and none of these appear to be aligned with the apical F–Xe bond.

The coordination of xenon in $XeF_5^+PtF_6^-$ (*16*) is very similar to that in XeF_6. The pyramidal XeF_5^+ has mean bond length of 1.89 Å, and there are four additional fluorines (Fig. 1) below the base of the pyramid with Xe---F equal to 2.52, 2.65, 2.95, and 2.95 Å. These interactions are staggered relative to the primary bonds forming the base of the pyramid. Very similar again is the coordination found in the addition compound $XeF_2 \cdot IF_5$ (*108*), in which the iodine in the pyramidal IF_5 molecule has four close contacts with I---F of 3.14 Å in the same staggered configuration. In none of these compounds do the secondary interactions show directional properties.

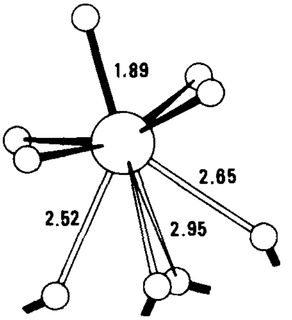

FIG. 1. XeF_5^+ in $XeF_5^+PtF_6^-$. Large circle, Xe; small circles, F. Redrawn from Bartlett *et al.* (*16*).

By contrast, in $XeF^+Sb_2F_{11}^-$ (*126*) the XeF^+ has a bond length of 1.84 Å and the next neighbor is at 2.35 Å, forming an almost linear bridge to the Sb_2F_{11} ion (Fig. 2). A very similar arrangement is found in $Xe_2F_3^+AsF_6^-$ (*142*), with one fluorine linking two F–Xe groups (Fig. 3). The terminal distances are 1.90 Å and both bridge distances are 2.14 Å. Both these compounds can be thought of as containing straightforward

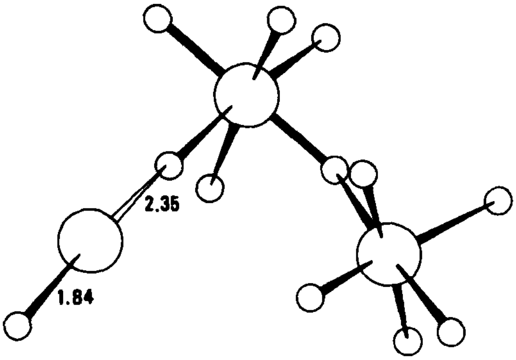

FIG. 2. $XeF^+Sb_2F_{11}^-$. Large circles, Xe and Sb; small circles, F. Redrawn from McRae *et al.* (*126*).

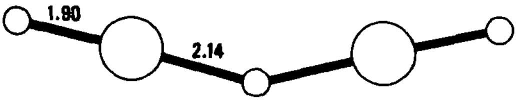

FIG. 3. $Xe_2F_3^+$ in $Xe_2F_3^+AsF_6^-$. Large circles, Xe; small circles, F. Redrawn from Sladky *et al.* (*142*).

fluorine bridges, but for the first, the asymmetry makes a description involving a secondary interaction equally valid.

For the polymeric $(XeO_3F^-)_n$ ion (*97*) (Fig. 4) two explanations are also possible. The Xe–F distances of 2.36 and 2.48 Å are only slightly different, and so the choice is between standard fluorine bridges, donating electron pairs, or secondary interactions between XeO_3 molecules and F^- ions. In both cases, pseudo-octahedral coordination would be expected, but in the first there should be six sterically active electron

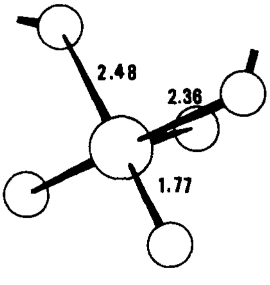

FIG. 4. $(XeO_3F^-)_n$ in $K^+XeO_3F^-$. Large circle, Xe; small circles, F (bridging) and O (terminal). Redrawn from Hodgson and Ibers (*97*).

pairs and in the second four. One piece of evidence supports the second view. This is that the XeO_3 moiety is very similar in dimensions to XeO_3 itself with O–Xe–O angles averaging 100°. For six electron pairs with one vacant position lone pair–bonded pair repulsion would be expected to give angles rather less than 90°. It is also interesting that the shortest Xe–O, 1.75 Å, is opposite the vacant position, while the longest, 1.79 Å, is opposite the shorter Xe---F bond.

XeO_3 is considered below, with HIO_3.

III. Group VII*

A. CHLORINE AND BROMINE

Although short secondary bonds are most prominent with iodine, there are some examples among chlorine and bromine compounds. In ClF_3 (*30*) the shortest intermolecular contacts have Cl–F equal to 3.06 (twice) and 3.17 Å (twice) (with others rather longer) fairly evenly arranged on the unobstructed sides of the T-shaped molecule, and these are close to the expected van der Waals distance of 3.22 Å. BrF_3 is similar (*31*), although the structure has not been fully refined. However, $ClF_2^+SbF_6^-$ (*62*) and $BrF_2^+SbF_6^-$ (*57*) are very different (Fig. 5) and show directed secondary interactions. In each, the halogen atom has a square-planar environment, with two fluorines at normal bonding distances and two further away, 2.38 Å for ClF_2^+ and 2.29 Å for BrF_2^+.

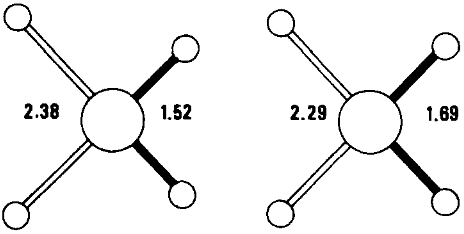

FIG. 5. ClF_2^+ (left) in $ClF_2^+SbF_6^-$ and BrF_2^+ (right) in $BrF_2^+SbF_6^-$. Large circles, Cl and Br; small circles, F. Redrawn from Edwards and Sills (*62*).

In *N*-chlorosuccinimide (*28*) there is a linear N–Cl---O grouping with Cl---O equal to 2.88 Å, compared to a van der Waals distance of 3.27 Å.

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* Summarized in Table II.

TABLE II

SECONDARY BONDS TO GROUP VIII AND VII ELEMENTS[a, b]

Compound	Ref.	Fig.	Linear group	Angle	Length		Single	van der Waals	Difference secondary minus single	Accuracy and notes
			Y–A---X	at A	Y–A	A---X	A–X	A---X		
$XeF^+Sb_2F_{11}$	*126*	2	F Xe F	(180)	1.84	2.35	1.93	3.47	0.51	[c]
$Xe_2F_3^+AsF_6^-$	*142*	3	F Xe F	178	1.90	2.14	1.93	3.47	0.24	[c]
$K^+XeO_3F^-$	*97*	4	O Xe F	171	1.76	2.48	1.93	3.47	0.55	[c]
				172	1.79	2.36	—	—	0.43	—
XeO_3	*145*	—	O Xe O	159	1.74	2.89	1.95	3.52	0.94	[c]
				163	1.76	2.80	—	—	0.85	—
				172	1.77	2.89	—	—	0.94	—
$ClF_2^+SbF_6^-$	*62*	5	F Cl F	176	1.57	2.33	1.63	3.22	0.74	[c]
				176	1.58	2.43	—	—	0.85	
$BrF_2^+SbF_6^-$	*57*	5	F Br F	178	1.69	2.29	1.75	3.32	0.60	[c]
n-Chlorosuccinimide	*28*	—	N Cl O	170	1.69	2.88	1.65	3.27	1.23	[c]
$POBr_3$	*128*	—	P Br O	169	2.14	3.08	1.77	3.37	1.31	[c]
Oxalyl bromide	*84*	—	C Br O	169	1.84	3.27	1.77	3.37	1.41	Original results inconsistent
$NH_4^+IO_3^-$	*111*	6	O I O	168	1.77	2.83	1.94	3.50	0.89	[d]
				172	1.81	2.78	—	—	0.84	—
				174	1.84	2.82	—	—	0.88	—
$Li^+IO_3^-$	*52a*	—	O I O	165	1.81	2.89	1.94	3.50	0.95	Three times[d]
$Na^+IO_3^-$	*125*	—	O I O	(166)	(1.83)	(3.01)	1.94	3.50	(1.07)	—
Rb^+IO_3	*5*	—	O I O	168	1.80	2.76	1.94	3.50	0.82	Three times[d]
$Ce^{4+}(IO_3^-)_4 \cdot H_2O$	*105*	—	O I O	160	1.81	2.93	1.94	3.50	0.99	I1[c]
				160	1.83	3.00	—	—	1.06	—
				164	1.84	2.99	—	—	1.05	—
				170	1.82	2.78	—	—	0.84	I2
				174	1.82	2.56	—	—	0.62	—

						152	1.83	2.99	—	—	1.05	—
						169	1.82	2.75	—	—	0.81	I3
						161	1.83	3.07	—	—	1.13	—
						175	1.86	2.52	—	—	0.58	—
						167	1.77	3.05	—	—	1.11	I4
						172	1.82	2.65	—	—	0.71	—
						174	1.82	2.55	—	—	0.61	—
$Cu^{2+}IO_3^-OH^-$	*80*	—	O	I	O	172	1.80	2.50	1.94	3.50	0.56	[c]
						172	1.83	2.70	—	—	0.76	Twice
α-HIO_3	*78*	—	O	I	O	163	1.78	2.88	1.94	3.50	0.94	[d]
						166	1.82	2.78	—	—	0.84	—
						174	1.90	2.50	—	—	0.56	—
HI_3O_8	*70*	7	O	I	O	171	1.78	2.71	1.94	3.50	0.77	I1[c]
						161	1.80	2.62	—	—	0.68	—
						168	1.97	2.58	—	—	0.64	—
						168	1.78	2.56	—	—	0.62	I2
						169	1.79	2.83	—	—	0.89	—
						174	1.95	2.38	—	—	0.44	—
						178	1.81	2.59	—	—	0.65	I3
						177	1.90	2.54	—	—	0.60	—
I_2O_5	*140*	—	O	I	O	169	1.76	2.93	1.94	3.50	0.99	I1[c]
						176	1.78	2.72	—	—	0.78	—
						173	1.92	2.44	—	—	0.50	—
						172	1.82	2.53	—	—	0.59	I2
						171	1.94	2.24	—	—	0.30	—
p-$ClC_6H_4IO_2$	*11*	—	O	I	O	160	1.60	2.95	1.94	3.50	1.01	—
						172	1.69	2.85	—	—	0.91	—
			C	I	O	163	1.92	2.71	—	—	0.77	—
$K^+IO_2F_2^-$	*131*	—	O	I	O	170	1.92	2.89	1.94	3.50	0.95	—
						161	1.94	2.81	—	—	0.87	—
$Cs^+_2I_8^{2-}$	*88*	8	I	I	I	175	2.80	3.42	2.56	3.96	0.86	Twice[c]
$[N(CH_3)_4]^+I_9^-$	*107*	—	I	I	I	168	2.67	3.43	2.56	3.96	0.85	—
						178	2.67	3.24	—	—	0.68	—
						169	2.91	3.24	—	—	0.68	—

continued

TABLE II—*continued*

Compound	Ref.	Fig.	Linear group Y–A---X			Angle At A	Length Y–A	Length A---X	Single A–X	van der Waals A---X	Difference secondary minus single	Accuracy and notes
I_2	*20*		I	I	I	170	2.72	3.50	2.56	3.96	0.94	[d]
α-ICl	*23*	9	Cl	I	I	179	2.44	3.08	2.56	3.96	0.52	[c]
			Cl	I	Cl	179	2.37	3.00	2.27	3.73	0.73	—
β-ICl	*41*		Cl	I	I	180	2.44	3.06	2.56	3.96	0.50	[c]
			Cl	I	Cl	175	2.35	2.94	2.27	3.73	0.67	—
$ICl_2^+SbCl_6^-$	*150*		Cl	I	Cl	174	2.29	3.00	2.27	3.73	0.73	[c]
						177	2.33	2.85	—	—	0.58	—
$ICl_2^+AlCl_4^-$	*150*	10	Cl	I	Cl	174	2.26	2.86	2.27	3.73	0.59	[c]
						176	2.29	2.88	—	—	0.61	—
I_2Cl_6	*24*		Cl	I	Cl	175	2.38	2.68	2.27	3.73	0.41	Twice each[c]
						175	2.39	2.72	—	—	0.45	—
$(C_6H_5)_2I^+Cl^-$	*112*	11	C	I	Cl	179	2.08	3.08	2.27	3.73	0.81	[c]
						179	2.08	3.24	—	—	0.97	—
$(C_6H_5)_2I^+I^-$	*112*		C	I	I	(180)	(2.08)	3.34	2.56	3.96	0.78	[c]
$C_6H_5ICl_2$	*12*	12	C	I	Cl	164	2.02	3.45	2.27	3.73	1.13	[c]

[a] *Notes to Tables II–V*: The standard single bond lengths and the van der Waals distances are derived from the figures in Table I. The *Difference* column gives the difference between the A---X interaction length and an A–X single bond length. The latter is taken as the standard A–X single bond length unless (*a*) Y is the same as X, (*b*) Y–A is formally a single bond, and (*c*) Y–A is shorter than the standard A–X single bond length. In this situation, the estimate of the single bond length found within the molecule is likely to be more valid than the standard value; for example, see $XeF^+Sb_2F_{11}^-$ in Table II.

[b] Parentheses around a figure indicate either that it cannot be computed from published information or that it appears particularly unreliable.

[c] Standard deviation of A---X is 0.04 Å or better, corresponding approximately to a standard deviation for the angle Y–A---X of 2° or better (if X and Y are the same).

[d] Standard deviation of A---X is 0.01 Å or better, corresponding approximately to a standard deviation of 0.5° for the angle Y–A---X (if X and Y are the same).

