Bond Length, Polarity, and Electronegativity

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The question of bond shortening in heteronuclear bonds is reconsidered in the light of the results obtained with an ionic approximation to chemical bonding. A definite answer can only be given when the relation between an elements valence-state-ionization energy and -electron affinity is understood. Two empirical bond shortening relations, i.e. those of Schomaker-Stevenson and Huggins, are shown to be incompatible.

1. Introduction. Several empirical relations have been proposed for the evaluation of one of the most important molecular constants, the equilibrium internuclear separation. It was anticipated quite early that the bond lengths \( r_{AB} \) of a number of heteronuclear bonds AB can be regenerated simply by adding the covalent radii \( r_A \) and \( r_B \) of the bonding partners A and B. These covalent radii \( r_x \) are obtained from the observed bond lengths \( r_{XX} \) in the homonuclear bonds XX. Nevertheless, it was frequently argued that relatively small negative corrections on this additivity rule (indicating bond contraction) are necessary to obtain better agreement with experiment. The final form to be given to these corrections however remains a point of discussion and has even led to a reevaluation of the covalent radii of elements.

In this report, the question about the additivity of bond lengths is reconsidered in the light of the ionic approximation to chemical bonding, recently advanced. In order to illustrate the difficulties involved, two well known empirical bond shortening relations will be examined in detail.

2. The dissimilarity between two empirical bond shortening relations. If bond shortening in heteronuclear bonds AB is defined as the difference between the sum of the covalent radii \( (r_A + r_B) \) and the equilibrium internuclear separation \( r_{AB} \), the electronegativity difference between the bonding partners on the Pauling electronegativity scale can, according to Schomaker and Stevenson, be used as a measure for bond shortening:

\[
r_{AB} = r_A + r_B - \beta |Z_B^{(P)} - Z_A^{(P)}|,
\]

The "constant" \( \beta \) equals 0.09 Å per unit of electronegativity-difference, although frequently other values for it have been proposed. The validity of this rule has been discussed extensively.

Huggins suggested a bond shortening relation of the form:

\[
r_{AB} = r_A + r_B - (\alpha^{-1}) \ln D_{AA}/(1/2) (D_{AA} + D_{BB})
\]

wherein \( \alpha \) ought to be a constant with a value \( 4 \leq \alpha \leq 6 \) Å\(^{-1}\) and \( D_{AA}, D_{BB} \) and \( D_{AB} \) represent the dissociation energies of the bonds AA, BB and AB respectively. Rather arbitrarily however, \( \alpha \) was given a value of 4.6 Å\(^{-1}\).

A quantity such as \( D_{AB}/(1/2) (D_{AA} + D_{BB}) \) was shown to be equal to \( (1 + F^2) \), wherein I is the ion-character or polarity of the bond AB and is given by \( I = (D_{BB} - D_{AA})/(D_{AA} + D_{BB}) \). These (corrected) \( D_{XX} \) values can be taken as a more absolute measure for the electronegativity of element X and may easily be converted into Pauling-scale electronegativities \( \chi_X^{(P)} \) by means of the relation:

\[
D_{XX} = a \chi_X^{(P)} + b
\]

whereby \( a \) and \( b \) are constants.

The Schomaker-Stevenson rule (1) is then transformed in

\[
r_{AB} = r_A + r_B - (\beta/a) (D_{BB} - D_{AA})
\]

\[
= r_A + r_B - (\beta/a) I (D_{AA} + D_{BB})
\]

The relation advanced by Huggins can be written as

\[
r_{AB} = r_A + r_B - (\alpha^{-1}) F^2 (1 - F^2/2)
\]

if the approximation \( \ln (1 + F^2) \approx F^2 (1 - F^2/2) \) is used. From a comparison of Eqs. (5) and (6) one immediately follows

\[
a \beta/a = I (1 - F^2/2)/(D_{AA} + D_{BB})
\]

which is not constant at all.

It seems therefore that, in first approximation, these two empirical bond shortening relations are incompatible. One rule [Eq. (4)], predicts the bond contraction to depend on \( (Z_B - Z_A) \) whereas the other one [Eq. (6)], reveals a dependence on \( (Z_B - Z_A)^2 \) for the same quantity.

According to a reference recently cited by Glidewell, Robiette already investigated the two corresponding equations:

\[
r_{AB} = r_A + r_B - k_1 (Z_B - Z_A)
\]

\[
r_{AB} = r_A + r_B - k_2 (Z_B - Z_A)^2
\]

He concluded that a quadratic correction, as in Eq. (8 b) was substantially better than a linear one, as in Eq. (8 a), indicating that Huggins relation should be preferred over the Schomaker-Stevenson-rule.

If this would be the case, Eq. (7) suggests refinements in the \( \beta \)-values, appearing in Eq. (1), in agreement with the different \( \beta \)-values already proposed by Pauling and Gordy but the validity of a quadratic dependence would imply that \( \beta \) should be calculated separately for each bond AB. As these results need further confirmation however, we will
now try to find some criterion to be fulfilled by the equilibrium internuclear separation in heteronuclear bonds AB, without making any a priori assumption about its relation to the sum of the covalent radii.

