filtrate was concentrated under reduced pressure to yield a crop of light yellow crystals. The yield of dried product was 6.8 g. or about 44% based on mustard gas. Sublimation of the product yielded a white solid, m.p. 107.0–107.5°.

Anal. Calcd. for C_4H_8SSe: C, 28.74; H, 4.82; S, 19.18. Found: C, 28.56; H, 4.96; S, 19.35.

The sublimation left a yellow residue (10–15% of total yield) which is presumably a polymeric material and/or polyselenide which would account for the yellow color of the crude product.

X-Ray Diffraction.—Small, single crystals of I suitable for X-ray diffraction studies were obtained by slow evaporation of solutions in methanol. Selected crystals were sealed in thin-walled capillaries to prevent vaporization. Zero and upper level Weissenberg photographs about the *b* or prism axis were prepared by use of copper radiation. Precession photographs of the *hk*0 and 0*kl* nets were also prepared. These photographs strongly suggested isomorphism of I with 1,4-diselenane[6] and with 1,4-dithiane.[7] Measurement of the films gave the unit cell dimensions shown in Table I.

TABLE I

CRYSTALLOGRAPHIC AND PHYSICAL DATA ON THE ISOMORPHOUS SERIES: 1,4-DITHIANE, 1,4-SELENOTHIANE, AND 1,4-DISELENANE

	$C_4H_8S_2$	C_4H_8SSe	$C_4H_8Se_2$
a, Å.	6.763 ± 0.002	6.867 ± 0.006	6.97 ± 0.02
b, Å.	5.464 ± 0.005	5.552 ± 0.010	5.62 ± 0.02
c, Å.	7.844 ± 0.003	7.956 ± 0.006	8.01 ± 0.02
β, deg.	92.67 ± 0.04	93.13 ± 0.10	93.6 ± 0.1
Vol. of unit cell, Å.^{3}	289.7	302.9	313
d, g. cm.$^{-3}$	1.377	1.832	2.27
M.p., °C.	112	107.0–107.5	113.0–113.5

Discussion

Crystallographic and physical data on the isomorphous series 1,4-dithiane, 1,4-selenothiane, and 1,4-diselenane are listed for ready comparison in Table I. Gibson and Johnson[1] noted that the melting point of I is not depressed by addition of 1,4-dithiane and concluded that solid solutions are formed. This conclusion is in keeping with the results of the X-ray studies.

The presence of two molecules of I per unit cell in the space group $P2_1/n$ requires that the molecules be centrosymmetric. This requirement can be satisfied only by a random disorder in which the crystallization process fails to differentiate between the S and Se ends of the molecules. This disorder would not only obscure the true positions of sulfur and selenium, but also those of the carbon atoms, since the C–S and C–Se distances are different. For this reason a detailed structural study of I by X-ray diffraction appears to have little merit.

Acknowledgments.—The authors wish to thank the National Science Foundation for financial assistance (Grant No. NSF-G 12884), Heather King for the chemical analysis, and Hanelore Maddox for preparing and measuring one of the Weissenberg photographs.

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(6) R. E. Marsh and J. D. McCullough, *J. Am. Chem. Soc.*, **73**, 1106 (1951).

(7) R. E. Marsh, *Acta Cryst.*, **8**, 91 (1955).

Correspondence

Partial Charge and Bonding Energy

Sir:

Bond energy (*H*) may reasonably be expected to be greater the more polar the bond, the higher its order (*n*), and the shorter the bond length (*R*). This expectation is realized in many binary halides and calcides. When the partial charge on halogen, δ_X, is plotted graphically *vs.* RH/n, a straight line connecting the free halogen X_2 with the salt NaX is found to include most of the binary halides. This is true of chlorides, bromides, and iodides. A linear relationship holds also for fluorides but F_2 with its unusually low bond energy understandably lies off the line. Results for chlorides are shown in Fig. 1; those for the other halides are closely similar. The equations for these relationships are of the form

$$\delta_X = A\frac{RH}{n} + B \qquad (1)$$

When δ_X is expressed as fraction of electronic charge *e*, *H* as kcal., and *R* in a.u., then *A*, of dimension $1/e$, and *B*, of dimension *e*, are constants having the following values: fluorides −0.00130, 0.066; chlorides −0.00114, 0.065; bromides −0.00111, 0.068; and iodides −0.00105, 0.071.