Two compounds show bromine–oxygen interactions. In phosphorus oxybromide, the molecules are linked into infinite chains by almost linear P–Br---O interactions with Br---O distance of 3.08 Å (*128*), whereas in oxalyl bromide (*84*) there is an O---Br interaction having a length of 3.27 Å. This is not much shorter than the van der Waals distance of 3.37 Å, but again there is a linear grouping, C–Br---O.

B. IODINE WITH OXYGEN

The short contacts formed by iodine fall into two groups, those with oxygen and those with halogens. With one exception oxygen contacts have only been found for I^V (iodic acid and related compounds), but this is probably an accidental restriction. Periodate almost always occurs as the IO_6 group in which the regular octahedron will not allow extra iodine contacts, while I^{III} oxygen compounds are generally unstable, and crystal structures have not been determined. There is some spectroscopic evidence that $(IO)_2SO_4$, I_2O_4, and related compounds contain iodine–oxygen secondary bonds similar to those in iodates (*51*).

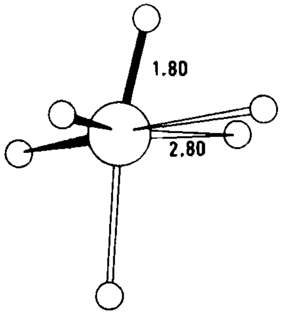


FIG. 6. IO_3^- in $NH_4^+IO_3^-$. Large circle, I; small circles, O. Redrawn from Keve *et al.* (*111*).

The recently determined structure of $NH_4^+IO_3^-$ (*111*) (Fig. 6) can be taken as a typical example of the I^V coordination. The structure is related to that of perovskite in its cell dimensions, but the octahedron of oxygen atoms around each iodine atom is very distorted, so that there are three near and three distant neighbors (1.80 and 2.80 Å). An equivalent description is as a pyramidal IO_3^- ion with three close contacts. The expected van der Waals distance is 3.50 Å.

The same arrangement occurs in $LiIO_3$ (*52a, 132*), $NaIO_3$ (*125*), and $RbIO_3$ (*5*) and is very likely in KIO_3, $CsIO_3$, and $TlIO_3$, which are almost isomorphous with NH_4IO_3 (*6*). In zirconium iodate (*116*), however, the iodate has five neighbors, at an average distance of 2.87 Å, forming with the three oxygens of the iodate group, a crude antiprism around the iodines, presumably with nondirected interactions. Ceric iodate (*49*) is similar, the iodate having five neighbors, three nearer (2.88 Å) and two further (3.27 Å). The packing in these two may well be controlled by the coordination around the metal atom because in $Ce(IO_3)_4 \cdot H_2O$ (*105*) all four iodines are surrounded by distorted octahedra. The iodine atom in $Cu(IO_3)OH$ (*80*) also has this coordination.

Perhaps the most interesting of this group is α-HIO_3 (*78*), where, although there are some hydrogen bonds, the molecular packing is controlled by the intermolecular interactions. This is conclusively proved because XeO_3 (*145*), though lacking hydrogen bonds, is isostructural with α-HIO_3. In both compounds the central atom is surrounded by a distorted octahedron of oxygen atoms. The short Xe–O is slightly shorter than the short I–O (1.76 vs. 1.83 Å) and the long Xe---O is slightly longer than the long I---O (2.87 vs. 2.75 Å). In the addition compound, $HIO_3 \cdot I_2O_5$ (*70*), the iodine of the HIO_3 molecule has only two short intermolecular contacts, but each iodine of the I_2O_5 molecule has three contacts (Fig. 7), completing its octahedron. In I_2O_5 itself (*140*), one of the iodine atoms forms three secondary bonds, but the other has only two, its pseudo-octahedral coordination consisting of three short and two long bonds and one vacant position. If the hydroxy group of iodic acid is replaced by an aryl group, as in *p*-chloroiodoxybenzene (*11*), the iodine still makes a short oxygen contact (2.77 Å). Similarly, in one compound of iodine(VII), KIO_2F_2, where the iodine is linked to only four bonded atoms, there are two oxygen atoms (I---O, 2.81, 2.89 Å) which complete an octahedron (*131*).

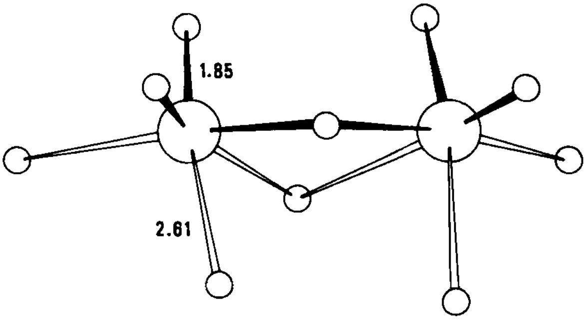


FIG. 7. The I_2O_5 moiety in HI_3O_8. Large circles, I; small circles, O. Redrawn from Feikema and Vos (*70*).

C. Iodine with Halogens

The structures of the polyhalogens and polyhalides were reviewed in 1961 (*153*), and recently their bonding has been examined (*154*). This will be considered below. These compounds show great variations in bond lengths, and it is perhaps more difficult for secondary bonds to be distinguished from primary bonds than from van der Waals interactions. Only typical examples are included here and details of other structures can be found in Refs. (*153*) and (*154*).

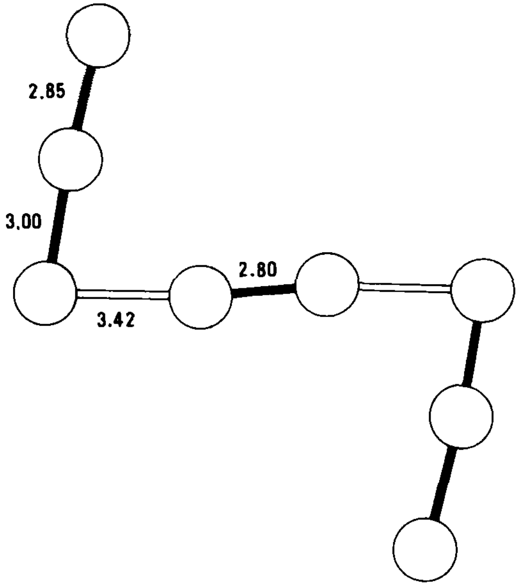


FIG. 8. I_8^{2-} in Cs_2I_8. Redrawn from Havinga *et al.* (*88*).

In Cs_2I_8 (*88*) the I_8^{2-} anion (Fig. 8) consists of an I_2 molecule which interacts at each end with I_3^- ions, with I---I equal to 3.42 Å. The van der Waals distance is 3.96 Å. A very similar structure is found in $N(CH_3)_4I_9$ (*107*), in which three I_2 molecules are attached to one I_3^- at distances of 3.24 (twice) and 3.43 Å. In solid I_2 (*20*) the intermolecular distance is 3.496 Å, and the intramolecular distance, 2.715 Å, is 0.05 Å longer than in the gas phase (*109*), whereas in I_8^{2-} it is longer still, 2.80 Å. Two modifications of ICl (Fig. 9) show similar interactions (*23*, *41*) with a very short I---I of 3.06 or 3.08 Å linking the molecules into zigzag chains; this is hardly longer than the bond distance in iodine itself.

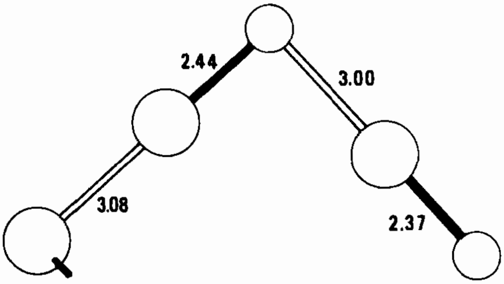


FIG. 9. α-ICl. Large circles, I; small circles, Cl (*23*).

There are also significant I---Cl interactions of 3.00 or 2.94 Å compared to a van der Waals distance of 3.73 Å.

Rather shorter I---Cl interactions occur in two compounds formally containing ICl_2^+, i.e. $ISbCl_8$ and $IAlCl_6$ (*150*). In both, the iodine atoms have two close chlorine atoms (2.29 Å, mean) and two completing a square plane at 2.90 Å (mean), which form part of the $SbCl_6^-$ or $AlCl_4^-$ groups (Fig. 10).

In the dimeric I_2Cl_6 (*24*) the bridges are symmetrical, but the I–Cl distances are 2.70 Å, only slightly shorter than the interaction distances in $IAlCl_6$ and $ISbCl_8$; the terminal I–Cl distances are rather long, 2.38 Å. The length of the bridge bonds suggests that it is equally valid to describe I_2Cl_6 either as a bridged molecule or as two ICl_2^+ groups interacting with two Cl^- ions. Both diphenyl iodonium chloride, $[(C_6H_5)_2ICl]_2$, and the corresponding bromide (*112*) have bridged structures (Fig. 11) in which the terminal iodine atoms are four-coordinated by two phenyl groups and two bridge atoms. For the chloride, the bridge is asymmetric with

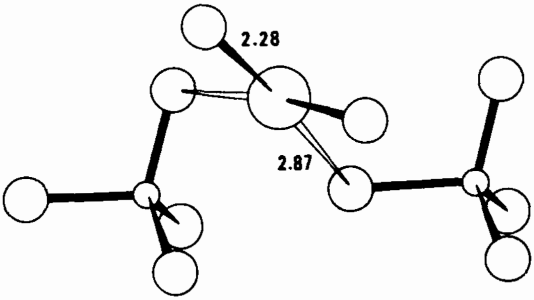


FIG. 10. $ICl_2^+AlCl_4^-$. Large circle, I; medium circles, Cl; small circle, Al. Redrawn from Vonk and Wiebanga (*150*).

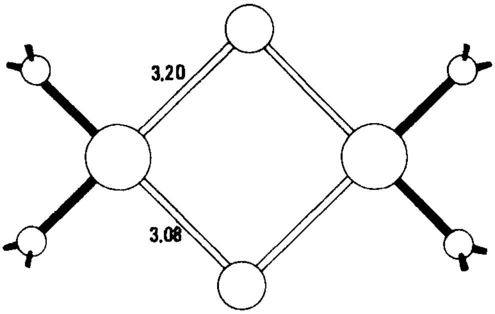


Fig. 11. Two central atoms of $[(C_6H_5)_2ICl]_2$. Large circles, I; medium circles, Cl; small circles, C (*112*).

I–Cl equal to 3.08 and 3.20 Å; but for the iodide it is symmetric, with I–I equal to 3.34 Å. For both, the distances are much longer than the normal single bond lengths (I–Cl, 2.27 Å; I–I, 2.56 Å) and the bonds can clearly be called secondary. In iodobenzene dichloride, $C_6H_5ICl_2$ (*12*) (Fig. 12), the iodine is linked to a phenyl group and two chlorine atoms at normal distances (I–Cl, 2.45 Å) and a square is completed by a weak I---Cl interaction of 3.40 Å.

Two compounds may show I---F interactions. Diphenyl iodonium borofluoride (*144*) has three I–F interactions between 2.94 and 3.00 Å (compared to the van der Waals distance of 3.45 Å), but only one C–I---F angle is close to 180°. In IOF_3 (*149*) many short I–F distances have been reported, but details have not been published.

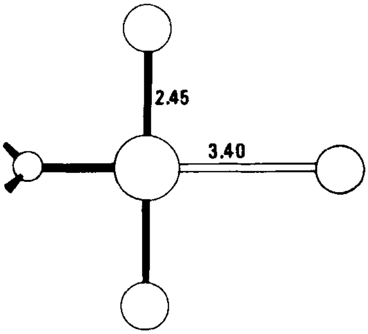


Fig. 12. The central atoms of $C_6H_5ICl_2$. Large circles, I; medium circles, Cl; small circles, C (*12*).

IV. Group VI*

The great majority of interactions of elements in this group are formed by selenium and tellurium. Sulfur is found in several adducts with charge-transfer interactions (*86*), while both it and selenium form thiothiophthene-like compounds containing bonds of order less than unity, which have been reviewed recently (*113*). Neither of these groups are considered further here.

A. With Oxygen and Sulfur

Both selenium and tellurium dioxide show secondary interactions leading to octahedral environments. In selenium dioxide (*122*) there are three primary Se–O bonds in a pyramid, length 1.78 Å (mean), and three secondary bonds, length 2.72 Å. Tellurium dioxide exists in two modifications, both related to TiO_2 structures, and both with four short and two long *cis* Te–O bonds. In the tetragonal modification (*117*) (Fig. 13), the distances are Te–O, 1.91 Å, and Te---O, 2.89 Å; in the orthorhombic modification, tellurite (*106*), the distances are 2.11 and 2.73 Å. Tellurium catecholate (*121*)

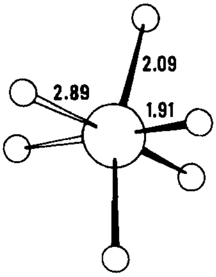
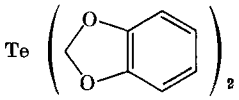


Fig. 13. TeO_2 (tetragonal). Large circle, Te; small circles, O. Redrawn from Leciejecwitz (*117*).



has the same primary coordination with Te–O, 2.01 Å, but forms only one secondary bond, Te---O, 2.64 Å.

* Summarized in Table III.

Selenous acid (*152*), H_2SeO_3, is similar to iodic acid in having three primary and three secondary bonds, with lengths of 1.74, and 3.06 Å (mean), while benzeneselinic acid (*29*), $C_6H_5SeO_2H$, forms one secondary interaction, with a C–Se---O linear system and Se---O equal to 3.16 Å, and also a weak O–Se---O interaction. Unlike iodates, salts of selenium and tellurium oxyacids have not been found to show short interactions, although rather few have been examined.*

In contrast to the four similar Te–O distances in tellurium catecholate, tellurium diethylxanthate (*104*) has two shorter Te–S, 2.49 Å, and two longer distances, 2.88 Å; these could be regarded as long dative bonds or as short secondary interactions. The atoms are coplanar, but the S–Te---S groups are rather far from linear, with bond angles of 149° (Fig. 14). In the largest gap, a further Te---S interaction occurs of a length of 3.61 Å, still rather short compared to the van der Waals distance of 3.86 Å.

