2015

Bond Length - Bond Valence Relationships for Carbon - Carbon and Carbon - Oxygen Bonds

C. Harris

Arkansas Tech University

F. D. Hardcastle

Arkansas Tech University, fhardcastle@atu.edu

Follow this and additional works at: <https://scholarworks.uark.edu/jaas>

Part of the [Organic Chemistry Commons](#)

Recommended Citation

Harris, C. and Hardcastle, F. D. (2015) "Bond Length - Bond Valence Relationships for Carbon - Carbon and Carbon - Oxygen Bonds," *Journal of the Arkansas Academy of Science*: Vol. 69 , Article 11.

DOI: <https://doi.org/10.54119/jaas.2015.6905>

Available at: <https://scholarworks.uark.edu/jaas/vol69/iss1/11>

This article is available for use under the Creative Commons license: Attribution-NoDerivatives 4.0 International (CC BY-ND 4.0). Users are able to read, download, copy, print, distribute, search, link to the full texts of these articles, or use them for any other lawful purpose, without asking prior permission from the publisher or the author.

This Article is brought to you for free and open access by ScholarWorks@UARK. It has been accepted for inclusion in Journal of the Arkansas Academy of Science by an authorized editor of ScholarWorks@UARK. For more information, please contact scholar@uark.edu.

Bond Length – Bond Valence Relationships for Carbon – Carbon and Carbon – Oxygen Bonds

C. Harris and F.D. Hardcastle*

Department of Physical Sciences, Arkansas Tech University, Russellville, AR 72801

*Correspondence: fhardcastle@atu.edu

Running Title: Bond Length – Bond Valence Relationships for C-C and C-O Bonds

Abstract

In the present study, relationships are developed for determining bond orders (also referred to as bond valences or bond numbers) from published bond lengths for carbon-carbon (C-C) and carbon-oxygen (C-O) bonds. The relationships are based on Pauling's empirical formula $s = \exp((R_o - R)/b)$, where s is the bond order, R is the corresponding bond length, R_o is the unit valence bond length, and b is a fitting parameter. We use a recently derived relationship for the b parameter in terms of the bonding atoms' published atomic orbital exponents. The resulting equations were checked against published x-ray diffraction (XRD) data for 176 carbon systems with 540 published C-C bond lengths, and 50 oxygen systems having 72 published C-O bond lengths. The C-C and C-O bond length-valence relationships are shown to have sufficient applicability and accuracy for use in any bonding environment, regardless of physical state or oxidation number.

Introduction

In 1929, Linus Pauling published his five rules of chemical bonding which could be used for predicting crystal structures (Pauling 1929). Pauling's second rule is that of local charge neutrality, commonly known as the valence sum rule, which states that the charge of an anion is neutralized by the sum of the adjacent cationic charges, while any cationic charge is neutralized by adjacent anionic charges. In terms of bond valence, the total valence at any one atom is equal to the sum of that atom's individual bond valences. In 1947, Pauling published the following empirical bond length-valence relationship:

$$s = \exp\left(\frac{R_o - R}{b}\right) \quad (1)$$

where s is the bond valence, which corresponds to the number of lone pairs of electrons contributing to the bond, R_o is the length of a chemical bond with unit valence, R is an observed bond length, and b is an empirical fitting parameter (Pauling 1947). A wide range of determined values for the b parameter, anywhere from 0.25 to 0.65 Å (Hardcastle 2013), led to many inconsistencies in valence values, an issue that hindered the ability of chemists to compare findings. As a result, it was proposed that a universal value of 0.37 Å for b be established as the average from the crystallographic data (Brown and Altermatt 1985). This resulted in consistent relationships having only one fitting parameter, R_o ; however, when applied to shorter and longer bonds, the calculated valence was shown to be less reliable owing to the inaccuracy of b .