The partial charge is calculated[1] from the principle of electronegativity equalization[2] supplemented by two assumptions. The principle of electronegativity equalization may be stated: *When two or more atoms initially different in electronegativity form a compound, their electronegativities change to the same intermediate value in the compound.* This intermediate value is taken to be the geometric mean of the electronegativities of all the component atoms before compound formation. The reduction in electronegativity of the initially more electronegative element, in a binary compound, results from its acquisition of a partial negative charge through uneven sharing of the valence electrons. Similarly, the initially less electronegative element becomes more electronegative through its retention of less than a half share of the valence electrons and thus in effect by its acquisition of a partial positive charge. To estimate these partial charges quantitatively it is necessary to assume (1) that electronegativity varies linearly with partial charge, and (2) that a particular bond has a fixed and known ionicity. The first assumption is reasonable in view of what is known of the relationship between ionization energies and electronegativities of cations.[3] The second assumption must, in

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(1) R. T. Sanderson, "Chemical Periodicity," Reinhold Publishing Corp., New York, N. Y., 1960, p. 42.

(2) R. T. Sanderson, *Science*, **114**, 670 (1951).

(3) Reference 1, p. 40.

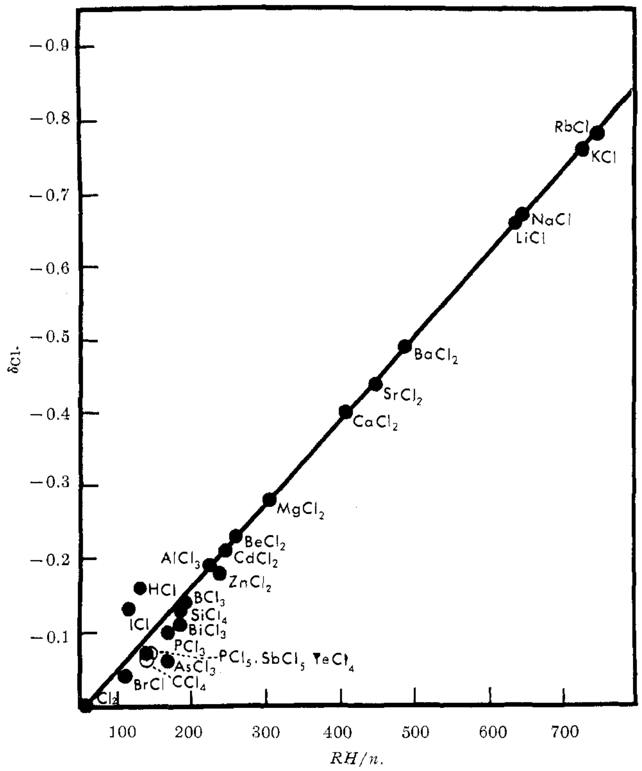

Figure 1.

the absence of conclusive evidence about the exact polarity of any bond, be arbitrary. An isolated molecule of NaF is taken to be 75% ionic.[3] The electronegativity of NaF is calculated as the geometric mean of the electronegativity of Na, 0.70, and F, 5.75 (Sanderson scale[4]), which is 2.01. Acquisition of an electronic charge of −0.75 (electron) has reduced the electronegativity of fluorine by 5.75 − 2.01 = 3.74. If the fluorine had acquired the electron completely, the change in electronegativity would have been 3.74/0.75 = 4.99. In a similar manner it is determined that complete loss of one electron would have increased the electronegativity of sodium by 1.74.