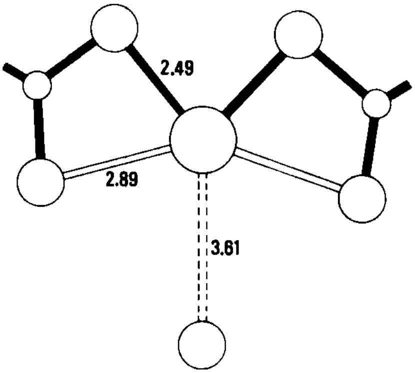


FIG. 14. The central atoms of $Te(S_2COC_2H_5)_2$. Large circle, Te; medium cicles, S; small circles, C. Redrawn from Husebye (*104*).

In tellurium bis(dimethyldithiophosphate), $Te[S_2P(OCH_3)_2]_2$ (*103*) (Fig. 15), the four sulfur atoms form a much distorted square around the tellurium with short Te–S, 2.44 Å, and long (cis), 3.31 Å, distances. Two of the selenium atoms in the dimeric anion $[Se(SeCN)_3]_2^{2-}$ (*87*) have similar environments (Fig. 16). The planar ion can be regarded as two $Se(SeCN)_2$ molecules bridged by two $SeCN^-$ ions with weak symmetrical interactions, and the mean distances are: short, 2.41 Å; long, 3.18 Å. By contrast, an asymmetric planar Te_2S_6-bridged system occurs in trithiourea tellurium hydrogen difluoride (*74*); the terminal Te–S bonds

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* But see Appendix.

TABLE III

SECONDARY BONDS TO GROUP VI ELEMENTS[a, b]

Compound	Ref.	Fig.	Linear group Y–A···X	Angle at A	Length		Single A–X	van der Waals A···X	Difference secondary minus single	Accuracy and notes
					Y–A	A···X				
SeO_2	*122*	—	O Se O	(167)	(1.75)	(2.61)	1.80	3.42	(0.81)	—
				(156)	(1.79)	(2.78)	—	—	(0.99)	Twice
TeO_2, tetragonal	*117*	13	O Te O	180	1.91	2.89	1.98	3.58	0.98	Twice
TeO_2, tellurite	*106*	—	O Te O	165	2.19	2.88	1.98	3.58	0.90	—
				166	2.25	2.79	—	—	0.81	—
$Te(O_2C_6H_4)_2$	*121*	—	O Te O	154	1.98	2.65	1.98	3.58	0.67	[c]
H_2SeO_3	*152*	—	O Se O	172	1.73	3.01	1.80	3.42	1.21	—
				162	1.75	3.16	—	—	1.36	—
				150	1.76	3.00	—	—	1.20	—
$C_6H_5SeO_2H$	*29*	—	C Se O	178	1.90	3.16	1.80	3.42	1.36	[c]
			O Se O	170	1.71	3.32	—	—	1.52	—
$Te(S_2COC_2H_5)_2$	*104*	14	S Te S	150	2.49	2.86	2.36	3.86	0.50	Twice[c]
$Te[S_2P(OCH_3)_2]_2$	*103*	15	S Te S	173	2.44	3.31	2.36	3.86	0.95	Twice[d]
$[Se(SeCN)_3]_2^{2-}$	*87*	16	Se Se Se	175	2.40	3.21	2.28	3.80	0.93	[d]
				177	2.40	3.24	—	—	0.96	—
				173	2.41	3.17	—	—	0.89	—
				173	2.42	3.02	—	—	0.74	—
$[TeSC(NH_2)_2]_2^{2+}(HF_2^-)_2$	*74*	—	S Te S	173	2.47	3.02	2.36	3.86	0.66	[c]
TeF_4	*56*	—	F Te F	165	1.87	2.26	1.96	3.53	0.39	[c]
$TeCl_4$	*36*	—	Cl Te Cl	(180)	2.31	2.91	2.31	3.81	0.60	Te1[d]
				—	2.32	2.90	—	—	0.59	—
				—	2.32	2.95	—	—	0.64	—
				—	2.30	2.95	—	—	0.64	Te2
				—	2.32	2.96	—	—	0.65	—
				—	2.32	2.92	—	—	0.61	—

$SeOF_2 \cdot NbF_5$	*58*	—	F	Se	F	170	1.68	2.69	1.78	3.37	1.01	Twice[c]
			O	Se	F	166	1.60	2.88	—	—	1.10	—
$SeF_3^+Nb_2F_{11}^-$	*59*	18	F	Se	F	174	1.64	2.42	1.78	3.37	0.78	[c]
						172	1.66	2.47	—	—	0.83	—
						171	1.67	2.40	—	—	0.76	—
$SeF_3^+NbF_6^-$	*60*	—	F	Se	F	176	1.69	2.33	1.78	3.37	0.55	Se1[c]
						176	1.72	2.41	—	—	0.63	—
						174	1.77	2.24	—	—	0.46	—
						177	1.73	2.43	—	—	0.65	Se2 three times[c]
$SeCl_3^+AlCl_4^-$	*143*	—	Cl	Se	Cl	171	2.07	3.03	2.13	3.65	0.96	[c]
						165	2.11	3.05	—	—	0.94	—
						166	2.13	3.11	—	—	0.98	—
$SeOCl_2 \cdot SbCl_5$	*93*	—	Cl	Se	Cl	170	2.13	3.05	2.13	3.65	0.92	[c]
$2SeOCl_2 \cdot SnCl_4$	*92*	—	Cl	Se	Cl	170	2.13	3.01	2.13	3.65	0.88	[d]
			O	Se	Cl	152	1.73	3.34	—	—	1.21	—
$SeOCl_2 \cdot 2C_5H_5N$	*119*	—	O	Se	Cl	170	1.59	3.65	2.13	3.65	1.52	[c]
$(C_9H_8NO)^+SeOCl_3^-$	*48*	19	O	Se	Cl	161	1.59	3.38	2.13	3.65	1.25	[c]
			Cl	Se	Cl	162	2.27	2.96	—	—	0.83	—
						165	2.23	2.99	—	—	0.86	—
$(C_5H_6N^+)_2$ $SeOCl_3^- Cl^-$	*151*	20	Cl	Se	Cl	168	2.25	2.99	2.13	3.65	0.86	[d]
$[(CH_3)_4N^+]_2$ $Cl_2(SeOCl_2)_{10}^{2-}$	*91*	21	Cl	Se	Cl	170	2.20	3.09	2.13	3.65	0.96	Se1[d]
			Cl	Se	O	143	2.18	3.14	1.80	3.42	1.34	—
			Cl	Se	Cl	162	2.20	3.05	2.13	3.65	0.92	Se2
			O	Se	Cl	157	1.57	3.60	—	—	1.47	—
			Cl	Se	O	156	2.20	2.85	1.80	3.42	1.05	—
			Cl	Se	Cl	161	2.22	2.97	2.13	3.65	0.84	Se3
			O	Se	Cl	165	1.58	3.44	—	—	1.31	—
			Cl	Se	O	157	2.20	2.89	1.80	3.42	1.09	—
			Cl	Se	Cl	171	2.17	3.66	2.13	3.65	1.53	Se4
			Cl	Se	O	170	2.17	2.87	1.80	3.42	1.07	—
			Cl	Se	Cl	168	2.20	3.05	2.13	3.65	0.92	Se5

continued

TABLE III—*continued*

Compound	Ref.	Fig.	Linear group Y–A---X	Angle at A	Length		Single A–X	van der Waals A---X	Difference secondary minus single	Accuracy and notes
					Y–A	A---X				
			O Se O	163	2.24	2.93	—	—	0.80	—
				158	1.62	3.12	1.80	3.42	1.32	—
$(CH_3)_3S^+I^-$	*156*	—	C S I	176	1.77	3.95	2.32	3.78	1.63	[c]
$(CH_3)_3Se^+I^-$	*98*	—	C Se I	179	1.96	3.78	2.42	3.88	1.46	[d]
$(CH_3)_3Te^+CH_3TeI_4^-$	*64*	22	C Te I	149	2.01	3.97	2.60	4.04	1.37	Cation[d]
				170	2.08	4.00	—	—	1.40	—
				173	2.13	3.84	—	—	1.24	—
				166	2.15	3.88	—	—	1.28	Anion
Thiuret hydriodide	*77*	—	S S I	167	2.09	3.62	2.32	3.78	1.30	[c]
$C_4H_8SeI_2$	*99*	—	I Se I	167	2.76	3.64	2.42	3.88	1.22	[d]
$C_6H_5TeCl \cdot SC(NH_2)_2$	*75*	23	C Te Cl	164	2.12	3.71	2.31	3.81	1.40	[c]
$C_6H_5TeBr \cdot SC(NH_2)_2$	*76*	—	C Te Br	164	2.12	3.77	2.43	3.91	1.34	[c]
$C_6H_5Te[SC(NH_2)_2]_2{}^+Cl^-$	*76*	—	C Te Cl	163	2.11	3.61	2.31	3.81	1.30	[c]
$(CH_3)_2TeCl_2$	*46*	24	C Te Cl	163	2.08	3.52	2.31	3.81	1.21	[d]
				171	2.10	3.46	—	—	1.15	—
$[p\text{-}ClC_6H_4Se]_2$	*115*	—	Se Se Cl	166	2.33	3.66	2.13	3.65	1.53	—
$[p\text{-}ClC_6H_4Te]_2$	*115*	—	Te Te Cl	(180)	2.70	(3.79)	2.31	3.81	1.48	—

[a] See footnote [a], Table II.

[b] Parentheses around a figure indicate either that it cannot be computed from published information or that it appears particularly unreliable.

[c] Standard deviation of A---X is 0.04 Å or better, corresponding approximately to a standard deviation for the angle Y–A---X of 2° or better (if X and Y are the same).

[d] Standard deviation of A---X is 0.01 Å or better, corresponding approximately to a standard deviation of 0.5° for the angle Y–A---X (if X and Y are the same).

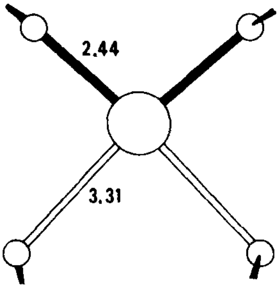


FIG. 15. The central atoms of $Te[S_2P(OCH_3)_2]_2$. Large circle, Te; small circles, S. Redrawn from Husebye (*103*).

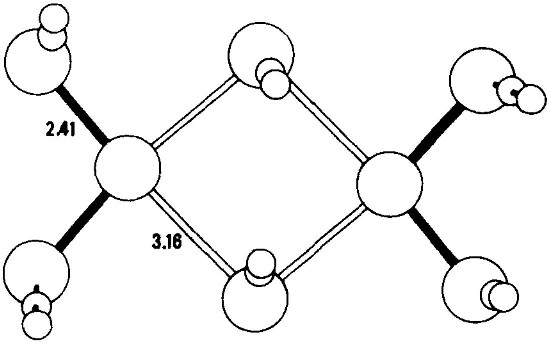


FIG. 16. $[Se(SeCN)_3]_2^{2-}$. Large circles, Se; small circles, C and N. Redrawn from Hauge (*87*).

are 2.47 and 2.53 Å, with bridge bonds of 2.86 Å opposite the long terminal bonds and 3.02 Å opposite the short terminal bonds.

B. WITH HALOGENS

Tellurium tetrafluoride (*56*) also shows asymmetric bridges, having endless chains

$$F\text{–}TeF_3\text{–}F\text{–}TeF_3{}^-$$

with bridge distances of 2.08 and 2.26 Å (terminal Te–F of 1.89 Å); the weaker bridge bond can be regarded as a strong secondary interaction. The coordination is octahedral, with one vacant (apex) position and the two bridge atoms are cis-equatorial. This can also be regarded, very approximately, as $TeF_3{}^+F^-$, with strong interaction between the ions.

The same structure type has been proposed from spectroscopic evidence for selenium and tellurium tetrachloride, tetrabromide, and tetraiodide (*2*, *83*, *89*) and has recently been proved for $TeCl_4$ (*36*) (Fig. 17). Tetrameric units are built up of $TeCl_3^+$ ions symmetrically bridged by Cl^- ions. Each tellurium has three short Te–Cl bonds, 2.32 Å, and three long bonds, 2.92 Å. $SeCl_4$ and $TeBr_4$ are isomorphous with this compound.

Both SF_4 and SeF_4 are monomeric in the vapor phase, but the Raman spectra of the solids suggest the presence of fluorine bridging (*13*).

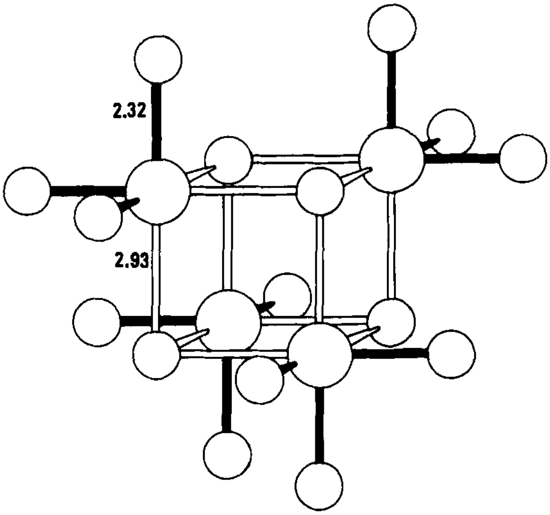


FIG. 17. $TeCl_4$. Large circles, Te; small circles, Cl. Redrawn from Buss and Krebs (*36*).