Theory

In 2013, Hardcastle derived Pauling's bond length-valence, including a new definition for the b fitting parameter (Hardcastle 2013). Since then, a slight modification has been made (Hardcastle *unpublished data*), resulting in the following equation:

$$b = \frac{2a_o}{(\xi_1 + \xi_2)} \quad (2)$$

where b is dependent upon the Bohr radius of a hydrogen atom, a_o (0.529 Å), and the sum of the orbital exponent values for each of the atoms contributing to the bond. This definition results in values for b that are specific to the type of chemical bond, a much more accurate alternative to the average universal value of 0.37 Å assumed for any type of bond. Using published values for atomic orbital exponents to determine the value of the b parameter for any bond, and substituting this value into Equation (1), results in a bond length-valence relationship specific to that bond type.

Uncertainty in R_o

With a definition for the b parameter, R_o is left as the only fitting parameter in Equation (1). The precise length of a C-O bond having a bond order of exactly one (a true C-O single bond) is a matter of debate, but has been estimated between 1.33 and 1.43 Å by Allen (Allen et al 1987) and at 1.39 Å by Brese and O'Keeffe, which they refer to as the "bond-valence parameter" because they were using $b = 0.37$ Å as a universal constant (Brese and O'Keeffe 1991). For the C-C bond length of unit valence, however, most investigators agree on the published C-C length found for crystalline diamond at $R_o = 1.542$ Å (Brown 2002) as representing the C-C bond length of unit valence.

Results and Discussion

The atomic orbital exponents for carbon and oxygen are from data published by Clementi and Raimondi (1963), with values of 1.5679 and 2.2266 respectively. Substituting these values into Equation (2), results in b parameters of 0.337 Å for C-C bonds and 0.279 Å for C-O bonds. Note that both of these values are much lower than the previously assumed universal constant of 0.37 Å. This leaves R_o , the bond length of unit valence, as the only remaining fitting parameter. In the case of C-C bonds, our initial guess would be the C-C bond length in diamond at $R_o = 1.542$ Å. But for C-O bonds, this value could be anywhere from 1.33 (Allen et al 1987) to 1.43 Å (Schomaker and Stevenson 1941).

The total atom valence for a carbon-centered environment was predicted to be 4.00, carbon having four electrons available for bonding, while the atom valence for an oxygen-centered environment was predicted to be 2.00. These predictions were based upon the number of bonding electrons available (oxidation state) in each atom, 4 for carbon and 2 for oxygen. Comparing the calculated atomic valences to the predicted valences, the total error for the C-O bonding was minimized by manipulating R_o . Clementi's orbital exponents were not changed to minimize error, but were held constant.

X-ray diffraction data, limited to results published in the year 2000 or later, was collected for C-C and C-O bond lengths, totaling 612 bonds (176 carbon environments and 50 oxygen environments). Each environment is represented by an individual table within Table 1. Bond lengths were recorded and converted to bond valence values, which were then totaled for the atom valence. Data analysis and error

minimization led to two specific relationships, one for C-C bonds:

$$s = \exp\left(\frac{1.5420 - R}{0.337}\right) \quad (3)$$

and one for C-O bonds:

$$s = \exp\left(\frac{1.3669 - R}{0.279}\right) \quad (4)$$

Each equation was shown to produce accurate valence values from published bond length data. The error in the data (XRD data and valence sum rule) was minimized at $R_o = 1.5420$ Å for C-C bonds, consistent with the C-C bond length of diamond, and $R_o = 1.3669$ Å for C-O bonds, consistent with the estimated 1.33-1.44 Å range for a C-O bond of unit valence.

Conclusion

Bond length – bond valence relationships, based on Pauling's formula, provide useful tools for the prediction and evaluation of crystal structures when used with the valence sum rule. In the present study, atomic orbital exponents were used to independently determine the value of the b parameter (previously either a floating fitting parameter, or set as a universal constant at 0.37 Å) for C-C and C-O bonds at 0.337 and 0.279 Å, respectively. This approach resulted in bond length – valence relationships for C-C and C-O bonds by using published crystallographically determined bond lengths for 612 bonds and the valence sum rule. The optimized bond lengths of unit valence are minimized at $R_o = 1.5420$ Å for C-C bonds, consistent with the C-C bond length of diamond, and $R_o = 1.3669$ Å for C-O bonds, consistent with the estimated 1.33-1.44 Å range for a C-O bond of unit valence.

Acknowledgments

The authors would like to thank Arkansas Tech University for the use of its facilities and funding from the Arkansas Space Grant Consortium (ASGC).