The partial charge of a combined atom is defined as the ratio of the change in electronegativity that occurred when the atom combined to the change that would have occurred had an electron been transferred completely (with appropriate sign to indicate whether the electronegativity increased (positive) or decreased (negative)). For example, to determine the partial charge on fluorine in some other compound, one determines the electronegativity of this compound and from it the change in electronegativity undergone by fluorine. This change, divided by 4.99 and assigned a minus sign, is taken as the partial charge on fluorine in that compound. If this is a binary fluoride, the partial charge on the other element is easily determined from that of fluorine, since the sum over the compound must be zero. Dividing this charge into the change in electronegativity undergone by the other element in forming the fluoride gives the change in electronegativity that would correspond to unit charge for that element. In this way a table of electronegativity changes corresponding to acquisition of unit charge has been computed for all elements for which reliable electronegativity values are known.[5] Partial charges on halogens, oxygen, and sulfur used in this work were calculated as just described, using the following revised electronegativity values: (the first number given is on the scale used for the calculations; the second number is the equivalent value on the Pauling scale[6]) K, 0.41–0.74; Rb, 0.33–0.70; Cs, 0.29–0.69; Be, 2.39–1.61; Mg, 1.99–1.42; Sr, 1.00–0.96; Ba, 0.78–0.93; and Al, 2.25–1.54.

The *H* values of eq. 1 are the standard heats of atomization, in kilocalories per equivalent weight, of the compounds at 25°. These were computed from standard heats of formation[7] of the compounds and standard heats of formation of the elements as monatomic gases at 25°. They represent the *total* bonding energy per equivalent. In gases this is conventional bonding energy but in liquids and solids it also includes all other cohesive forces.

The internuclear distance *R*, measured in Ångstrom units, was obtained mainly from familiar compilations[8,9] and, especially in solids, is not always known with certainty. Where the bond lengths in a solid are unequal, the shortest reported distance was used. In several instances the sum of ionic radii was used if a measurement was unavailable and the value appeared consistent with reported values for similar compounds.

To determine the bond order in a crystal of a binary compound it is necessary to recognize that *all* the outermost shell electrons of both kinds of atoms must be regarded as bonding electrons. In sodium chloride, for example, there are not just two but eight electrons of each pair of atoms directly involved in the bonding (as will be discussed below). Each atom forms six bonds with only eight electrons instead of twelve, so the bond order is taken as 8/12 or 0.67. (It is interesting to note that CsCl, CsBr, and CsI with bond order 0.5 for 8:8 coordination do not fit eq. 1, but with bond order 0.67 for 6:6 coordination and bond energy corrected accordingly,[9] they do.)

Equation 1 is, of course, limited as a means of calculating the total bonding energy by any uncertainties in evaluating partial charge, bond length, or bond order. Assuming that the bond order can be correctly assigned, that the bond length is exact in the alkali halides but within ±0.02 Å. elsewhere, and that the partial charge is correct to the nearest 0.02 electron, one can calculate total bonding energies within reasonable limits of

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(4) Reference 1, p. 31.

(5) Reference 1, p. 43.

(6) R. T. Sanderson, *J. Chem. Phys.*, **23**, 2567 (1955).

(7) Circular 500, National Bureau of Standards, 1952; JANAF Interim Thermochemical Tables, Dow Chemical Co., Midland, Mich., 1960.

(8) A. F. Wells, "Structural Inorganic Chemistry," 3rd Ed., Oxford University Press, 1962; L. E. Sutton, "Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958; R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1948, 1960; "Structure Reports," International Union of Crystallography, Oosthoek, Utrecht, 1928, 1959.

(9) L. Pauling, "Nature of the Chemical Bond," 3rd Ed., Cornell Univrsity Press, Ithaca, N. Y., 1960.

accuracy for 71% of all binary halides (68 of 96) for which necessary data are available. Some representative examples are given in Table I.