However, TeF_5^-, has been shown to be monomeric, by spectroscopic (*1a*) and crystallographic evidence (*61*).

Weak interactions occur in the adduct of $SeOF_2$ with NbF_5 (*58*) where the pyramidal $SeOF_2$ molecule (Se–F, 1.68 Å) makes three further contacts [Se---F, 2.75 Å (mean)] to complete an octahedron. The cation SeF_3^+ (Fig. 18) in both $SeF_3^+Nb_2F_{11}^-$ (*59*) and $SeF_3^+NbF_6^-$ (*60*) is very similar, but has rather shorter distances: Se–F, 1.66 and 1.73 Å; Se---F, 2.43 and 2.35 Å, respectively. The corresponding chlorine-containing cation in $SeCl_3^+AlCl_4^-$ (*143*) has Se–Cl equal to 2.18 Å and Se---Cl equal to 3.08 Å (mean) with the same geometry.

The structures of six compounds containing selenium oxychloride or its derivatives have been determined. All show secondary bonding resulting in distorted octahedra, sometimes with one or two vacant

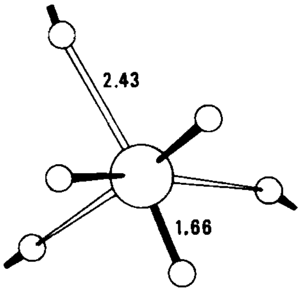
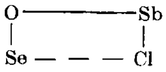


FIG. 18. SeF_3^+ in $SeF_3^+Nb_2F_{11}^-$. Large circle, Se; small circles, F. Redrawn from Edwards and Jones (*59*).

positions. In two compounds, $SeOCl_2 \cdot SbCl_5$ (*93*) and $2SeOCl_2 \cdot SnCl_4$ (*92*), the oxygen atom of the $SeOCl_2$ molecule acts as a donor. Each contains a Cl–Se - - - Cl interaction to a Cl of another molecule, with Se - - - Cl of 3.05 or 3.01 Å, and the second also has a weaker O–Se - - - Cl. Both also contain intramolecular interactions involving four-membered rings, such as



but it is not clear whether these are significant. In $SeOCl_2 \cdot 2C_5H_5N$ (*119*) the selenium accepts two electron pairs from pyridine molecules becoming five-coordinate, and the sixth position is occupied by a long Se - - - Cl interaction, 3.65 Å. The $SeOCl_3^-$ ion has been examined in two compounds. When the cation is 8-hydroxyquinolinium (*48*), the anion can be viewed as polymerized into chains by symmetrical chlorine bridges (Fig. 19).

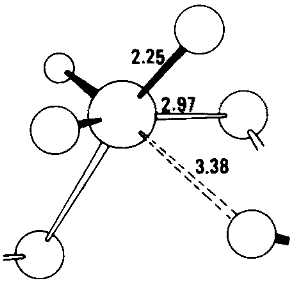


FIG. 19. $[SeOCl_3^-]_n$ in $C_9H_8NO^+SeOCl_3^-$. Large circle, Se; medium circles, Cl; small circle, O. Redrawn from Cordes (*48*).

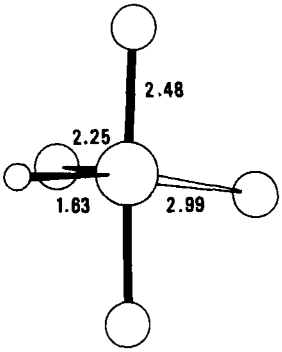


FIG. 20. $SeOCl_3^-$ in $[C_5H_6N^+]_2SeOCl_3^-Cl^-$. Large circle, Se; medium circles, Cl; small circle, O. Redrawn from Wang and Cordes (*151*).

This gives a five-coordinate selenium, and the sixth position is filled by a weak Se---Cl intramolecular interaction. However, the Se–Cl bridge bonds are also long, 2.97 Å, and it is valid to consider the complex as being built up of $SeOCl_2$ molecules bound together by interactions with chloride ions. In $(C_5H_6N^+)_2SeOCl_3^-Cl^-$ (*151*) there are discrete $SeOCl_3^-$ ions, each of which interacts with one chloride ion, with Se---Cl equal to 2.99 Å, to give a five-coordinate selenium atom (Fig. 20). As a culmination of the secondary interactions of $SeOCl_2$, the complex $(CH_3)_4NCl\cdot5SeOCl_2$ (*94*) contains a $[Cl_2(SeOCl_2)_{10}]^{2-}$ anion, a centrosymmetrical species held together entirely by secondary bonds (Fig. 21).

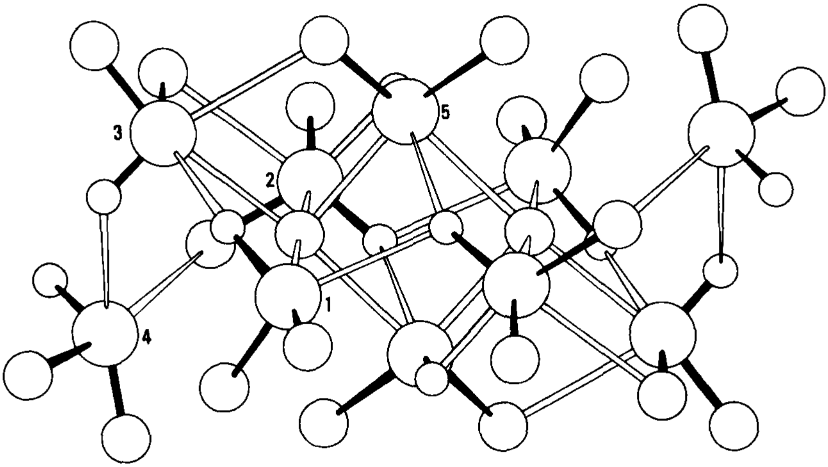


FIG. 21. $Cl_2(SeOCl_2)_{10}^{2-}$, in $(CH_3)_4NCl\cdot5SeOCl_2$. Large circles, Se; medium circles, Cl; small circles, O. The five different selenium atoms are numbered. Redrawn from Hermodsson (*94*).

These are mainly Se---Cl distances of about 3.20 Å, but there are some Se---O. Six of the selenium atoms achieve six-coordination, and four five-coordination, although some of the interactions are rather long.

An interesting group of compounds for which S, Se, and Te (=X) can all be compared contain the ion $(CH_3)_3X^+$, interacting with iodine. These are pyramidal, and the first two have one linear C–X---I grouping, while the third has three, completing an octahedron. The interacting distances are S---I, 3.89 Å (*156*); Se---I, 3.78 Å (*98*); Te---I, 3.95 Å (mean) (*64*). Iodide is the anion for the first two, but the third occurs in the compound $(CH_3)_3Te^+CH_3TeI_4^-$ (Fig. 22); the anion is octahedral, with one empty position and this position is filled with a further Te---I interaction of length 3.88 Å. Although the S---I contact is no shorter than the van der Waals distance of 3.78 Å, the linearity and the similarity to the other compounds suggests that there is a directed interaction, even though it is very weak. A rather shorter S---I interaction is known, 3.62 Å, in thiuret hydriodide (*77*) with an approximately linear S–S–I grouping. However, in 2,2′-diiododiethyl trisulfide (*54*), a S---I contact of 3.74 Å without directional properties may well be due to van der Waals forces only. An Se---I interaction occurs between molecules of the tetrahydroselenophene·iodine adduct (*99*) with the linear grouping I–I–Se---I and distances Se–I, 2.76 Å and Se---I, 3.64 Å.

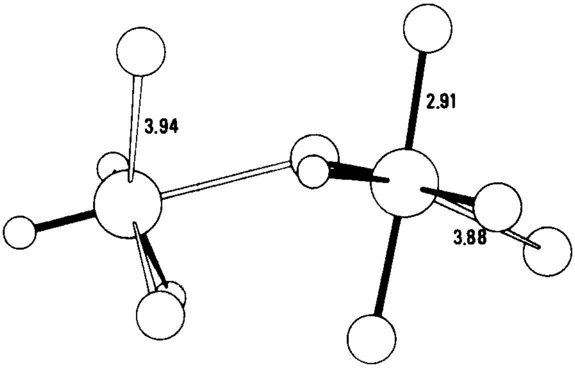


FIG. 22. $(CH_3)_3Te^+CH_3TeI_4^-$. Large circles, Te; medium circles, I; small circles, C. Redrawn from Einstein *et al.* (*64*).

Tellurium to chlorine and bromine interactions are found in several compounds of Te(II). Typical of these is the complex of thiourea with benzene tellurium chloride (*75*). This is a T-shaped molecule, with Te–C as the stem, Te–Cl (3.00 Å) and Te–S as the arms, and a Te---Cl interaction forming a distorted square with a length of 3.71 Å (Fig. 23).

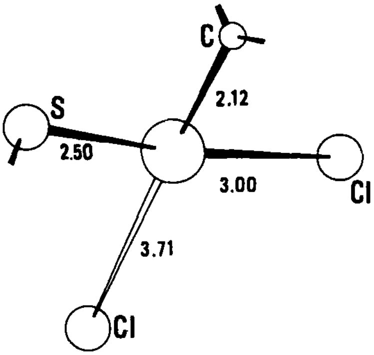


FIG. 23. The central atoms in $C_6H_5TeSC(NH_2)Cl$. Large circle, Te; medium circles, Cl and S; small circle, C. Redrawn from Foss and Husebye (*75*).

The corresponding bromide (*76*) has Te–Br, 3.11 Å, and Te---Br, 3.77 Å. If two molecules of thiourea (*76*) are complexed, a chloride ion is released to give $PhTe(tu)_2{}^+Cl^-$, but the chlorine is only 3.61 Å away, in line with the carbon atom, completing a distorted square. A similar C–Te---Cl is found in a Te(IV) compound, dimethyl tellurium dichloride (*46*), which has two short Te–Cl distances, 2.51 Å, and two longer ones, 3.49 Å, which complete an octahedron (Fig. 24). In *p,p'*-dichlorodiphenyl ditelluride (*115*), the grouping Cl---Te–Te---Cl is approximately linear, with Cl---Te somewhat longer, 3.79 Å (mean). The corresponding selenium compound (*115*) is isomorphous; its Cl---Se distances are slightly shorter (3.72 Å). Neither of these are significantly shorter than the expected van der Waals distances of 3.81 and 3.65 Å, but the geometry suggests directed interactions.

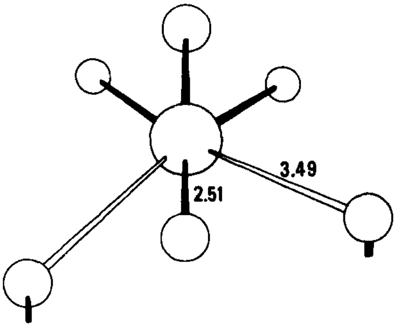


FIG. 24. $(CH_3)_2TeCl_2$. Large circle, Te; medium circles, Cl; small circles, C. Redrawn from Christofferson *et al.* (*46*).

A number of tellurium(II)–thiourea complexes show Te–hal bonds rather longer than the standard single bond length. These have been reviewed by Foss (*73*) and explained in terms of trans interactions; in these compounds, as with the polyhalides, the distinction between primary and secondary bonds becomes blurred.

V. Group V*

Nitrogen is concerned in some charge-transfer bonded adducts (*86*) and in the interactions formed by cyanides which are considered below, but apart from this, neither it nor phosphorus appears to be the principal atom of directed secondary bonds, while for bismuth, only two examples have been found. Arsenic and antimony interact mainly with chalcogens and halogens, but an Sb---N interaction of 2.53 Å occurs in $SbCl_3 \cdot C_6H_5NH_2$ (*101*) (Fig. 25). The Cl–Sb bond in the group Cl–Sb---N is 2.52 Å, considerably longer than in isolated $SbCl_3$ (2.37 Å) or in the other two bonds in the adduct (2.33 Å). There is an As---As interaction of 3.24 Å in dimethylarsinodimethyldithioarsinate (*39*) (Fig. 26); as could be expected, this occurs between pyramidal As^{III} groups rather than tetrahedral As^{V} groups, and the atoms S–As---As–S are approximately linear. In one compound, the adduct of antimony trichloride and

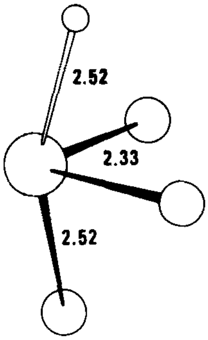


FIG. 25. The central atoms in $SbCl_3 \cdot C_6H_5NH_2$. Large circle, Sb; medium circles, Cl; small circle, N. Redrawn from Hulme (*101*).

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* Summarized in Table IV.

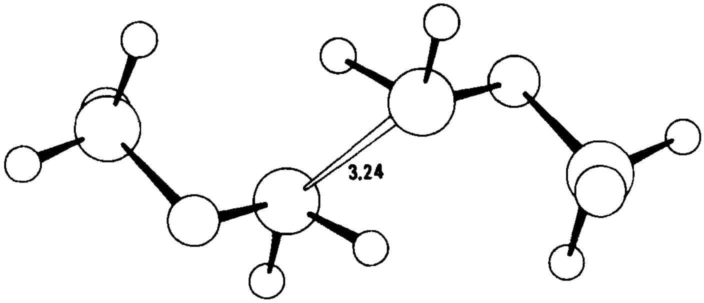
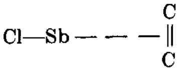


FIG. 26. $(CH_3)_2AsSAsS(CH_3)_2$. Large circles, As; medium circles, S; small circles, C. Redrawn from Camerman and Trotter (*39*).

naphthalene (*102*), there is an interaction with the π electrons of the naphthalene. In the group



$$\mathrm{Cl{-}Sb}\,-\,-\,-\begin{array}{c}\mathrm{C}\\ \| \\ \mathrm{C}\end{array}$$

the Cl–Sb bond, 2.367 Å, is 0.02 Å longer than the other two Cl–Sb bonds; the distance to the π bond is 3.2 Å which is long, but the structure clearly shows that this is a directed interaction.

