Electronegativity Order of Group IV Elements:
Evidence from Molecular Geometry

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Electronegativities, Group IV Elements

Electronegativities for Group IV elements A have been estimated from the bond lengths observed in AX_2 and AX_4 molecules (X = F, Cl, Br). The order of electronegativities established by this method is $\chi_C > \chi_{Ge} > \chi_{Sn} > \chi_{Si}$.

The molecular geometries of several dihalocarbene analogs AX_2 have been recently determined. The parameters are cited in Table I. It was thought to be of interest to estimate electronegativities for group IV elements from this newly available set of geometrical data. The utility of using geometrical data in estimating electronegativities was recently demonstrated for sulfone [9] and sulfonyl chloride [10] molecules. In particular, the group electronegativities of some RSO_2 groups have been estimated [10] from the S–Cl bond lengths of sulfonyl chlorides using the Schomaker-Stevenson equation [11] and parameters from Pauling [12] in addition to the experimentally determined S–Cl bond lengths [13].

In the present case an expression for the bond length suggested more recently by Robiette [14] and used successfully by Glidewell [15] and Hargittai [13] has been chosen,

$$r(\text{A–X}) = r_A + r_X - c|\chi_X - \chi_A|^2,$$

where r_A and r_X are covalent radii from Glidewell [15],

r_C	76.7 pm	r_F	70.9 pm
r_{Si}	116.9	r_{Cl}	99.4
r_{Ge}	120.2	r_{Br}	114.2
r_{Sn}	138.6		

χ_X are the halogen electronegativities from Pauling [12], viz. 4.0, 3.0, and 2.8 for fluorine, chlorine, and bromine, respectively, and $c = 7.3$ pm.

Using the A–X bond lengths from Table I, the following electronegativities were calculated (here averages of available results are given):

$$\chi_C\ 2.6,\quad \chi_{Si}\ 1.9,\quad \chi_{Ge}\ 2.5,\quad \chi_{Sn}\ 2.3.$$

The internal consistency of the χ_X values is shown in Fig. 1.

Table I. Bond lengths and bond angles in carbene-analogue AX_2 molecules from experimental determination.

A		X F	Cl	Br
C	r, pm	130.35(1)		
	$\angle$, °	104.8		
	Ref.	[6]		
Si	r, pm	159.01(1)	208.3(4)	224.3(5)
	$\angle$, °	100.8	102.8(6)	102.7(3)
	Ref.	[7]	[1]	[1]
Ge	r, pm	173.21(1)	218.6(4)	233.7(13)
	$\angle$, °	97.2	100.3	101.2
	Ref.	[8]	[3]	[2]
Sn	r, pm		234.6(7)	250*
	$\angle$, °		99	
	Ref.		[5]	

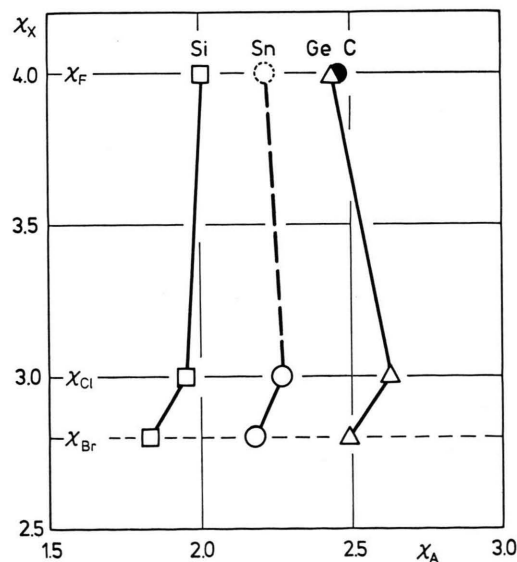* Preliminary result. Private communication from Dr. Gy. Schultz, 1982.

Fig. 1. Electronegativities of group IV elements A as estimated from the bond lengths of their dihalide molecules AX_2. (The dashed line indicates that the structure of SnF_2 is not yet known and that the tin electronegativity in SnF_2 was estimated on the basis of the other data.)

The most important observation here is that the silicon electronegativity value is smaller than that of germanium. The various uncertainties involved in this approach are not thought to have a serious influence on this result. The most important potential sources of error include the limited number of reference molecules considered, the approximate character of the equation, and the values chosen for covalent radii and reference electronegativities. The actual magnitude of the uncertainties is difficult to estimate.

There is, of course, the additional uncertainty in the experimental bond lengths, but in this case the effect is easy to estimate. A change in $r(A–X)$ of 0.5 pm would introduce a change of almost 0.1 in the calculated electronegativities χ_A.