TABLE I

REPRESENTATIVE CALCULATIONS OF TOTAL BONDING ENERGY

Compd.	δ_X	R, Å.	n	H (calcd.)	H (lit.)
LiF	−0.74	2.01	0.67	206 ± 4	202
NaCl	−0.67	2.81	0.67	153 ± 4	153
$CaCl_2$	−0.40	2.80	1.00	145 ± 8	145
KBr	−0.72	3.29	0.67	144 ± 3	142
RbI	−0.66	3.66	0.67	127 ± 3	124
BaI_2	−0.39	3.51	1.00	125 ± 6	118
CdF_2	−0.27	2.34	1.00	110 ± 8	115
BCl_3	−0.14	1.76	1.00	102 ± 8	109
CF_4	−0.09	1.32	1.00	91 ± 14	103
$AlBr_3$	−0.16	2.30	1.00	89 ± 9	94
$ZnCl_2$	−0.18	2.52	1.00	85 ± 8	94
$SiCl_4$	−0.13	2.01	1.00	85 ± 10	93
MgI_2	−0.17	2.81	1.00	82 ± 7	86
SiI_4	−0.07	2.43	1.00	55 ± 9	59

It is interesting, and perhaps quite significant, to observe (as in Fig. 1) that most of the deviations from eq. 1 are in compounds of low bond polarity (usually molecular compounds) and in the direction of larger than expected RH/n values. This fact suggests that the bonds in these compounds may actually involve a greater number of electrons than indicated by normal covalence, enough to increase the bond order beyond the assigned value. In highly condensed solids the bond order is expected to be the maximum fixed by the coordination numbers and the number of available electrons, whereas in these molecular compounds outer d-orbitals on the other element may attract otherwise unshared electrons of the halogen to impart at least slight multiplicity to otherwise single covalent bonds. In other words, it seems possible that a more correct evaluation of bond order could bring most of the remaining halides into agreement with eq. 1, although it is perhaps more likely that other factors determine this deviation. The relationships among oxides and sulfides, as shown for oxides in Fig. 2, are obviously more complex. They suggest strongly that although bond strengths in these compounds do appear to be related to polarity, length, and order, certain other factors that could be neglected in the halides cannot be neglected here.

Equation 1 warrants more careful consideration to see whether a more detailed interpretation is possible. Except for fluorine, whose low dissociation energy appears to reflect intershell repulsions observable mainly in certain period 2 elements, the diatomic halogens fit this relationship, as the limiting case where the bond polarity is zero. At this point, $ARH/n = -B$. In the halogens, n is 1, $R = 2r$, where r is the covalent radius of X, and $H = D/2$, where D is the energy of atomization of X_2. Then $B = -ArD$. Substituting this in eq. 1 and solving for H gives