A. WITH OXYGEN AND SULFUR

Both arsenious and antimonous oxides exist as molecular and polymerized species in the solid state; in the cubic (molecular) form (*9*), the central atoms have three near oxygens in a pyramid and three further completing an octahedron: As–O, 1.8 Å; As---O, 3.0 Å; Sb–O, 2.0 Å, and Sb---O, 2.9 Å. The monoclinic form (*17*, *18*) of As_2O_3 does not show similar contacts, while the structure of valentinite (*155*), although apparently containing Sb_2O_3 chains, has not been accurately determined. Bismuth in bismuth silicate (eulytite) has the same environment with Bi–O, 2.15 Å, and Bi---O, 2.63 Å (*139*). By contrast, several other arsenic and antimony oxy compounds do not show secondary contacts, one example being potassium di-*o*-phenylene dioxyarsenate (*141* and see references therein).

Compounds with thio acids have quite different structures, and two xanthates and two diethyl(dithiocarbamates) contain distorted octahedra. In $As(S_2COC_2H_5)_3$ (*42*) the distances are As–S, 2.28 Å, and As---S, 2.94 Å, while the antimony compound (*82*) has Sb–S, 2.52 Å, and Sb---S, 3.00 Å. As $[S_2CN(C_2H_5)_2]_3$ has As–S, 2.35 Å, and As---S, 2.85 Å (*47*) (Fig. 27); phenylarsine bis(diethyl dithiocarbamate) (*15*) is

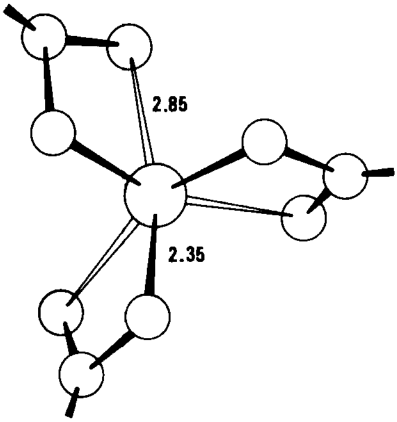


FIG. 27. The central atoms in $As[S_2CN(C_2H_5)_2]_3$. Large circle, As; small circles, S (next to As) and C. Redrawn from Colapietro *et al.* (*47*).

very similar with two S–As---S groupings and distances of 2.33 and 2.87 Å. Antimony triiodide forms an adduct with 1,4-dithiane (*19*), containing Sb---S links, 3.30 Å; the Sb-I bonds opposite these interactions are 0.02 Å longer than the third Sb–I bond.

B. WITH HALOGENS

The structure of solid arsenic trifluoride has not been determined, but in antimony trifluoride (*55*) there are three short, pyramidal Sb–F bonds of 1.92 Å and three longer bonds of 2.61 Å, completing an octahedron (Fig. 28). In the adduct, $AsF_3 \cdot SbF_5$ (*63*), the arsenic is also in a distorted octahedron, but the fluorine atoms show several degrees of interaction (Fig. 29). Two near, 1.64 Å, with one at 2.01 Å forming a bridge to a SbF_5 group, make up a distinct adduct molecule, but there is

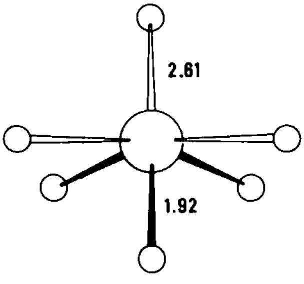


FIG. 28. SbF_3. Large circle, Sb; small circles, F. Redrawn from Edwards (*55*).

a second bridge through a fluorine at 2.39 Å and two longer contacts of 2.73 Å; the van der Waals distance is 3.32 Å. Infrared evidence shows that the anion SbF_4^- exists both as monomeric and polymeric species, with large cation size favoring the former (*1a*); in $NaSbF_4$ (*38*), one fluorine of each unit forms an asymmetric bridge, with Sb–F of 2.19 and 2.51 Å, and there is a weaker Sb - - - F interaction of 2.84 Å as well, giving overall six-coordination. Unexpectedly, in view of the infrared work, $KSbF_4$ (*37*) has been reported to have more symmetric bridges with Sb–F of 2.18 and 2.29 Å; it has secondary interactions of 2.90 and 2.98 Å, but there are no linear groups.

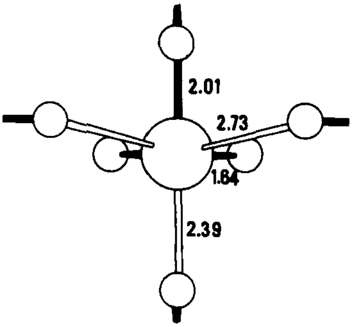


FIG. 29. $AsF_3 \cdot SbF_5$. Large circle, As; small circles, F. Redrawn from Edwards and Sills (*63*).

Although SbF_3 and SbI_3 (below) show secondary links, it seems that neither $AsBr_3$ (*25*), $SbCl_3$ (*120*), nor $SbBr_3$ (*25*, *50*) do so. In $SbCl_3$, the bond distance is 2.35 Å, whereas the next nearest neighbors are at 3.5 Å. However, in $Cs_3As_2Cl_9$ (*96*), the arsenic is reported to be in a distorted octahedron with As–Cl, 2.25 Å, and As - - - Cl, 2.76 Å; there is a series of isomorphous compounds containing either As or Sb with Cl, Br, or I. This was an early determination in two dimensions only, but the results are not dissimilar to more recent work on pyridinium tetrachloroantimonite (*130*), where the $SbCl_4^-$ ions are linked by asymmetric bridges with Sb–Cl, 2.38 Å, and Sb - - - Cl, 3.12 Å.

The triiodides of arsenic, antimony, and bismuth form an interesting series (*146*, *148*). All are isomorphous, with octahedra of iodine atoms containing the central atoms. Arsenic and antimony are significantly displaced from the centers of the octahedra, to give three near and three far X–I distances, but for Bi no irregularity can be detected. The bond distances are as tabulated below.

	Short (Å)	Long (Å)
AsI_3	2.556	3.56
SbI_3	2.868	3.32
BiI_3	3.1	3.1

VI. Group IV*

There are very few relevant interactions involving group IV elements because (*a*) the earlier members almost always have regular tetrahedral coordination, and (*b*) for the later members, the description *nonmetal* is doubtfully appropriate. One example is GeF_2 (*147*) (Fig. 30) which is not dissimilar to SbF_3 and SeF_3^+. It is polymerized into a chain with almost symmetrical bridges (Ge–F, 1.91 and 2.09 Å) and each germanium is coordinated to a pyramid of fluorine atoms, but in a fourth position opposite the longer Ge–F bridge bond, there is another fluorine at 2.57 Å. A number of Sn(IV) compounds are polymerized, and the bridges range from symmetrical, as in dimethyltin fluorine (*138*) with a regular octahedron, to highly unsymmetrical, as in dimethyltin chloride (*52*) with Sn–Cl bonds of 2.40 and 3.54 Å. Here, the tin coordination is still basically tetrahedral, but the CH_3–Sn–CH_3 angle has widened to 123° toward the octahedral angle of 180° (Fig. 31). $(CH_3)_2Sn(NCS)_2$ (*43, 71*) is similar to the chloride, having two Sn---S interactions, and the distortion toward octahedral is greater, with CH_3–Sn–CH_3 being 148°. $(CH_3)_3Sn(NCS)$ (*43, 85*) is reported to show a similar Sn---S interaction leading to five-coordinate tin, but details have not yet been published. In tribenzyltin acetate (*8*) (Fig. 32) the bridge is moderately asymmetrical, with Sn–O equal to 2.14 and 2.65 Å. The coordination is almost

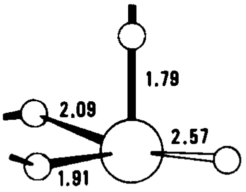


FIG. 30. GeF_2. Large circle, Ge; small circles, F. Redrawn from Trotter *et al.* (*147*).

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* Summarized in Table IV.

TABLE IV

Secondary Bonds to Group V and IV Elements[a, b]

Compound	Ref.	Fig.	Linear group Y–A···X	Angle at A	Length Y–A	Length A···X	Single A–X	van der Waals A···X	Difference secondary minus single	Accuracy and notes
$SbCl_3 \cdot C_6H_5NH_2$	*101*	25	Cl Sb N	166	2.52	2.53	2.06	3.60	0.47	[c]
$(CH_3)_2AsSAsS(CH_3)_2$	*39*	26	S As As	162	2.28	3.24	2.36	3.70	0.88	[d]
As_2O_3, cubic	*9*	—	O As O	—	1.8	3.0	1.84	3.37	1.2	Three times
Sb_2O_3, cubic	*9*	—	O Sb O	—	2.0	2.9	2.02	3.57	0.9	Three times
$Bi_4(SiO_4)_3$	*139*	—	O Bi O	156	2.15	2.62	2.21	3.67	0.47	Three times
$As(S_2COC_2H_5)_3$	*42*	—	S As S	160	2.28	2.94	2.22	3.65	0.72	Three times[d]
$Sb(S_2COC_2H_5)_3$	*82*	—	S Sb S	152	2.52	3.00	2.40	3.85	0.60	Three times[d]
$As[S_2CN(C_2H_5)_2]_3$	*47*	27	S As S	(177)	2.34	2.90	2.22	3.65	0.68	[d]
				—	2.35	2.81	—	—	0.59	—
				—	2.36	2.82	—	—	0.60	—
$C_6H_5As[S_2CN(C_2H_5)_2]_2$	*15*	—	S As S	152	2.32	2.91	2.22	3.65	0.69	[d]
				153	2.33	2.84	—	—	0.62	—
$SbI_3 \cdot S_2C_4H_4$	*19*	—	I Sb S	169	2.77	3.27	2.40	3.85	0.87	[d]
				171	2.77	3.34	—	—	0.94	—

SbF_3	*55*	28	F	Sb	F	162	1.90	2.63	2.00	3.52	0.63	[c]
						156	1.94	2.60	—	—	0.60	Twice
$AsF_3 \cdot SbF_5$	*63*	29	F	As	F	164	1.64	2.73	1.82	3.32	1.09	Twice[c]
						163	2.01	2.39	—	—	0.57	—
$NaSbF_4$	*38*	—	F	Sb	F	152	1.93	2.51	2.00	3.52	0.58	—
						170	2.03	2.84	—	—	0.84	—
$Cs_3As_2Cl_9$	*96*	—	Cl	As	Cl	172	2.25	2.75	2.17	3.60	0.57	Three times
$(C_5H_6N)^+SbCl_4^-$	*130*	—	Cl	Sb	Cl	(180)	2.38	3.12	2.35	3.80	0.72	Published coordinates inconsistent[d]
AsI_3	*146*	—	I	As	I	161	2.56	3.50	2.46	3.83	1.04	Three times
SbI_3	*148*	—	I	Sb	I	171	2.87	3.32	2.64	4.03	0.68	Three times
BiI_3	*148*	—	I	Bi	I	(180)	(3.1)	(3.1)	2.73	4.13	(0.37)	Three times
GeF_2	*147*	30	F	Ge	F	162	2.09	2.57	1.86	3.42	0.71	[c]
$(CH_3)_2SnCl_2$	*52*	31	Cl	Sn	Cl	164	2.40	3.54	2.39	3.85	1.15	[c]
$(CH_3)_2Sn(NCS)_2$	*71*	—	N	Sn	S	163	2.14	3.20	2.44	3.90	0.74	[c]
$(C_7H_7)_3SnO_2CCH_3$	*8*	32	O	Sn	O	169	2.14	2.65	2.06	3.62	0.59	[c]

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[a] See footnote *a*, Table II.

[b] Parentheses around a figure indicate either that it cannot be computed from published information or that it appears particularly unreliable.

[c] Standard deviation of A···X is 0.04 Å or better, corresponding approximately to a standard deviation for the angle Y–A···X of 2° or better (if X and Y are the same).

[d] Standard deviation of A···X is 0.01 Å or better, corresponding approximately to a standard deviation of 0.5° for the angle Y–A···X (if X and Y are the same).

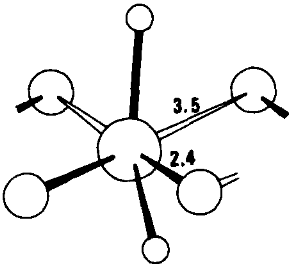

FIG. 31. $(CH_3)_2SnCl_2$. Large circle, Sn; medium circles, Cl; small circles, C. Redrawn from Davies *et al.* (*52*).

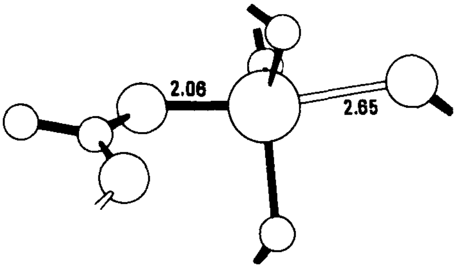

FIG. 32. The central atoms in $(C_6H_5CH_2)_3SnO_2CCH_3$. Large circle, Sn; medium circles, O; small circles, C (*8*).

trigonal-bipyramidal, but the average C–Sn–O (short) is 95° rather than 90° for a trigonal bipyramid or 109° for a tetrahedron. In other compounds, such as Na_2SnF_5 (*123*), which shows Sn–F bonds of various lengths, it is hardly valid to treat the tin as a nonmetal.

