Resonance of an unshared electron pair between two atoms connected by a single bond

(covalence intermediate between normal values/apparently tricovalent Sn and Ge/digermene/distannene)

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ABSTRACT   The reported structure of the dimer of a compound of bicovalent tin indicates that the tin-tin bond is of a new type. It can be described as involving resonance between two structures in which there is transfer of an electron pair from one tin atom to the other. The tin atoms are connected by a single covalent bond (each also forms two covalent bonds with carbon atoms), and an unshared electron pair resonates between the fourth sp^3 orbitals of the two atoms. Similar structures probably occur in digermene and distannene.

The usual values of the oxidation number of tin are +2 and +4, and in its covalent compounds tin usually forms either two or four covalent bonds. A structure of a compound of tin containing two tin atoms has been reported in which each tin atom seems to be forming three single covalent bonds with other atoms (the other tin atom and two carbon atoms) (1), and a recently reported quantum mechanical study (2) indicates that digermene, Ge_2H_4, and distannene, Sn_2H_4, have nonplanar structures rather than the double-bonded planar structure of ethylene, C_2H_4.

The gas-molecule electron-diffraction investigation (2) of bis(bistrimethylsilylmethyl)tin(II), $\{(CH_3)_3Si\}_2HCSnCH\{Si-(CH_3)_3\}_2$, has shown the tin atom to form two single bonds (length 224 pm) to the adjacent carbon atoms, with bond angle 96°. This is the structure expected for bicovalent tin: two of its four outer electrons constitute an unshared electron pair occupying an orbital with mainly s character, and the two bond orbitals have mainly p character, with the expected value (3) of the bond angle between 94° and 100°.

It might be expected that in the solid state the molecules of this substance would either retain their structure or form dimers with a tin-tin double bond and planar $C_2Sn = SnC_2$ structure. The crystal structure study (1) showed, however, that the C_2SnSnC_2 group is not planar; instead, it is pyramidal about each Sn atom, with angles CSnC = 112° and CSnSn = 115°. Moreover, the observed value, 276.4 pm, of the tin-tin bond length is far greater than the double-bond value (3), 260 pm, and only a small amount smaller than the single-bond value, 280 pm. It is accordingly certain that the bonds formed by the tin atoms are not those formed by either bicovalent or quadricovalent tin.

A rather similar molecule is known in which the C_2SnM group is planar and the metal-metal bond has the expected value. In the crystal $[\{(CH_3)_3Si\}_2HC]_2SnCr(CO)_5$, the atoms (4) $C_2SnCr-(CO)_2$ lie in one plane and the tin–chromium distance, 256.2 pm, is close to the value 255 pm calculated (3, 5) from the single-bond radii 140 pm for tin and 126 pm for chromium, with the bond number $n = 1.5$ corresponding to equal resonance among the six ligands of the chromium atom.

Table 1. Comparison of enthalpy of sublimation and promotion energy (kJ/mol) of group IV elements

Element	Enthalpy of sublimation	Promotion energy to first non s^2p^2 configuration	Ratio
C	719	403	1.78
Si	368	475	0.77
Ge	328	448	0.73
Sn	301	414	0.73
Pb	197	418	0.47

The normal valences of the group IV elements

The normal configuration of isolated atoms of C, Si, Ge, Sn, and Pb is ns^2np^2, $n = 2$–6, with Russell–Saunders states ^3P, ^1D, and ^1S. For this configuration bicovalence is expected, with the neutral atom having an unshared electron pair, ns^2, and using its two other electrons and two np orbitals for covalent bond formation. The excited configuration $ns\,np^3$ (states ^5S, ^3D, ^3P, ^3S, ^1D, and ^1P) would permit quadricovalence, with the bond orbitals being the four tetrahedrally directed sp^3 hybrid bond orbitals. If the promotion energy of an electron from the ns orbital to the np orbital is much greater than the energy of the two additional bonds, the element retains the normal configuration and is bicovalent, and if it is smaller, the element is quadricovalent.

A comparison of energy quantities is made in Table 1. The $sp^3 - s^2p^2$ difference in energy for the configurations could be obtained by averaging the energy of all the spectroscopic states based on each configuration, but in fact many of the states have not been observed. Moreover, it is known (6) that the quadricovalent state is not based on sp^3 alone, but has a considerable s^2p^2 component, so that the required promotion energy is less than the value calculated from the atomic energy levels. The lowest state based on $ns\,np^3$, the ^5S state, lies 403 kJ/mol above the ground state for C and 474 kJ/mol for Sn; it has not been observed for the others. Another rough measure of promotion energy is given in the third column of Table 1—the excitation energy from the normal state to the first excited state not based on the configuration ns^2np^2. The second column gives the enthalpy of sublimation, and the fourth column gives the ratio of these values to the corresponding values of the promotion energy. High values of this ratio should lead to quadricovalence and low values to bicovalence. This agrees with the observed chemical properties: C and Si form overwhelmingly quadricovalent compounds, Pb forms mainly bicovalent compounds, and Ge and Sn form compounds of both kinds. Also, the stable forms of elemental C, Si, and Ge are the nonmetallic quadricovalent diamond-type structures, and those of Sn and Pb are metallic structures based mainly on bivalence. At low temperatures Sn changes to the quadricovalent structure.

