

## Empirical Relationships between Tetrahedral Covalent Radii and Effective Nuclear Charge

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ALTHOUGH it has long been known<sup>1</sup> that the tetrahedral covalent single-bond radii of elements in a given row of the Periodic Table decrease as atomic number increases, few if any attempts have been made to find equations which relate the radii with atomic number. With the availability of accurate modern values for the lengths of single bonds between tetrahedrally co-ordinated atoms,<sup>2</sup> it has been possible to establish reliable experimental values for the tetrahedral covalent single-bond radii,  $R_{X4}(\text{obs})$ , of elements in the first (Li—Ne) row of the Periodic Table. These are given in Table 1. The list is based on a value for  $R_{C4}(\text{obs})$  of 0.767 Å, this being half the carbon-carbon bond length in ethane.<sup>3</sup> Other radii are derived from bond lengths,  $L_{XY}$ , in species of the types indicated, assuming a simple additivity rule

$$L_{XY} = R_{X4} + R_{Y4} \quad (1)$$

rather than a relation of the type suggested by Schomaker and Stevenson<sup>4</sup> where an electronegativity correction is applied.

The species noted in Table 1 are essentially free

species, that is, molecules and ions rather than the diamond-like macromolecular crystals studied by Pauling and Huggins,<sup>1</sup> but the new radii are strikingly similar to their values. The Schomaker-Stevenson radii,<sup>4</sup> which are based on bond lengths in molecules such as  $F_2$ ,  $H_2O_2$ , and  $H_2N \cdot NH_2$  together with the electronegativity correction, do not correspond. In the present approach the bonds in the above three molecules are considered as exceptions to the simpler additivity rule.

The decrease of the tetrahedral radii with increasing atomic number is normally explained as the result of increasing nuclear charge. In fact there appears to be a closely linear relationship between the radii and the reciprocal of Slater's<sup>5</sup> effective nuclear charge,  $Z_{\text{eff}}$ . Table 2 shows the good agreement between the observed radii and radii calculated using the relationship

$$R_{X4}(\text{calc}) = 1.234(1/Z_{\text{eff}})_X + 0.387. \quad (2)$$

For bonds between first-row elements certain conditions are evident which limit the types of bonds whose lengths can be predicted using

TABLE 1. Single-bond radii of first-row elements (Å)

Element X	Type of species*	Tetrahedral covalent radii		Covalent radii Free molecules (ref. 4)
		Free species (this study)†	Crystals (ref. 1)	
Li	Li <sub>2</sub>	1.336	—	1.34
Be	basic salts of carboxylic acids	0.99	1.06	—
B	R <sub>3</sub> N·BR <sub>3</sub>	0.87	0.88	0.81
C	R <sub>3</sub> C·CR <sub>3</sub>	0.767	0.77	0.772
N	[R <sub>3</sub> N·CR <sub>3</sub> ] <sup>+</sup>	0.707	0.70	0.74
	R <sub>2</sub> N·CR <sub>3</sub>			
	[R <sub>3</sub> N·NR <sub>3</sub> ] <sup>2+</sup>			
O	RO·CR <sub>3</sub>	0.655	0.66	0.74
F	F·CR <sub>3</sub>	0.618	0.64	0.72

\* R = alkyl or H

† Errors estimated to be less than 0.005 Å, except for Be and B.

TABLE 2. Variation of tetrahedral covalent radii, R<sub>X4</sub>, (Å) with effective nuclear charge, Z<sub>eff</sub>

Element X	(Z <sub>eff</sub> ) <sub>X</sub>	(1/Z <sub>eff</sub> ) <sub>X</sub>	R <sub>X4</sub> (calc)	R <sub>X4</sub> (obs)
Li	1.30	0.769	1.336	1.336
Be	1.95	0.513	1.020	0.99
B	2.60	0.385	0.862	0.87
C	3.25	0.308	0.767	0.767
N	3.90	0.256	0.703	0.707
O	4.55	0.220	0.658	0.655
F	5.20	0.192	0.624	0.618
Ne	5.85	0.171	0.598	—

Equations (1) and (2). These conditions are as follows:

- (i) the two atoms involved must be co-ordinated tetrahedrally;
- (ii) one, but not both, of the atoms may have lone pairs in some of the positions of tetrahedral co-ordination (this condition excludes the bonds upon which the Schomaker-Stevenson<sup>4</sup> radii are based);
- (iii) if two or more atoms with lone pairs are attached to a given atom, none of the bond lengths involved can be predicted on the simple basis (this condition excludes molecules such as CF<sub>4</sub> where the C-F bond is shorter than predicted).

The empirical nature of the two equations and the three conditions must be stressed. A number of key molecules still remain to be studied accurately before the proposals can be fully tested.

The data available at present for second-row

elements (Na—Ar) are not entirely satisfactory and moreover there are effects such as the possibility of *d*<sub>π</sub>-*p*<sub>π</sub> bonding to be considered. However, preliminary studies suggest a relationship:

$$R_{X_4}(\text{calc}) = 1.801(1/Z_{\text{eff}})_X + 0.720 \quad (3)$$

From Table 1 it is apparent that data at present available<sup>2</sup> suggest that the C-N bonds in molecules of the type R<sub>2</sub>N·CR<sub>3</sub> and ions of the type [R<sub>3</sub>N·CR<sub>3</sub>]<sup>+</sup> are equal. Further, present data also suggest that the N-N bond in the ion [H<sub>3</sub>N·NH<sub>3</sub>]<sup>2+</sup> has a length equal to twice the tetrahedral covalent radius of nitrogen. It is often suggested that charged species, particularly of the latter type, will have anomalous bond lengths, but this does not appear to be so.

Equation (2) may be used to calculate a tetrahedral covalent radius for neon which can then be used to predict bond lengths in hypothetical molecules such as Ne(BH<sub>3</sub>)<sub>4</sub>.

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<sup>1</sup> L. Pauling and M. L. Huggins, *Z. Krist.*, 1934, **87**, 205; L. Pauling, "The Nature of the Chemical Bond", Oxford University Press, 1963, p. 244.

<sup>2</sup> "Interatomic distances", *Chem. Soc. Special Publ.*, **11**, and **18**, ed., L. E. Sutton.

<sup>3</sup> L. S. Bartell and H. K. Higginbotham, *J. Chem. Phys.*, 1965, **42**, 851.

<sup>4</sup> V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.*, 1941, **63**, 37.

<sup>5</sup> J. C. Slater, *Phys. Rev.*, 1930, **36**, 57; C. A. Coulson, "Valence", Oxford University Press, 1956, p. 40.