VII. Cyanides*

Virtually all nonmetal cyanides that have been investigated show interactions between the nonmetal and the nitrogen of the cyanide, often giving a long linear group

$$\cdots X\text{–}C\text{–}N \cdots X\text{–}C\text{–}N \cdots X\text{–}$$

If the group is bent, it is bent at the nitrogen, showing that it is X that is the "principal atom." Despite this, these compounds have been

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* Summarized in Table V.

collected here because of their general similarity. They have been reviewed recently (*27*) with special reference to their intermolecular interactions.

Three halogen cyanides (*79*, *91*, *110*) have been examined, and for all, a linear infinite chain is required by the space group symmetry, but only for ClCN have the atomic positions been determined accurately. This has an interaction distance Cl---N of 3.01 Å. The approximate bond lengths suggest that the degree of interaction increases for I > Br > Cl [Table 3 in Hassel and Römming (*86*)]. Cyanuric chloride also shows a Cl---N interaction, somewhat longer than that in cyanogen chloride (*100*). Inclusion of an organic moiety between the halogen and the cyanide does not disturb the chain structure, as shown by IC≡C–CN (*22*) and a series of halogenophenyl cyanides and isocyanides (*27*, pp. 147, 134). These and several related compounds have been examined by Britton and co-workers, but the only complete publication is for *p*-iodobenzonitrile (*134*), in which the I---N distance is 3.18 Å, substantially longer than the probable 2.8 Å for ICN.

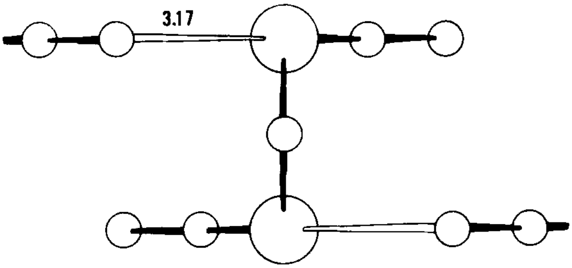

FIG. 33. $CH_2(SCN)_2$. Large circle, S; small circles, C and N. Redrawn from Konnert and Britton (*114*).

With sulfur and selenium, some dozen compounds have been examined (*114*) of which ten show interaction between S or Se and CN and are summarized in Table V; in an eleventh, tetracyano-1,4-dithiin (*53*), there is a preferential interaction between the CN groups and the double bonds. The sulfur or selenium atoms generally show distorted square-planar coordination, with two near neighbors and two far S---N interactions. With $CH_2(SCN)_2$ (*114*) (Fig. 33) there is only one S---N interaction, whereas with $(CH_3)_2SC(CN)_2$ (*45*) the sulfur forms three primary bonds and so has the ability to form three secondary bonds completing a distorted octahedron. The shortest interactions are 2.95 Å for S---N in $S(CN)_2$ (*65*) and 2.98 Å for Se---N in $Se(SCN)_2$ (*127*). Most of the

TABLE V

SECONDARY BONDS FORMED BY CYANIDES[a, b]

Compound	Ref.	Fig.	Linear group Y–A---N	Angle CN---A	Angle YA---N	Length Y–A	Length A---N	Standard single A–N	van der Waals A---N	Difference A---N minus single	Accuracy and notes
ClCN	*91*	—	C Cl N	180	180	1.57	3.01	1.69	3.30	1.32	[c]
BrCN	*79*	—	C Br N	180	180	(1.79)	(2.86)	1.82	3.40	(1.04)	—
ICN	*110*	—	C I N	180	180	(2.03)	(2.79)	1.98	3.53	(0.81)	—
IC≡CN	*22, 27*	—	C I N	(180)	(180)	(2.03)	(2.81)	1.98	3.53	(0.83)	—
p-IC_6H_4CN	*134*	—	C I N	180	180	2.06	3.18	1.98	3.53	1.20	[d]
$CH_2(SCN)_2$	*114*	33	C S N	132	176	1.68	3.17	1.74	3.35	1.43	[d]
$(CH_3)_2SC(CN)_2$	*45*	—	C S N	140	171	1.73	3.29	1.74	3.35	1.55	[c]
				114	162	1.80	3.35	—	—	1.61	—
				119	174	1.82	3.45	—	—	1.71	—
$S(CN)_2$	*65*	—	C S N	138	176	1.72	2.95	1.74	3.35	1.21	[c]
				148	170	1.74	2.98	—	—	1.24	—
$Se(CN)_2$	*65, 90*	—	C Se N	(145)	(180)	(1.8)	(2.4)	1.84	3.45	(0.6)	Very poor. Space group doubtful
$S(SCN)_2$	*69*	—	S S N	139	166	2.12	3.12	1.74	3.35	1.38	S1 twice Atom 1 is central, atom 2 attached to cyanide
			S S N	119	162	2.12	3.25	—	—	1.51	S2
			C S N	115	169	1.69	3.12	—	—	1.38	—
$Se(SCN)_2$	*127*	—	S Se N	133	168	2.21	2.98	1.84	3.45	1.14	Se1 twice
			Se S N	122	167	2.21	3.32	1.74	3.35	1.58	S2
			C S N	115	172	1.69	3.03	—	—	1.29	—
$Se(SeCN)_2$	*4, 124*	34	Se Se N	129	168	2.30	3.16	1.84	3.45	1.32	Se1 twice[c]
			Se Se N	126	164	2.30	3.27	—	—	1.43	Se2
			C Se N	122	172	1.92	3.07	—	—	1.23	—

p-$C_6H_4(SeCN)_2$	*124*	—	C	Se	N	162	175	1.84	3.06	1.84	3.45	1.22	C of CN[c]
						113	168	1.91	3.32	—	—	1.48	C of C_6H_4
$(CH_2SCN)_2$	*26*	—	C	S	N	140	169	1.63	3.28	1.74	3.35	1.54	C of CN[c]
						119	177	1.80	3.39	—	—	1.65	C of CH_2
$C_4(CN)_4S$	*133*	—	C	S	N	127	174	1.69	3.22	1.74	3.35	1.48	[c]
						124	171	1.72	3.26	—	—	1.52	—
$P(CN)_3$	*67*	—	C	P	N	148	165	1.77	2.99	1.80	3.35	1.19	[c]
						154	164	1.79	2.97	—	—	1.17	—
						155	166	1.80	2.85	—	—	1.05	—
$As(CN)_3$	*66, 135*	35	C	As	N	166	162	1.97	2.74	1.88	3.40	0.86	[c]
$CH_3As(CN)_2$	*135*	—	C	As	N	149	165	1.99	2.93	1.88	3.40	1.05	C of CN[c]
						150	160	1.97	3.32	—	—	1.44	—
						106	165	2.00	3.32	—	—	1.44	C of CH_3
$(CH_3)_2AsCN$	*40*	—	C	As	N	168	168	2.00	3.18	1.88	3.40	1.30	C of CN[c]
SiH_3CN	*7*	—	C	Si	N	(180)	(180)	—	—	—	—	—	Distances not known accurately
$(CH_3)_3GeCN$	*137*	—	C	Ge	N	180	180	1.98	3.57	1.92	3.50	1.65	—
$(CH_3)_2Ge(CN)_2$	*27*	—	C	Ge	N	(180)	(180)	—	3.20	1.92	3.52	1.28	—
$(CH_3)_2Si(CN)_2$	*27*	—	C	Si	N	(180)	(180)	—	3.53	1.67	3.65	1.86	—
$(CH_3)_3SnCN$	*136*	—	X	Sn	X	180	180	2.49	2.49	2.10	3.65	0.39	X = either C or N[c]

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[a] See footnote *a*, Table II.

[b] Parentheses around a figure indicate either that it cannot be computed from published information or that it appears particularly unreliable.

[c] Standard deviation of A---X is 0.04 Å or better, corresponding approximately to a standard deviation for the angle Y–A---X of 2° or better (if X and Y are the same).

[d] Standard deviation of A---X is 0.01 Å or better, corresponding approximately to a standard deviation of 0.5° for the angle Y–A---X (if X and Y are the same).

others are weak with an S---N of about 3.2 Å, compared to the van der Waals distance of 3.35 Å, but the directional properties suggest that these are real secondary bonds. In the isomorphous series $S(SCN)_2$ (*69*), $Se(SCN)_2$ (*127*), and $Se(SeCN)_2$ (*4*, *124*), all the S and Se atoms achieve distorted square coordination, and Fig. 34 shows the molecular packing in $Se(SeCN)_2$. This group of compounds is sufficiently extensive for two effects on bond lengths to appear. The shortest interactions are of the type NC–X---NC forming a linear chain, with cyanide opposite the secondary bond. If the chain is bent at the nitrogen, i.e.,

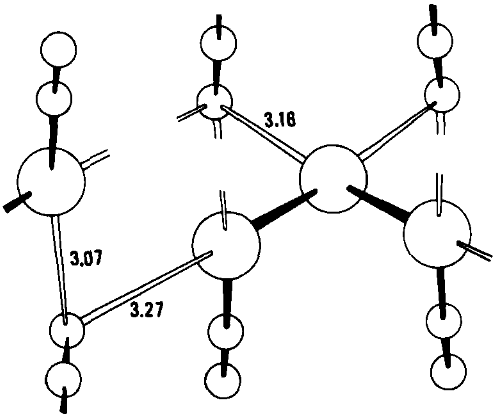
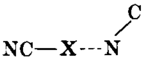


FIG. 34. $Se(SeCN)_2$. Large circles, Se; small circles, C and N. Redrawn from McDonald and Pettit (*124*).



$$\mathrm{NC{-}X{\cdots}}\overset{\diagup\!C}{\mathrm{N}}$$

the interaction is longer, and it is also longer in compounds of type R–X---NC with alkyl or aryl groups opposite the secondary bond.

Several group V cyanides have been examined. $P(CN)_3$ (*67*) has three interactions completing an octahedron with P---N equal to 2.93 Å. By contrast, in $As(CN)_3$ (*66*, *135*) (Fig. 35), there is only one interaction, but it is much stronger, 2.74 Å. On substitution with first one and then a second methyl group (*40*, *135*), the interaction weakens to 2.94 and 3.18 Å. In $CH_3As(CN)_2$ (*135*) there are also weaker H_3C–As---N and NC–As---N interactions, both with As---N of 3.32 Å.

With group IV, an incomplete study (*7*) on silyl cyanide, which has an unexpectedly high melting point, has shown a linear chain, ---Si–C–N---Si, but the bond lengths were not determined accurately.

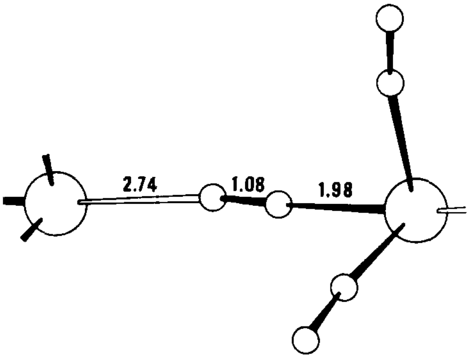


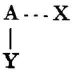
FIG. 35. As(CN)$_3$. Large circles, As; small circles, C and N. Redrawn from Emerson and Britton (*66*).

Trimethylgermyl cyanide (*137*) again has an abnormal melting point and the crystal structure determination shows a linear chain. The interaction is weak (3.57 Å), but probably real, as the C–Ge–C angles are slightly wider than tetrahedral (average 115°). Further evidence that this is real comes from the structure of $(CH_3)_2Ge(CN)_2$, (*27*, p. 115 f.), where the interaction is stronger, 3.20 Å; the change parallels that found for $As(CN)_3$ and $CH_3As(CN)_2$. In $(CH_3)_2Si(CN)_2$ (*27*, p. 155 f.), the overall structure is retained, but the interaction is very weak, with Si---N of 3.53 Å. Trimethyltin cyanide (*136*) has approximately the same structure as the germanium compound, but with one great difference. The CN group is now detached and is equidistant between two tin atoms, which are coordinated by three methyl groups in a plane; the cyanide group is disordered, but a linear group Sn---C–N---Sn is retained. It appears that trimethyllead cyanide also has this structure (*44*).

VIII. Conclusion

A. ANGLES

The crystallographic results given above have been interpreted in terms of linear interactions, but some workers (*140*, *154*) have suggested that the relevant features are right-angled interactions,



$$\begin{array}{l} \mathrm{A}\cdots\mathrm{X} \\ | \\ \mathrm{Y} \end{array}$$

The strongest evidence for the linear group comes from those compounds where there is only one primary bond from the central atom, when the secondary bond is always found to be in line with, rather than at right angles to it.

Tables II–V include as many angles as are known, and taking their accuracy into consideration, it can be seen that deviations of up to 15° from the straight line are common, but that few exceed this. When they do, of course, it becomes difficult to recognize a particular linear Y–A - - - X group, and so the preceding statement is equivalent to saying that only in very few compounds with secondary bonds are linear groups absent or doubtful.

B. GEOMETRY

Whatever the nature of the bonding in the linear interactions, the resulting geometries can be analyzed, and with a set of simple rules, can be understood. Considering both primary and secondary bonds (and sometimes vacant positions), the central atom may have one of four coordinations: the centrosymmetric line, square, and octahedron, or the pseudo-centrosymmetric trigonal-bipyramid (with an axial secondary bond). Using this classification, the observed geometries are given in Table VI.

The rules that explain these structures are: (1) The geometry of the primary bonds of the central atom is governed in the usual way by the number of lone and bonded electron pairs; (2) secondary bonds can form in any direction in line with primary bonds, but (3) not in the same direction as a lone pair on the central atom.

As riders to (2) can be added (*a*) that secondary bonds are rare with the elements P, S, or Cl, and (*b*) that the number of secondary bonds may be restricted by packing considerations.