Bond Length – Bond Valence Relationships for C-C and C-O Bonds

Table 1. Bond valence calculations from published XRD data.

<i>Carbon Environments</i>			C13	1.338	1.831	C9	Valence	C36	1.403	1.510	C2	Valence			
Alonso et al. 2009			C17	1.508	1.106	C4	1.429	1.398	C43	1.517	1.077	C1	1.423	1.423	
			O1	1.360	1.025	C8	1.390	1.569		4.035	C3	1.204	2.723		
					3.962	C10	1.525	1.052				4.146			
C11	Valence		C16	Valence			4.019	C39	Valence		C3	Valence			
C10	1.474	1.223	C15	1.341	1.814		C40	Valence	C34	1.398	1.532	C2	1.204	2.723	
O2	1.210	1.755	C21	1.504	1.119	C35	1.410	1.479	C38	1.398	1.532	C4	1.431	1.390	
O3	1.304	1.253	O1	1.361	1.021	C39	1.397	1.537	C40	1.520	1.067			4.113	
		4.232			3.955	C41	1.517	1.077	Borbulevych et al. 2002				C6	Valence	
C11	Valence		C12	Valence				4.093	C8	Valence		C5	1.423	1.423	
C10	1.475	1.220	C1	1.393	1.555		C36	Valence	C7	1.500	1.133	C7	1.200	2.756	
O2	1.213	1.737	C13	1.425	1.414	C35	1.413	1.466	C9	1.540	1.006			4.179	
O3	1.349	1.066	C15	1.427	1.406	C37	1.395	1.546	O5	1.432	0.792		C7	Valence	
		4.023			4.376	C44	1.522	1.061	O6	1.430	0.797	C6	1.200	2.756	
C11	Valence		C3	Valence				4.073			3.728	C8	1.423	1.423	
C10	1.460	1.275	C2	1.381	1.612		C4	Valence			C4	Valence		4.179	
O2	1.225	1.663	C4	1.442	1.345	C3	1.426	1.410	C3	1.410	1.479		C9	Valence	
O3	1.331	1.137	C5	1.430	1.394	C5	1.390	1.569	C5	1.462	1.268	C8	1.423	1.423	
		4.076			4.350	C9	1.518	1.074	C9	1.420	1.436	C10	1.205	2.715	
C11	Valence		C6	Valence				4.053			4.182			4.138	
C10	1.468	1.245	C5	1.474	1.223		C8	Valence	Burlakov et al. 2015				C10	Valence	
O1	1.230	1.634	C7	1.387	1.583	C3	1.416	1.453	C7	Valence		C9	1.205	2.715	
O2	1.318	1.192	C11	1.383	1.602	C7	1.394	1.551	C6	1.430	1.394	C11	1.430	1.394	
		4.071			4.408	C12	1.519	1.071	C8	1.203	2.731			4.109	
C8	Valence		C26	Valence				4.074			4.125		C13	Valence	
C7	1.483	1.191	C25	1.502	1.126		C21	Valence			C2	Valence	C12	1.425	1.414
C9	1.514	1.087	C27	1.540	1.006	C20	1.408	1.488	C1	1.205	2.715	C14	1.199	2.764	
C10	1.336	1.841	C28	1.526	1.049	C22	1.400	1.523	C3	1.424	1.419			4.178	
		4.119	C29	1.531	1.033	C26	1.520	1.067			4.134		C14	Valence	
C8	Valence				4.214			4.078	Chen et al. 2009			C13	1.199	2.764	