$$H = n\delta_X/AR + nDr/R \qquad (2)$$

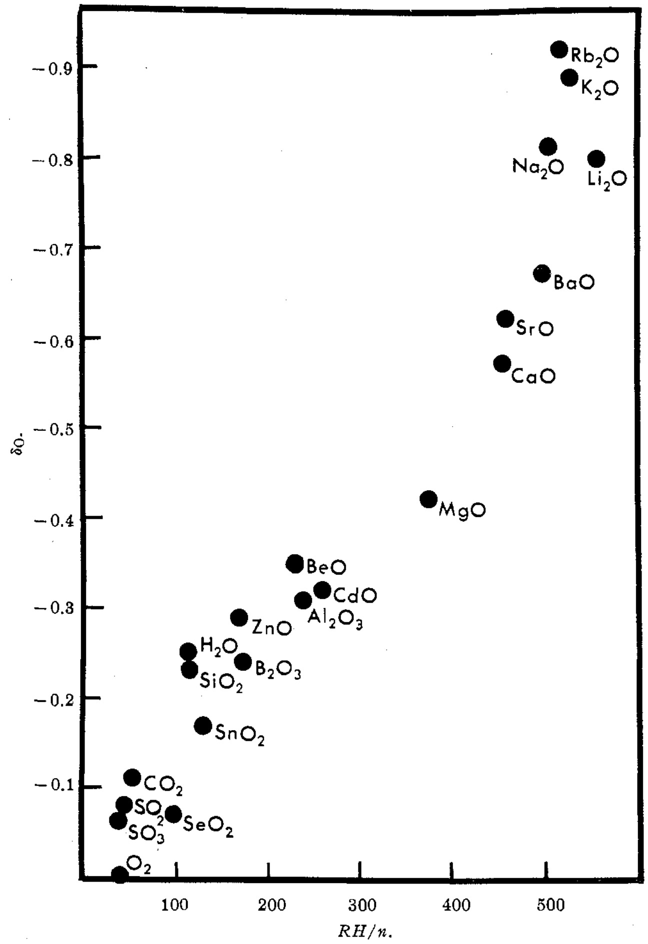

Figure 2.

The second term is in units of energy (kcal.) since the units of r and R cancel. In the first term, since δ_X is given as a fraction of the electronic charge it must be multiplied by $330e$ (the e arising from the dimension $1/e$ of A) to convert this term to energy units (kcal./equiv.). This necessitates a change in constant A to $\alpha = 330A$. The final general equation for halides (except fluorides) is then

$$H = n\left[\frac{330e\delta_X}{\alpha R} + \frac{rD}{R}\right] \qquad (3)$$

For $MgCl_2$, for example, $n = 1$, $R = 2.46$, $\delta_X = -0.28$, $e = -1.00$, $\alpha = 0.376$, $r = 0.99$, and $D = 57.2$. From these, H is calculated to be 123 kcal., the same as determined from thermodynamic data.

H/n, the equivalent total bonding energy per pair of valence electrons, is seen from eq. 3 to be the sum of two terms, $330e\delta_X/\alpha R$ and rD/R. The latter seems to be the atomization energy per equivalent ($D/2$) in the X_2 molecule adjusted for the reduction of energy with increasing bond length by multiplying by the factor $2r/R$. The former has the form of a coulombic energy (ee'/R) modified by a factor, $1/\alpha$ (= about 2.7). It is hoped that future studies will reveal whether this analysis is valid and, if so, what the significance of this factor is.

Especially interesting in this study is the suggestion of a unified theory of bonding that is evident when typically "covalent" and typically "ionic" compounds come so close to fitting the same simple relationship involving bond strength. One of the most uncertain aspects of the estimation of partial charge using the concept of electronegativity equalization has always been the arbitrary nature of the choice of 75% ionicity for an isolated molecule of NaF. Although this value has seemed reasonable in the light of measured dipole moments of diatomic molecules, which agree as well as might be expected with values calculated from partial charge,[10] and although its absolute accuracy is unimportant in the majority of applications where *relative* charge values permit all manner of useful comparisons, insights, and interpretations,[11] nevertheless it results in partial charges for atoms in "ionic" compounds that are far removed from the ionic charges that, even though polarization effects are considered, are implicit in accepted theory. For example, the partial charge estimated for chlorine in $MgCl_2$ is -0.28 instead of -1.00; in CaO the partial charge on oxygen is -0.57 instead of -2.00. What is the significance of this discrepancy?

Some light is directed on this question by recognition of the fundamental qualities of ions with respect to electron donor–acceptor interaction. For a cation certainly has the requisites of an electron acceptor, and a simple anion always has an outer shell of electron pairs readily available for sharing because of the high negative charge on the atom. Donor–acceptor interaction therefore seems inevitable when cations and anions are in such close contact as they are in a crystal. The extent to which such interaction exists may be related to the partial charges. Consistent with this view are the facts that (1) a negatively charged atom improves as donor as it becomes more negative,[12] and (2) the coordination number of the negative atom in a crystal increases with higher negative charge. This relationship is illustrated by the data for fluorides in Table II. To account for the common coordination of six or eight atoms around one which has only four outermost orbitals, we need only to recognize the resonance principle[13] that greater stability results from a larger number of partial bonds, where possible, than from an equivalent number of two-electron bonds.