There are a very few exceptions to (1), involving group IV elements, in which the overall geometry has changed, partly or completely, from that predicted for the primary bonds (tetrahedral) toward either trigonal-bipyramidal or octahedral. These can be seen as special cases, because they are the only examples where the primary coordination contains no vacant positions. Thus, the introduction of bonds to extra atoms can be expected to distort the original tetrahedron. As an example, in $(CH_3)_2SnCl_2$ where the secondary bonds to chlorine are rather long, the angles CH_3–Sn–CH_3 and Cl–Sn–Cl are 123.5° and 93°, rather than 109° for the original tetrahedron or 180° for a perfect octahedron. A similar situation might be found with an AB_5 molecule with five bonding pairs

TABLE VI

GEOMETRY OF SECONDARY INTERACTIONS[a]

Line

Primary: 1 Electron pairs: 4 Secondary: 1

XeF^+ (II, 2); $Xe_2F_3^+$ (II, 3); $POBr_3$ (II); I_8^{2-} (II, 8); ICl (II, 9); *n*-Chlorosuccinimide (II); ClCN (V)

Square

Primary: 2 Electron pairs: 4 Secondary: 1 Vacant: 1

$CH_2(SCN)_2$ (V, 33)

Primary: 2 Electron pairs: 4 Secondary: 2

ClF_2^+ (II, 5); BrF_2^+ (II, 5); ICl_2^+ (II, 10); $(C_6H_5)_2ICl_2$ (II, 12); $Te[S_2P(OCH_3)_2]_2$ (III, 15); $[Se(SeCN)_3]_2^{2-}$ (III, 16); $Se(SeCN)_2$ (V, 34)

Primary: 3 Electron pairs: 5 Secondary: 1

$C_6H_5ICl_2$ (II, 11); $C_6H_5Te(SC(NH_2)_2Cl$ (III, 23)

Trigonal bipyramid

Primary: 4 Electron pairs: 4 Secondary: 1

$(C_6H_5CH_2)_3Sn(OCOCH_3)$ (IV, 32); $(CH_3)_3GeCN$ (V)

Octahedron

Primary: 3 Electron pairs: 4 Secondary: 1 Vacant: 2

$SeOCl_2 \cdot SbCl_5$ (III); $(CH_3)_3Se^+$ (III); $C_6H_5SeO_2H$ (III); $SbCl_3 \cdot C_6H_5NH_2$ (IV, 25); $(CH_3)_2AsSAsS(CH_3)_2$ (IV, 26); GeF_2 (IV, 30); $As(CN)_3$ (V, 35)

Primary: 3 Electron pairs: 4 Secondary: 2 Vacant: 1

XeO_3F^- (II, 4); I_2O_5 (II); $Cl_2(SeOCl_2)_{10}^{2-}$ (III, 21)

Primary: 3 Electron pairs: 4 Secondary: 3

IO_3^- (II, 6); I_2O_5 (in HI_3O_8; II, 7); H_2SeO_3 (III); $TeCl_4$ (III, 17); SeF_3^+ (III, 18); $SeCl_3^+$ (III); $SeOF_2$ (III); $(SeOCl_3^-)_n$ (III, 19); $Cl_2(SeOCl_2)_{10}^{2-}$ (III, 21); $(CH_3)_3Te^+$ (III, 22); $Bi_4(SiO_4)_3$ (IV); $As[S_2CN(C_2H_5)_2]_3$ (IV, 27); SbF_3 (IV, 28); $AsF_3 \cdot SbF_5$ (IV, 29); AsI_3 (IV); $P(CN)_3$ (V)

Primary: 4 Electron pairs: 5 Secondary: 1 Vacant: 1

$Te(O_2C_6H_4)_2$ (III); TeF_4 (III); $SeOCl_3^-$ (III, 20).

Primary: 4 Electron pairs: 5 Secondary: 2

$IO_2F_2^-$ (II); TeO_2 (III, 13); $(CH_3)_2TeCl_2$ (III, 24)

Primary: 5 Electron pairs: 6 Secondary: 1

$CH_3TeI_4^-$ (III, 22); $SeOCl_2 \cdot 2C_5H_5N$ (III)

Distorted octahedron

Primary: 4 Electron pairs: 4 Secondary: 2

$(CH_3)_2SnCl_2$ (IV, 31); $(CH_3)_2Sn(NCS)_2$ (IV)

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[a] Typical examples only are included. After each is given the table number and, if it is illustrated, the figure number.

forming one secondary bond and becoming octahedral, but no example has been reported.

The effect of (3) is demonstrated by considering the geometry defined by six electron pairs (5 bonding and 1 lone pair) giving a square-pyramidal molecule. Three species containing this arrangement, XeF_6, XeF_5^+, and IF_5, do not have a secondary bond in line with the apical atom. With AB_4 molecules having six electron pairs no secondary bonding is possible because the geometry is a square, e.g., XeF_4. One can predict that an AB_3 species with six electron pairs would not form secondary bonds, but the only likely species of this type, XeF_3^-, has not been prepared. The underlying reason is that the octahedron defined by the original six electron pairs is centrosymmetrical.

There are two exceptions to (3) and the preceding discussion; they are CH_3TeI_4 and $SeOCl_2 \cdot 2C_5H_5N$. Both form five primary bonds with square-pyramidal geometry, but *do* have a secondary interaction occupying the sixth position of an octahedron. It is possible that their bonding should be attributed to *p* electrons only, in which case there will not be six sterically active electron pairs in the original molecules. A parallel can be drawn with $TeCl_6^{2-}$ (*68*) and $TeBr_6^{2-}$ (*14*), having regular octahedral geometry but formally seven electron pairs.

C. DISTANCES

The problems of definition of van der Waals radii, etc., discussed in the Introduction make it difficult to use secondary bond distances as a measure of interaction strength, but there are two possible approaches to this.

At least one worker (*62*) has used the *ratio* (secondary bond length)/(primary bond length) as a measure of the strength of the secondary bond, but this must almost certainly be invalid. For a very weak interaction, almost at the van der Waals distance (taken to be 1.50 Å longer than a single bond) the ratio will be (primary bond length + 1.50)/(primary bond length), and this can clearly vary, for example, from 1.3 for Te–Br to 2.1 for Cl–F interactions. For a stronger interaction, the ratio will be just as dependent on the participating elements.

The alternative approach uses the *difference* (secondary bond length minus single bond length). This is supported by the calculations (discussed below) of Wiebenga and Kracht (*154*) of bond orders in polyhalogens. Their plot of this difference ($R - R_{cov}$) against bond order is shown in Fig. 36; their bond orders are in the range 0.4 to 1.0 corresponding to length differences 0.7 to 0.0 Å. Part of the shortening from the van der Waals distance is assumed to be due to electrostatic attraction

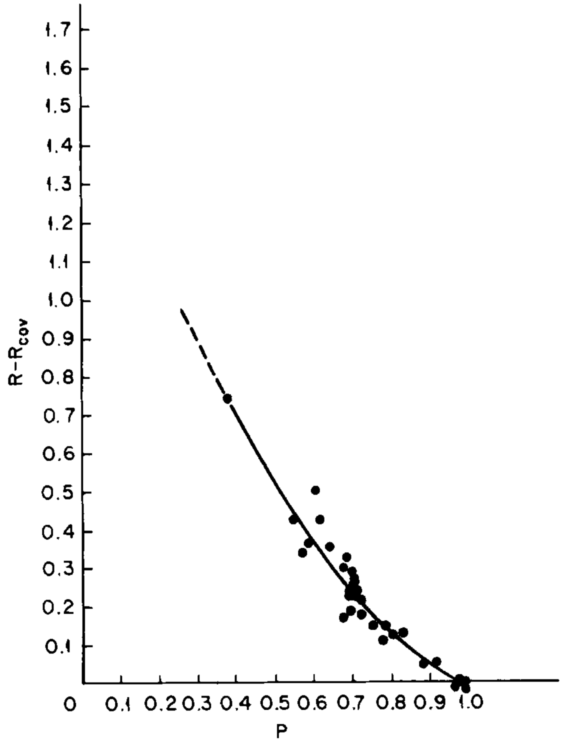

FIG. 36. The relationship between bond order and bond length minus standard single-bond length for polyhalogens. From Wiebenga and Kracht (*154*).

and a calculated correction is made for this (mostly small, but as much as 0.3 Å in one case). This correction presents a problem for the estimation of secondary bond orders from the bond length differences, because it uses both the charges on the individual atoms and the force constant of the bond being corrected, information which is not normally available. In the future with this correction, reliable estimates of bond order can probably be obtained, but at present they can only be semiquantitative.

From the data two trends can be established for the strength of secondary bonds. In the system Y–A---X, Y and X are often identical and there is not much evidence of the result of changing Y alone. However, if A is changed, the effect is clear. When A becomes more electropositive, the interaction becomes stronger. Good examples of this are F–Br---F and F–Cl---F in BrF_2^+ and ClF_2^+, with secondary distances of 2.29 and 2.38 Å, respectively, or I–X---I in AsI_3, SbI_3, and BiI_3 with distances of 3.50, 3.32, and 3.1 Å, and there are many others. Similarly, if the atom A is positively charged, it forms stronger interactions than the same atom when neutral.

One might expect that making X (or X and Y together) more electronegative would also strengthen the bond, but this is not necessarily so. There are few examples where compounds with similar geometries can be compared, but one case is O–As - - - O in As_2O_3, 3.0 Å, S–As - - - S in $As[S_2CN(C_2H_5)_2]_3$, 2.84 Å (mean), and corresponding bond length differences of 1.16 and 0.82 Å. Although the first determination is inaccurate, the large decrease make it almost certain that here As - - - S is stronger than As - - - O. Similarly, in $C_6H_5Te(tu)Cl$ and $C_6H_5Te(tu)Br$, the bond length differences are 0.40 and 0.34 Å, and it is again likely that Te - - - Cl is weaker than Te - - - Br. Further evidence can be obtained by considering the effect of making all of A, X, and Y more electropositive without changing their relative electronegativity. This clearly strengthens the interaction in some cases. Cl–I - - - Cl in ICl_2^+ can be compared with F–Cl - - - F and F–Br - - - F in ClF_2^+ and BrF_2^+, with bond length differences of 0.63 (mean), 0.80 (mean), and 0.60 Å, where I - - - Cl is stronger than Cl - - - F and no weaker than Br - - - F. Taking the first trend into consideration, it appears from this that the interaction tends to be strengthened if X becomes *less*, not more electronegative.

D. BONDING

With as much empirical information available as possible, the nature of the secondary bonding itself can be considered. One simple explanation is that nothing more than electrostatic attraction is responsible, with the lone pair(s) of the central atom taking up some space. This is not unattractive for octahedra with three primary and three secondary bonds, but it does not explain the pseudo-octahedral geometry when one or two secondary bonds are not formed. Also, with two primary bonds there is no obvious reason why only two secondary attractions should be strong. This explanation, then, is plausible for SeF_3^+ forming an octahedron, but not useful for BrF_2^+ forming a square, two compounds whose bonding should be very similar.

What follows is put forward as a theory for secondary bonds that may be more satisfactory than the electrostatic view. In general terms, a dative interaction is suggested between a lone pair on the "outer" atom (X) and an empty orbital on the "cental" atom (A). Further, reasoning from the linearity of the bond, it is likely that the empty orbital is the σ^* orbital of the primary bond, Y–A; this can be expected to project furthest in space in the direction away from Y. Considering both primary and secondary bonds together, the three atomic orbitals involved will give three molecular orbitals, occupied by two electron pairs. If the three atoms are arranged symmetrically, there are occupied bonding and nonbonding orbitals and an unoccupied antibonding orbital, and the result is a weak bond between each pair of atoms. With an unsymmetrical arrangement, the bonding orbital is concentrated between the close pair, giving a strong bond, and the nonbonding one is concentrated on the other side and (with a small contribution from the bonding orbital) gives a weak bond. The overall scheme is identical to that put forward for the hydrogen bond, which has the same possibility of asymmetry, O–H---O, or symmetry, $(F–H–F)^-$.

In theory, the formation of a secondary bond should produce a weakening of the primary bond (effectively one bonding electron pair spread over two bonds). But this will only be true if there is no change at all in the orbitals involved; there are generally *d* orbitals on the central atom of the correct symmetry to mix with the bonding or nonbonding three-center orbitals, and the formation of the secondary bond might lead to greater interaction with these *d* orbitals. In this case, the primary bond might be unchanged, or even strengthened by forming the secondary bond. The best evidence of either effect is found with iodine and the polyiodides, where the intramolecular I–I is significantly longer than in the gas phase; some similar examples have been noted during the main part of the chapter. There are also cases in which a primary bond that is long because of the nature of the structure, e.g., the bridge I–O in I_2O_5, has the shortest secondary bond opposite it. Hassel and Römming (*86a*) have shown that for iodine in charge-transfer bonded adducts and trihalides, there is a linear correlation with Y–I lengthening as I---X shortens.

The two trends noted for the strength of the secondary bonds can be understood qualitatively from this model. When the central atom (A) becomes more electropositive, the bonding and antibonding orbitals of the primary bond will both become less compact, leading to better overlap with the distant lone-pair orbital of the outer atom (X); there will also be a greater electrostatic force between the central and outer atoms. Similarly, when the outer atom becomes more electropositive, the lone-pair orbital will become less compact and will overlap better with the σ^* orbital of the central atom. In both cases, the greater diffuseness of the orbitals is the first step toward full delocalization of electrons, the first step toward metallic bonding; one or two compounds with secondary bonds do have a metallic luster.

This model corresponds closely to that suggested for charge-transfer bonded species (*10*), and it has already been noted that the two types of bond are geometrically similar. The electron pair donation is effectively a charge transfer, and it would be possible to give the whole class of secondary bonds this label. However, as presently recognized, charge-transfer interactions are always thought of as weak. It is therefore better to introduce the new term *secondary bond* which can cover a whole range of interactions including charge-transfer bonds, than to extend that term far beyond its present use.