Similar calculations were also performed on the basis of the available bond lengths of AX_4 molecules, where the data are of widely varying accuracy. The bond length parameters taken were CF_4 131.7 pm [16], CCl_4 176.6 [17], SiF_4 155.3 [18], $SiCl_4$ 202.0 [19],

GeF_4 167 [20], $GeCl_4$ 211.3 [17], $GeBr_4$ 227.2 [21], and $SnCl_4$ 228.1 [22]. The resulting estimated χ_A values are 2.6, 1.7, 2.0 and 1.8 for A = C, Si, Ge, and Sn, respectively. Thus, the data for both series of molecules, AX_2 and AX_4, yield electronegativities decreasing in the same order:

$$\chi_C > \chi_{Ge} > \chi_{Sn} > \chi_{Si}.$$

This order is in agreement with information collected on the electronegativities of group IV elements from other chemical and physical evidence as summarized by Moody and Thomas [23] but differs considerably from that cited in the Pauling scale, where χ_C is 2.5 while χ_A is 1.8 for the three elements silicon, germanium and tin.

The present results can be utilized in estimating bond lengths in dihalocarbene analogs whose structures have not yet been determined. Thus, for example, the Sn–F bond length in SnF_2 is predicted to be 186 pm.

[1] I. Hargittai, Gy. Schultz, J. Tremmel, N. D. Kagramanov, A. K. Maltsev, and O. M. Nefedov, J. Am. Chem. Soc. 105, 2895 (1983).
[2] Gy. Schultz, J. Tremmel, I. Hargittai, N. D. Kagramanov, A. K. Maltsev, and O. M. Nefedov, J. Mol. Struct. 82, 107 (1982).
[3] Gy. Schultz, J. Tremmel, I. Hargittai, I. Berecz, S. Bohátka, N. D. Kagramanov, A. K. Maltsev, and O. M. Nefedov, J. Mol. Struct. 55, 207 (1979).
[4] I. Hargittai, J. Tremmel, A. A. Ishchenko, A. A. Ivanov, L. S. Ivashkevich, and V. P. Spiridonov, J. Mol. Struct. 42, 147 (1977).
[5] A. A. Ishchenko, L. S. Ivashkevich, E. Z. Zasorin, V. P. Spiridonov, and A. A. Ivanov, Sixth Austin Symposium on Gas Phase Molecular Structure, Austin, Texas 1976.
[6] W. H. Kirchhoff, D. R. Lide, and F. X. Powell, J. Mol. Spectrosc. 47, 491 (1973).
[7] H. Shoji, T. Tanaka, and E. Hirota, J. Mol. Spectrosc. 47, 268 (1973).
[8] H. Takeo, R. F. Curl, and P. W. Wilson, J. Mol. Spectrosc. 38, 464 (1971); H. Takeo and R. F. Curl, J. Mol. Spectrosc. 43, 21 (1972).
[9] I. Hargittai, Z. Naturforsch. 34a, 755 (1979).
[10] 1. Hargittai and C. Bliefert, Z. Naturforsch. 35b, 1953 (1980).
[11] V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. 63, 37 (1941).
[12] L. Pauling, The Nature of the Chemical Bond.

Edition Cornell University Press, Ithaca N. Y. 1960.
[13] I. Hargittai, The Structure of Volatile Sulphur Compounds. Akadémiai Kiadó, Budapest 1981 (in Hungarian). Revised English version, Reidel Publ. Co., Dordrecht, in press.
[14] A. G. Robiette, private communication cited by Glidewell [15].
[15] C. Glidewell, Inorg. Chim. Acta 20, 113 (1976).
[16] As a matter of fact using the original Schomaker-Stevenson formula and the covalent radii communicated by Pauling [12] resulted in the same order of electronegativities.
[17] C. W. W. Hoffman and R. L. Livingston, J. Chem. Phys. 21, 565 (1953).
[18] Y. Morino, Y. Nakamura, and T. Iijima, J. Chem. Phys. 32, 643 (1960).
[19] K. Hagen and K. Hedberg, J. Chem. Phys. 59, 1549 (1973).
[20] R. R. Ryan and K. Hedberg, J. Chem. Phys. 50, 4986 (1969).
[21] A. D. Caunt, H. Mackle, and L. E. Sutton, Trans. Faraday Soc. 47, 943 (1951).
[22] G. G. B. Souza and J. D. Wieser, J. Mol. Struct. 25, 442 (1975).
[23] H. Fujii and M. Kimura, Bull. Chem. Soc. Jpn. 43, 1933 (1970).
[24] G. J. Moody and J. D. R. Thomas, Dipole Moments in Inorganic Chemistry. Edward Arnold, London 1971.