Electronegativity and Bond Type. 3. Origins of Bond Type

Gordon Sproul

Department of Chemistry, University of South Carolina at Beaufort, Beaufort, South Carolina 29902

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Using the bond character of numerous solid binary compounds, graphs of two functions of electronegativity can provide information on the atomic contributions to bonding. While a plot of the difference and average electronegativity, $\Delta\chi$ vs $\chi$, shows the historical isosceles triangle, other plots provide additional insight into bonding. The graph of lower and higher electronegativity, $\chi_{lo}$ vs $\chi_{hi}$, indicates that it is the individual electronegativity values of bonded atoms that uniquely determine bond type. When $\Delta\chi$ is plotted against $\chi_{lo}$, the data forms a right triangle aligned with the axes, implying that these functions best correlate with bond type.

It is obvious that, in order to maintain the full information contained in two variables (such as the electronegativities of two bonded atoms), two independent functions of those variables are necessary. Selection of the two functions of electronegativity $\Delta\chi$ and $\chi$ has been somewhat arbitrary and corresponds with historical precedent. As already indicated, a plot of $\Delta\chi$ vs $\chi$ reproduces historically described triangles. The function $\Delta\chi$ was used by Pauling, it has nevertheless provided a qualitative measure of ionic character. For the other variable, $\chi$, various types of mean of electronegativities have been proposed, but the one most commonly used is the geometric mean. A graph of $\Delta\chi$ vs the geometric mean of the electronegativities, $\chi_{geo}$, was plotted (Figure 2) and evaluated against the tripartite hypothesis. It was found that, for this particular data set of electronegativities, $\Delta\chi$ vs $\chi$ gives a better agreement fraction of 0.97 than $\Delta\chi$ vs $\chi_{geo}$ which gives an agreement fraction of only 0.94. (The agreement fraction is the ratio of the number of compounds falling within the expected bond-type region to the number of compounds considered.)

While the difference appears small, it is significant since nearly twice as many compounds are misplaced from their expected bonding regions when the geometric mean is used rather than the arithmetic mean. The function $\chi$ will be used here because of its inherent simplicity and because it provides the better correlation with observed bonding properties.

Other combinations of functions of electronegativity could be considered; another will now be shown to provide interesting insights into the origins of chemical bonding. The simplest functions of electronegativities of bonded atoms are, of course, the unfunctionalized electronegativity arguments themselves. By plotting the lower value of electronegativity, $\chi_{lo}$, against the higher value of electronegativity, $\chi_{hi}$, a right triangle is produced (Figure 3). While this graph contains the same information as that in the isosceles triangles of $\Delta\chi$ vs $\chi$, the information is presented differently. This particular graphical presentation shows that the origin of lines demarcating the three bonding regions arises from the individual electronegativity values of the component atoms and does not appear to be due to some combination of these values. More particularly, it indicates that metallic bonding always occurs if $\chi_{hi}$ is less than a certain value (in the case of the electronegativity scale CE of Allen, $\chi_{hi}(Al)$ = 13.47 eV); ionic or covalent bonding will occur if $\chi_{hi}$ is greater than this same value; and ionic bonding is separated from...
Figure 1. Graph of $\Delta \chi$ vs $\bar{\chi}$ for binary compounds. M, O, and I are metals, covalent molecules, and ionic compounds, respectively.

Figure 2. Graph of $\Delta \chi$ vs $\chi_{geo}$ for binary compounds. M, O, and I are metals, covalent molecules, and ionic compounds, respectively.
Figure 3. Graph of $\chi_0 \text{ vs } \chi_b$ for binary compounds. M, O, and I are metals, covalent molecules, and ionic compounds, respectively.

Figure 4. Graph of $\Delta \chi \text{ vs } \chi_0$ for binary compounds. M, O, and I are metals, covalent molecules, and ionic compounds, respectively.
covalent bonding by a line of demarcation manifested by a particular value of $x_{lo}$ ($x_{lo}(Al) = 9.46$ eV). The values for $x_{lo}$ and $x_{hi}$ for several scales of electronegativity have been previously published and are the same as the $x$-intercept of the analytical lines reported.\(^9\)

Alternative selections of variables can provide additional conceptual clarification. By plotting $\Delta x$ vs $x_{lo}$, a different right triangle is obtained (Figure 4). This graph, like the previous ones, shows that metallic bonding character is maintained as $x_{lo}$ increases, until $x_{lo}$ reaches a particular value, at which point a discontinuity of bond type occurs. This graph also shows the discontinuity as $\Delta x$ increases, again changing from metallic character at its minimum values. These graphs indicate, then, that there are two independent functions operating that determine bond type. This is similar to Sanderson’s description of bond type. Metallic delocalization of electrons diminishes and localization bonding,\(^15\) in which he recognized any increase in ionic bonding as necessitating a corresponding decrease in covalent bonding. Metallic delocalization of electrons diminishes and localization increases either ionically or covalently away from the metallic vertex, and an increase of ionic or covalent bonding occurs with the decrease of the other. This graph of $\Delta x$ vs $x_{lo}$, because it indicates bond-type data aligning with the Cartesian axes, indicates these two (or closely related) variables provide direct variation of bonding data with these functions. There are six simple electronegativity variables (both the lower and higher electronegativity arguments as well as the four simple mathematical functions of these): $x_{lo}$, $x_{hi}$ (the two arguments), $x$ (the additive mean), $\Delta x$ (the difference function), $x_{geo}$ (the multiplicative geometric mean), and $x_{lo}/x_{hi}$ (a ratio function). Of the 15 possible pairs of these, only the combination $\Delta x$ and $x_{lo}$ exhibits direct variation of bond type as a function of $\chi$. Therefore, $\Delta x$ and $x_{lo}$ are the two independent variables that may be the most useful when describing the relationship of electronegativity to binary compounds. Plots of $\Delta x$ vs $x_{lo}$ show that these two variables are the ones that may be the most useful when describing the relationship of electronegativity to the three bond types.

**Conclusion**

These observations, based on plots of well-characterized bond types using various combinations of functions of electronegativity, provide empirical direction for reevaluating the relationships between electronegativity and bonding. While a quantitative graph of $\Delta x$ vs $\chi$ provides a useful tripartite separation of bonding types, two other combinations of functions of electronegativity are shown to clarify the information it contains. A graph of $x_{lo}$ vs $x_{hi}$ indicates that the electronegativity values of the bonded atoms uniquely distinguish bond type in binary compounds. Plots of $\Delta x$ vs $x_{lo}$ show that these two variables are the ones that may be the most useful when describing the relationship of electronegativity to the three bond types.

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**References and Notes**