E. THEORETICAL CALCULATIONS

In the work of Wiebenga and Kracht (*154*) on the bonding of polyhalogens, a Hückel procedure was used, modified to allow for charges on the atoms and based only on *p* orbitals. The overlap integral was only given a nonzero value for two adjacent *p* orbitals directed at each other, and its variation with bond distance (R) was taken to be a linear function of $(R - R_{\text{covalent}})$, fitted to the known values for I_2 and I_3^-. It was assumed that all angles were 90° or 180°.

All the species examined have bond lengths longer than the standard covalent distances, and the bond orders were calculated corresponding to the observed geometries. These agreed well with the known distances (Fig. 36), which is not surprising in view of the assumed form of the overlap integral. A more independent test was a comparison of the calculated atomic charges with those obtained from nuclear quadrupole resonance and Mössbauer measurements, and the agreement was satisfactory; other comparisons also suggest that this theoretical model accounts rather well for the bonding in these compounds.

This model is in essence the same as that proposed above for secondary bonds, but is more sophisticated because it allows full delocalization rather than delocalization over a three-atom system only. In two species, ICl (solid) and I_8^{2-}, bonds were examined that have been termed secondary in the present study; the bond orders were 0.60 for the I---I–Cl interaction and 0.39 for the I---I–I interaction. This indicates very strongly that the secondary bond model can account satisfactorily for the observed interactions.

These two polyhalogen secondary bonds, although weak, are part of a continuous range of bond strength (Fig. 36), and to distinguish them as secondary might seem unnecessary. In principle, this is true, but in practice in most systems the possible continuous range of bond lengths has not been observed. The bonding is usually very asymmetric, and it is then valuable to distinguish the longer one as *secondary*, while recognizing that the bonding is of the same type in both the primary and secondary bond, apart from a possibly greater electrostatic component in the latter. The alternative in the past has been to ignore or discard the secondary bond, rather than, ideally, to treat it as equivalent to the primary one.

The predominance of asymmetric systems points to a problem that cannot yet be resolved. Above, the primary geometry was explained by electron pair repulsion, and in this model the electrons are in hybrid orbitals which include *d* orbitals. The asymmetry then appears as a consequence of the lone pairs. From the model of Wiebenga and Kracht, the lone pairs are in *s* or *p* orbitals directed at right angles to the molecular plane (if there is one). It is not clear whether asymmetry can arise naturally in this case, as calculations of geometries with minimum energy were not made. With I_3^-, the immediate cause of asymmetry seems to be an asymmetric crystal environment (*154*), and the same may be true of other systems. This makes it quite likely that *d* orbitals are not necessary for asymmetry; their contribution may only be in second-order effects, e.g., partial multiple bonding in I–O bonds of iodates. The trans effects proposed by Foss (*73*) can produce long bonds and asymmetric systems, but only when the atoms X and Y in the Y–A - - - X group are not the same.

The way to further understanding of secondary bonds may well be through calculations like those of Wiebenga and Kracht on more general systems, which might establish bond orders and polarities. Examination of electronic spectra might also give useful information.

Some much more detailed calculations have been made (*95*) on the interactions in solid halogens, which demonstrate the importance of charge-transfer interactions in these systems.

F. SIGNIFICANCE

The facts collected in this chapter are clearly very much at variance with bonding models that allow only single bonds at standard bond distances and interactions at van der Waals distances. In reality, in some types of compounds, secondary bonds occur in virtually every example examined, and the understanding of these compounds must be incomplete if secondary bonding is ignored. Its more general importance is as part of a continuum of bonding types, of particular importance in bridging the gap between covalent and metallic bonding. By including secondary bonding, we can go one stage further in bringing the whole range of chemical interaction into one conceptual group, where the nature of the bonding is controlled by the electronegativity of the participating atoms. This can be illustrated for bridging interactions –B–A–B– in Fig. 37.

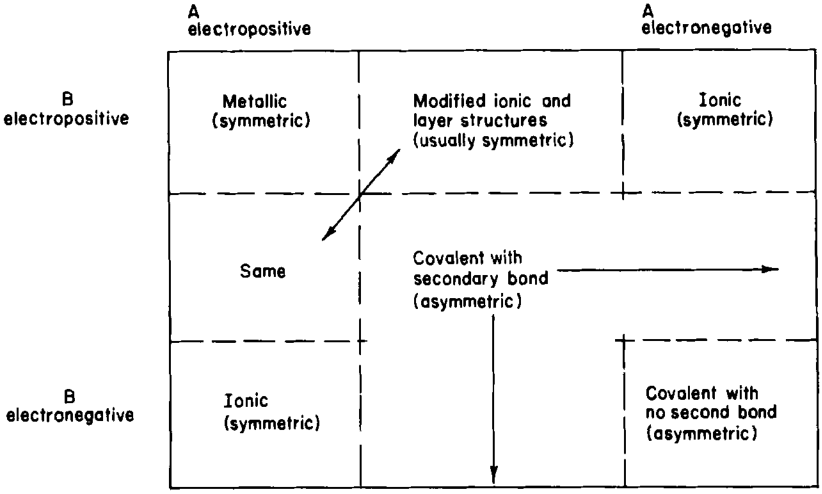

FIG. 37. The variation of bond type with electronegativity in a system B–A–B.

IX. Appendix

The following further structure determinations have been published up to the end of May 1972. Their results have not been incorporated into Tables II–V. The bond lengths are almost always accurate to better than 0.04 Å.

A. GROUP VII

An important discovery is that some 15 steroid molecules whose structures were determined as bromine derivatives have linear interactions C–Br---O and these appear to dominate the molecular packing. The Br---O distances are in the range 2.9–3.2 Å (*129a*). A chlorine oxygen interaction occurs in $POCl_3$. Its crystals are isomorphous with those of $POBr_3$ and contain a P–Cl---O grouping with P–Cl of 1.97 Å, Cl---O of 3.05 Å, and the angle at Cl of 165° (*127a*). The structure of $POBr_3$ has been refined in an alternative space group without significant change in the atomic positions (*145a*). In $BrF_4{}^+Sb_2F_{11}{}^-$ the bromine is surrounded by a distorted octahedron of fluorine atoms with four at 1.81 Å (avg.) and two (cis) at 2.24 and 2.49 Å. The F–Br---F angles are 168° and 175° (*118a*).

Four further iodate structures have been reported. In $Ca(IO_3)_2 \cdot 6H_2O$ the iodine has the usual distorted octahedral coordination (*25a*) while in $Sr(IO_3)_2 \cdot H_2O$, there are two linear O–I---O interactions but instead of a third I---O, there are two oxygen atoms at 3.2 Å (*126b*). In $KIO_3 \cdot HIO_3$ there are four independent iodine atoms. All have distorted octahedral environments but one has an extra iodine oxygen contact through the center of the widest face, between the three I---O interactions (*42b*). In $KIO_3 \cdot HIO_3 \cdot KCl$, there are I---Cl as well as I---O interactions. The octahedron around one iodine atom contains two unusually short I---O distances, 2.59 and 2.47 Å and one I---Cl of 3.03 Å. The octahedron of the second iodine has one I---O of 2.61 Å, one I---Cl of 3.07 Å and one vacant position (*25b*).

B. GROUP VI

The most important information is that a number of selenites and tellurites have distorted octahedra around Se or Te as would be expected by comparison with iodates. In $LiH_3(SeO_3)_2$, the three Se---O interactions range from 2.80 to 3.29 Å while the bonded Se–O vary between 1.65 and 1.77 Å (*126e*). The same coordination is reported for $NaD_3(SeO_3)_2$ (*126d*) and $NaH_3(SeO_3)_2$ (*108a*) while in $KH_3(SeO_3)_2$ two of the Se---O interactions are relatively short (3.00 Å, 3.22 Å) but the third (3.45 Å) is close to the van der Waals distance of 3.42 Å (*85a*). In $BaTeO_3 \cdot H_2O$, the Te–O distance is 1.85 Å, there are two linear O–Te---O interactions of 3.03 and 3.33 Å and one position of the octahedron is vacant (*126f*). The structure of H_2SeO_3 has been refined by neutron diffraction (*114b*) confirming the previous results. It is worth noting that although it has the same space group ($P2_12_12_1$) and similar cell dimensions to HIO_3, the two compounds are not isomorphous, unlike HIO_3 and XeO_3.

The short intramolecular S---S and S---O distances in thiothiophthenes and desaurins are reviewed (*121a*). Both Cl---S–S---Cl and Cl---S–C interactions (with Cl---S of 3.23 Å and 3.19 Å respectively) occur in 4-phenyl-1,2-dithiolium chloride monohydrate (*84a*) and there are similar interactions in the corresponding bromide (*100a*) and iodide (*100b*). The structure of thiuret hydriodide has been refined (*130a*) and the same paper discusses a number of other compounds containing S–S---Hal interactions.

In $TeCl_3^+AlCl_4^-$, the tellurium atom has 3 short Te–Cl bonds, 2.28 Å and 3 long ones, 3.06 Å in a distorted octahedron (*36b*), very similar to that in $TeCl_4$, whose structure determination has been published in detail (*36a*). In the compound $ClC_2H_4TeCl_3$, bridging chlorine atoms link the molecules into infinite chains. The tellurium has octahedral coordination with one vacant position, and in the Cl–Te---Cl groups, Cl–Te is 2.39 Å, Te---Cl is 2.72 Å (*113a*).

In $Te(CH_3)_2I_2$, each of the three independent tellurium atoms has a distorted octahedral environment with two Te–C of 2.10–2.16 Å, two short Te–I of 2.85–2.99 Å and two C–Te---I interactions with Te---I of 3.65–4.03 Å (*42c*).

C. GROUP V

The structures of two further adducts of $SbCl_3$ have been determined. In $SbCl_3 \cdot 2C_6H_5NH_2$, the antimony atom is in an octahedron with one position vacant. It forms two long interactions with nitrogen atoms of aniline molecules with Sb---N of 2.64 Å. The bond angle Cl–Sb---N is 166° and this Sb–Cl is 2.50 Å, substantially longer than the apical Sb–Cl, 2.36 Å (*101a*). A complex with phenanthrene, $C_{14}H_{10} \cdot 2SbCl_3$, is similar to the corresponding naphthalene complex (*52b*). In KSb_2F_7, SbF_3 and SbF_4^- units are linked into infinite chains by long interactions. The antimony atom in the SbF_4^- ion remains four-coordinate but the other one has distorted octahedral coordination with three short Sb–F, 1.92–1.96 Å, two long Sb---F, 2.41 Å and 2.57 Å and one vacant position (*126c*). In $BiCl_3$, which might be expected to show directed interactions, the bismuth has three near chlorines (2.46–2.52 Å) forming a pyramidal $BiCl_3$ group and five at 3.22–3.45 Å giving in all a bicapped trigonal prism (*126g*). Although two Cl–Bi---Cl groups are approximately linear (155°) it is clearly not valid to label these as directed to the exclusion of the others. If the bonding of the five chlorines is partly covalent, as a comparison with the van der Waals distance (3.90 Å) would suggest, then it must be of a more complex type than for most of the compounds described here. There is some support for this from a comparison (*126g*) with two molecules probably isomorphous with $BiCl_3$: $SbCl_3$ and β-$SbBr_3$. In these and in α-$SbBr_3$, the same bicapped trigonal prismatic coordination occurs and it is very significant that the Sb---Cl interaction (3.63 Å, avg.) is longer than the Bi---Cl interaction (3.31 Å, avg.).

In α-Bi_2O_3, one bismuth atom has distorted octahedral coordination with three short Bi–O, 2.14–2.29 Å and three longer, 2.48–2.80 Å; the second bismuth atom has three short, 2.08–2.21 Å, and two longer distances, 2.54, 2.63 Å, and the shortest Bi–O is opposite the vacant position (*126a*). Similar octahedra with one vacant position occur in the oxides $Bi_{12}GeO_{20}$ (*1*) and $Bi_2Ti_4O_{11}$ (*107a*) while a complete octahedron is found in bismuth formate (*142a*) with Bi–O, 2.34 Å and Bi---O, 2.50 Å.

D. GROUP IV

In trimethyl tin isothiocyanate, $(CH_3)_3SnNCS$, there is an Sn---S interaction, 3.13 Å, which links the molecules into chains; at the same time the C–Sn–C angle increases to 119° (avg.) and N–Sn–C is 95° (avg.), i.e., the molecule is close to a trigonal bipyramid (*72*).

E. CYANIDES

Further examples of halogen–cyanide interactions have been found: Cl---N of 3.22 Å in 2,4,6-trichlorobenzonitrile, Br---N of 3.06 Å in the corresponding bromo compound (*42a*) and Br---N of 3.03 Å in bromotricyanomethane (*154a*). Interestingly, chlorotricyanomethane forms no interactions (*154a*). In the two salts $K(SeCN)_3 \cdot \frac{1}{2}H_2O$ (*87b*) and $Rb(SeCN)_3 \cdot \frac{1}{2}H_2O$ (*87a*), Se---N interactions occur of length 3.47–3.60 Å, which provide square planar environments around each selenium with either three short and one long bond (central Se) or two short, one long bond and one vacant position (terminal Se). The whole series of group IV cyanides, $(CH_3)_2M(CN)_2$, M = Si–Pb, has been examined. With M = Si and Ge, there are weak interactions, N---Si, 3.48 Å, N---Ge, 3.28 Å, and the molecules are somewhat distorted from tetrahedral, $H_3C–Si–CH_3$, 120°, $H_3C–Ge–CH_3$, 121°. There are also very weak interactions, N---Si, 3.97 Å and N---Ge, 3.84 Å, about 0.3 Å *longer* than the expected van der Waals distances but which are linear and which appear to be significant. With M = Sn, both interactions are of equal length, Sn---N, 2.48 Å and the molecules are closer to octahedral, $H_3C–Sn–CH_3$, 149°. The compound with M = Pb appears to be similar to this, but single crystals could not be obtained (*114a*).

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