The resonating unshared electron pair

For the elements Ge and Sn, an intermediate structure can be assumed in molecules with a cluster of two atoms of these ele-

ments, in which an electron is transferred from one atom to the other and only one of the two atoms has an electron promoted out of the ns^2 unshared pair; the negatively charged atom has the configuration ns^2np^3, with an unshared ns^2 pair and three other electrons (in essentially p orbitals) forming three covalent bonds, and the positively charged atom has the configuration $ns\,np^2$, with three electrons in three sp^2 hybrid orbitals forming three covalent bonds and with one unoccupied orbital. The central group in the dimer of bis(bistrimethylsilylmethyl)tin would then resonate between the two structures
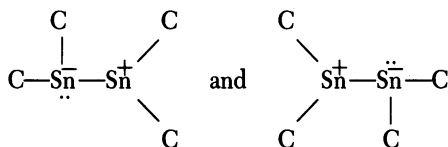
with a small contribution of the less stable intermediate structure that has an unpaired electron on each atom. The electron pair can be described as resonating between the positions on the two Sn atoms, with the resonance favored by the fact that the orbital that becomes occupied does not have to be vacated but was empty, available for occupancy. This vacant orbital is analogous to the metallic orbital in metals in permitting an increase in the resonance frequency and hence in the resonance energy.

The tin-tin bond in this compound is accordingly between a single bond and a double bond; it is a single bond plus a resonating-unshared-pair bond. The contribution made by the resonating unshared pair is expected to be somewhat less than that made by the three-electron bond in the superoxide ion and the nitric oxide molecule (7) (about 60% of that made by the single bond) because of the poorer overlap of the orbitals. An estimate of the contribution can be made by consideration of the observed tin-tin distance in the compound. This distance, 276.4 pm, is 3.6 pm less than the single-bond value, 280 pm, and this shortening corresponds (3) to bond number 1.12; that is, the unshared-electron-pair resonance corresponds to about 12% of a single bond and stabilizes the molecule by about 12% of the single-bond energy.

It is not unreasonable that a pair of Sn atoms should sometimes assume this intermediate structure between bicovalence and quadricovalence, with promotion of only one electron out of $5s^2$ (in this case from one atom to $5p$ of the other atom). For these atoms a double bond is less stable than two single bonds, mainly because of the strain of bending the two single bonds that constitute the double bond. Formation of an extra single bond in some molecules may provide enough energy to permit promotion of one electron, whereas the formation of the second bond of the double bond, with its smaller contribution to the stability of the molecule, might not be able to permit promotion of a second electron. The resonance energy of the unshared pair might compensate for the separation of electric charge in the proposed structure.

With the proposed structure, the CSnSn bond angle is expected to be midway between the value for Sn with an unshared pair (96° for p bonds with a little s character) and that for Sn without the unshared pair (120° for sp^2 bonds). The observed value, 115°, is 7° larger than the value expected by this simple argument.

The discussion of bond energy and promotion energy and of the usual valences indicates that structures involving a single bond and a resonating unshared electron pair might be formed in other compounds containing two atoms of either Ge or Sn. An interesting quantum mechanical calculation of molecules M_2H_4 with M = C, Si, or Ge has been made by Fjeldberg *et al.* (2). Their calculation of the energy of the molecule as a function of the fold

angle α between the M—M bond and the MH_2 plane of each monomer unit shows this function for ethylene to be essentially a parabola with minimum at $\alpha = 0°$, as expected for a double bond between the carbon atoms. For disilene the curve is U-shaped with a rather flat bottom, suggesting interaction with a structure favoring larger angles of α, and for digermene the curve has a maximum at $\alpha = 0°$ and minima at $\alpha = \pm 40°$, indicating a structure approaching the intermediate structure with a single bond plus a resonating unshared electron pair, which corresponds to about 55° for α. It is likely that other compounds $(R_2Ge)_2$ and $(R_2Sn)_2$ with this intermediate structure will be found, and also compounds $(RGa)_2$, $(RIn)_2$, and $(RTl)_2$.

Comparison with other bonds

In the R_2Sn dimer the covalence of Sn(II) is increased from 2 to 3 by the transfer of an electron from one Sn atom to the other. Other substances are known in which a single Sn(II) atom becomes tricovalent on adding an electron. An example (7) is Cs-$SnCl_3$. In this crystal an electron is transferred from Cs to Sn, which becomes Sn^- with electron configuration $5s^25p^3$. Three Sn—Cl bonds are formed with length 2.52 Å, a little larger than the single-bond value 2.39 Å. (Three weak bonds, length about 3.4 Å, are formed to other Cl atoms.) The ClSnCl bond angles are near 90°.

The resonance of the unshared electron pair in the R_2Sn dimer is associated with a decrease in the bond length below the Sn—Sn single-bond value, corresponding to an increase to the value 1.12 for the bond number. This indicates that the overlap of the two unshared-pair orbitals is only about one-fifth as great as for the bond orbitals. Resonance of an unshared pair between two orbitals should give the same increase in bond number as resonance of a single electron (the one-electron bond) or resonance of an odd electron and an electron pair (the three-electron bond), each of which corresponds to about 60% of a single covalent bond.

In the R_2Sn dimer there is an orbital for the unshared electron pair on each of the two Sn atoms; that is, there is an empty orbital on Sn^+ available for occupancy by the electron pair resonating from Sn^-. This empty orbital may be compared with the "metallic orbital" on the M^0 and M^+ atoms in a metal, which give the metal its characteristic properties (8). Thus, the Sn_2 group in the R_2Sn dimer may be considered to be a true metallic fragment, whereas the Sn_2 group in distannane, H_3Sn—SnH_3, is not.

The structures with a single bond plus a resonating unshared electron pair may also occur for a group IV element when two atoms are held by their other four single bonds to the other atoms in a molecule or crystal in such positions that a single bond can be formed, but an unstrained double bond, with its requirement of planarity, cannot.

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