C7	1.465	1.256	C20	Valence			C25	Valence	C2	Valence		C1	1.419	1.440	
C9	1.521	1.064	C19	1.515	1.083	C20	1.406	1.496	C1	1.431	1.390			4.204	
C10	1.347	1.782	C21	1.490	1.167	C24	1.392	1.560	C3	1.190	2.839	Chiang et al. 2001			
		4.103	C22	1.529	1.039	C29	1.520	1.067			4.228	C1	Valence		
C8	Valence		C23	1.513	1.090			4.124	C3	Valence		C1a	1.568	0.926	
C7	1.476	1.216			4.379		C35	Valence	C2	1.190	2.839	O4	1.254	1.499	
C9	1.511	1.096	C25	Valence		C34	1.408	1.488	C4	1.440	1.353	O3	1.251	1.515	
C10	1.339	1.825	C24	1.338	1.831	C36	1.394	1.551			4.192			3.940	
		4.137	C26	1.502	1.126	C40	1.517	1.077			C6	Valence	DiPasquale et al. 2006		
C8	Valence		O1	1.365	1.007			4.115	C5	1.430	1.394		C11	Valence	
C7	1.481	1.198			3.963		C39	Valence	C7	1.201	2.747	C12	1.522	1.061	
C9	1.468	1.245	C19	Valence		C34	1.408	1.488			4.141	C13	1.520	1.067	
C10	1.352	1.756	C18	1.338	1.831	C38	1.396	1.541			C7	Valence	C14	1.525	1.052
		4.200	C20	1.515	1.083	C43	1.518	1.074	C6	1.201	2.747	O2	1.458	0.721	
Andreu et al. 2009			O1	1.357	1.036			4.103	C8	1.436	1.369			3.901	
C4	Valence				3.950		C4	Valence			4.117	Draskovic et al. 2010			
C3	1.442	1.345	C17	Valence		C3	1.419	1.440			C9	Valence	C2	Valence	
O2	1.380	0.954	C1	1.391	1.564	C5	1.397	1.537	C8	1.430	1.394	C3	1.436	1.369	
O3	1.215	1.724	C18	1.420	1.436	C9	1.517	1.077	C10	1.190	2.839	C7	1.380	1.616	
		4.023	C24	1.424	1.419			4.054			4.232	O1	1.364	1.010	
C21	Valence				4.419		C8	Valence			C10	Valence		3.996	
C16	1.504	1.119		C8	Valence	C3	1.422	1.427	C9	1.190	2.839		C3	Valence	
C22	1.537	1.015	C7	1.498	1.139	C7	1.392	1.560	C11	1.440	1.353	C2	1.436	1.369	
C23	1.536	1.018	C9	1.374	1.645	C12	1.512	1.093			4.192	C4	1.429	1.398	
C24	1.527	1.045	C13	1.377	1.631			4.080			C13	Valence	O2	1.287	1.332
		4.198			4.415		C21	Valence	C12	1.430	1.394			4.099	
C17	Valence		Basuli et al. 2003			C20	1.419	1.440	C14	1.201	2.747		C4	Valence	
C14	1.508	1.106	C5	Valence		C22	1.398	1.532			4.141	C3	1.429	1.398	
C18	1.516	1.080	C4	1.421	1.431	C29	1.520	1.067			C14	Valence	C5	1.419	1.440
C19	1.535	1.021	C6	1.391	1.564			4.040	C13	1.201	2.747	C8	1.419	1.440	
C20	1.530	1.036	C13	1.518	1.074		C35	Valence	C1	1.436	1.369			4.278	
		4.243			4.070	C34	1.417	1.448			4.117	C10	Valence		