TABLE II

RELATION OF COORDINATION NUMBER OF FLUORINE TO ITS PARTIAL CHARGE

Compd.	δ_F	C.N.	Compd.	δ_F	C.N.
CsF	-0.89	6	CaF_2	-0.47	4
RbF	-0.88	6	MgF_2	-0.34	3
KF	-0.85	6	BeF_2	-0.29	2
NaF	-0.75	6	AlF_3	-0.24	2
LiF	-0.74	6	BF_3	-0.19	1
BaF_2	-0.56	4	SiF_4	-0.17	1
SrF_2	-0.51	4	CF_4	-0.09	1

DEPARTMENT OF CHEMISTRY
ARIZONA STATE UNIVERSITY
TEMPE, ARIZONA
R. T. SANDERSON

RECEIVED FEBRUARY 3, 1964

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(10) Reference 1, p. 45.

(11) R. T. Sanderson, "Chemical Periodicity," Reinhold Publishing Corp., New York, N. Y., 1960.

(12) Reference 1, pp. 56 *et seq.*, 105, 169, 228, 249.

(13) R. E. Rundle, *J. Chem. Phys.*, **17**, 671 (1949); R. T. Sanderson, *J. Chem. Educ.*, **38**, 382 (1961).

Metal Ion Induced Rearrangements

Sir:

The condensation of α-amino-β-thiols with dicarbonyl compounds does not lead to the Schiff bases which would be good tetradentate metal chelating agents, but instead results largely in the formation of thiazolidines (with β-mercaptoalkylamines) or benzothiazolines (with *o*-aminobenzenethiols).

Thompson and Busch[1] prepared tetradentate ligands in the form of nickel(II) chelates in high yields by the reaction of a mixture of 2-aminoethanethiol, α-diketone, and a nickel salt.

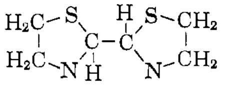
These authors assumed that the nickel ion influenced the condensation reaction by acting as a template, thus inhibiting the formation of thiazolidines. They did not consider the possible reaction of the thiazolidine with the metal ion to give the metal chelate. It has been reported, however, that 2,2′-bisbenzoxazolinyl rearranges in the presence of metal ions to give the corresponding Schiff base chelates.[2] It was therefore decided to determine whether bisthiazolinyls would undergo similar metal ion induced rearrangements.

For this purpose we have prepared the following three compounds, which are stable, white crystalline solids, by the condensation of glyoxal or diacetyl with 2-aminoethanethiol or *o*-aminobenzenethiol.

(I) 2,2′-Bisthiazolidinyl (m.p. 179–181° dec.). *Anal.* Calcd.: C, 40.87; H, 6.86; N, 15.89; S, 36.37. Found: C, 41.17; H, 6.38; N, 14.88; S, 38.72.

(II) 2,2′-Bisbenzthiazolinyl (decomposes above 160°). *Anal.* Calcd.: C, 61.71; H, 4.43; N, 10.29; S, 23.56. Found: C, 62.0; H, 4.0; N, 10.0; S, 22.7.

(III) 2,2′-Dimethyl-2,2′-bisbenzthiazolinyl (m.p. 149–150°). *Anal.* Calcd.: C, 63.96; H, 5.37; N, 9.33; S, 21.35. Found: C, 64.15; H, 5.37; N, 9.37; S, 21.39.



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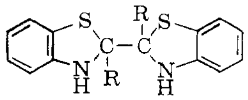

II, R = H
III, R = CH_3

Of these compounds, only II has been reported previously,[3] but this (brownish crystals, m.p. 283°) was probably the oxidation product, 2,2′-bisbenzthiazolyl.

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(1) M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.*, **84**, 1762 (1962).

(2) E. Bayer and G. Schenck, *Ber.*, **93**, 1184 (1960).

(3) M. Claasz, *ibid.*, **49**, 1141 (1916).