3. The ionic approximation to chemical bonding and the question of bond shortening. Although the primary aim of our recently introduced ionic approximation to chemical bonding was to obtain expressions for the bond energy, a particular interpretation of the formulae appearing therein leads to a simple condition to be applied on the equilibrium internuclear separation in heteronuclear bonds. Indeed, at the equilibrium distance $r_{AB}$, the valence electron energy of a bond AB, $\epsilon_{AB}$, may be written as

$$\epsilon_{AB} = IE_A + IE_B + E_{AB}$$  \hspace{1cm} (9)

where the bond energy $E_{AB}$ is expressed as a linear function of the electron affinities $EA$ of the bonding partners, $IE_X$ is the (valence-state-)ionization energy of element X and $n_X$ represents the equilibrium occupancy number of its valence orbital.

Imposing that an ionic approximation is valid, requires that only the energies of the two ionic structures $A^-B^+$ and $A^+B^-$ appear in the expression for the energy. Hence:

$$\epsilon_{AB} = (1/2) n_A (IE_A + EA_A) + (1/2) n_B (IE_B + EA_B)$$  \hspace{1cm} (10)

where the quantities $(IE_X + EA_X)$ obviously represent the energies of the ionic structures at infinite internuclear separation. However, there is no term referring to Coulomb attraction between the ions. It is therefore tempting to apply the criterion

$$e^2 / r_{AB} = (1/2) n_B IE_A + (1/2) n_A IE_B$$  \hspace{1cm} (12)

since in both ionic structures $A^-B^+$ and $A^+B^-$ the charge separation equals the elementary charge.

Equation (11) can then be rewritten as

$$\epsilon_{AB} = (1/2) n_A (IE_A + EA_A) + (1/2) n_B (IE_B + EA_B) + e^2 / r_{AB}$$  \hspace{1cm} (13)

where we have consistently made use of the criterion

$$e^2 / r_{XX} = IE_X$$  \hspace{1cm} (15)

applied earlier in our discussion of the ionic approximation to homonuclear bonds.

With the use of Eq. (15) one can now define a quantity $i$

$$i = (IE_B - IE_A) / (IE_A + IE_B) = (r_{AA} - r_{BB}) / (r_{AA} + r_{BB})$$  \hspace{1cm} (16)

which enables us to rewrite Eq. (12) as

$$r_{AB} = (r_A + r_B) (1 - i^2) / (1 - i)$$  \hspace{1cm} (17)

which is the bond length predicted with the use of an ionic approximation to chemical bonding.

Unless Born repulsion must be taken into account also, the effect of polarity on the equilibrium bond distance is such that

$$r_{AB} > (r_A + r_B), \text{ only if } I > i$$

$$r_{AB} = (r_A + r_B), \text{ only if } I = i, \text{ and}$$

$$r_{AB} < (r_A + r_B), \text{ only if } I < i.$$  

Hence, the question of bond shortening reduces to the most fundamental question whether or not there is a simple relation between $IE_X$ and $EA_X$. Of course, it is essential that the covalent radii of elements be known unequivocally, which seems highly problematic. Nevertheless, it seems safe to conclude that, in the absence of another correction term involving Born repulsion, the effect of polarity on the bond length—whether this should be negative or positive—should rather be represented by a correction term in higher power of the electronegativity-difference, as suggested by Huggins and Robiette, rather than by a linear term, as suggested by Schomaker and Stevenson. The fact that for this latter rule different $\beta$-values have already been proposed seems to be in favour of the present deductions.

As indicated above, the idea that heteronuclear bond lengths are short implies the inequality $i > I$. The relation between $I$ and $i$ is also important for determining the range of $I$-values for which our previously suggested relation

$$e^2 / r_{AB} \approx EA_A + EA_B$$  \hspace{1cm} (18)

valid for highly ionic bonds AB only, can be justified.

An evaluation of the relation between $I$ and $i$ however relies upon an understanding of the relation between $IE_X$ and $EA_X$, which, according to the ionic approximation to chemical bonding, is of basic importance for an understanding of chemical interactions. A particular solution to this problem will be forwarded in a forthcoming paper.

4. Conclusion. The ionic approximation to chemical bonding leads to a reasonable criterion to be imposed on the equilibrium internuclear separation in heteronuclear bonds, in complete agreement with our formerly introduced ionic approximation to
homonuclear bonding. In principle, Huggins and Robiette's bond shortening relations should be preferred over the Schomaker-Stevenson-rule—in the absence of Born repulsion correction terms—but, in general, the whole question of bond shortening is closely related to the relation between ionization energies and electron affinities. Unless this question is solved, it can not be concluded that heteronuclear bonds are likely to be short, as suggested by Pritchard and Skinner.

2. V. Schomaker and D. P. Stevenson, J. Amer. Chem. Soc. 63, 37 [1941].