C9	1.537	1.015	C3	1.190	2.839	C	Valence	Liu et al. 2013			4.409			
O3	1.246	1.543	C5	1.430	1.394	C1	1.376	C10	Valence	C9	Valence			
O4	1.265	1.441			4.232	C	1.386	C4	1.398	1.532	C8	1.378	1.626	
3.999				C9	Valence	O	1.378	C5	1.419	1.440	C10	1.401	1.519	
Gavenonis and Tilley			C8	1.420	1.436		4.184	C9	1.415	1.457	O1	1.377	0.964	
2004			C10	1.140	3.292		Valence			4.429			4.109	
	C2	Valence			4.728	C4	1.374		C9	Valence		C2	Valence	
C1	1.412	1.470		C3	Valence	C	1.386	C8	1.371	1.660	C3	1.452	1.306	
C3	1.397	1.537	C2	1.192	2.822	O	1.379	C10	1.415	1.457	O1	1.380	0.954	
C5	1.518	1.074	C4	1.475	1.220		4.191	O1	1.386	0.934	O2	1.203	1.800	
		4.081			4.041		Valence			4.051			4.060	
	C9	Valence		C11	Valence	C6	1.376		C2	Valence	Liu et al. 2014			
C8	1.428	1.402	C10	1.186	2.872	C	1.388	C3	1.437	1.365		C17	Valence	
C10	1.405	1.501	C12	1.459	1.279	O	1.377	O1	1.373	0.978	O2	1.198	1.833	
C14	1.502	1.126			4.151		4.178	O2	1.237	1.593	O3	1.304	1.253	
		4.029	Krawczuk and Stadnicka							3.937	O3A	1.304	1.253	
	C13	Valence	2012				C9	1.379		C10	Valence			4.339
C8	1.404	1.505		C2	Valence	C	1.388	C4	1.408	1.487		C7	Valence	
C12	1.399	1.528	C3	1.356	1.738	O	1.378	C5	1.411	1.474	O5	1.228	1.646	
C17	1.520	1.067	C9	1.490	1.168		4.161	C9	1.405	1.500	O6	1.289	1.322	
		4.101	O1	1.347	1.074		Valence			4.461	C4	1.519	1.071	
	C6	Valence			3.981	C1	1.430		C9	Valence			4.039	
C5	1.407	1.492		C5	Valence	C	1.400	C8	1.392	1.561		C6	Valence	
C7	1.396	1.541	C4	1.458	1.284	O	1.350	C10	1.405	1.500	O3	1.242	1.565	
C11	1.522	1.061	C6	1.356	1.737		3.979	O1	1.372	0.980	O4	1.272	1.405	
		4.095	O8	1.351	1.061		Valence			4.042	C2	1.505	1.116	
	C10	Valence			4.081	C4	1.320		C2	Valence			4.086	
C5	1.411	1.474	Lee et al. 2006				C	1.400	C3	1.453	1.303		C1	Valence
C9	1.409	1.483		C9	Valence	O	1.400	O1	1.395	0.906	O5	1.245	1.548	
C14	1.517	1.077	C8	1.522	1.062		4.342	O2	1.211	1.748	O6	1.254	1.499	
		4.035	C13	1.516	1.080		Valence			3.957	C2	1.513	1.090	
	C18	Valence	C14	1.521	1.065	C6	1.400		C10	Valence			4.137	
C17	1.421	1.431	O2	1.457	0.725	C	1.380	C4	1.438	1.361		C18	Valence	
C19	1.392	1.560			3.933	O	1.340	C5	1.408	1.488	O3	1.290	1.318	
C23	1.507	1.109	Leon et al. 2002					4.241	C9	1.409	1.483	O4	1.232	1.622
		4.101		C	Valence		Valence			4.332	C16	1.496	1.146	
	C22	Valence	C1	1.386	1.588	C9	1.420		C9	Valence			4.086	
C17	1.416	1.453	C	1.387	1.583	C	1.380	C8	1.370	1.665	Lu and Peters 2006			
C21	1.380	1.616	O	1.378	0.961	O	1.360	C10	1.409	1.483		C29	Valence	
C26	1.530	1.036			4.132		4.077	O1	1.379	0.958	C28	1.484	1.188	
		4.105		C	Valence	Liu et al. 2002					4.106	C30	1.397	1.537
	C30	Valence	C4	1.387	1.583		C3	Valence		C2	Valence	C34	1.399	1.528
C29	1.419	1.440	C	1.387	1.583	C1	1.508		C3	1.442	1.345			4.252
C31	1.393	1.555	O	1.387	0.930	C4	1.211		O1	1.382	0.947		C33	Valence
C35	1.516	1.080			4.097		3.773		O2	1.206	1.781	C28	1.431	1.390
		4.075		C	Valence		Valence			4.073		C32	1.389	1.574
	C34	Valence	C1	1.378	1.626	C3	1.211		C10	Valence	C38	1.517	1.077	
C29	1.410	1.479	C	1.390	1.569	C5	1.453		C4	1.435	1.373			4.040
C33	1.386	1.588	O	1.369	0.992		3.969		C5	1.408	1.488		C29	Valence
C38	1.526	1.049			4.188		Valence		C9	1.398	1.532	C28	1.419	1.440
		4.115		C	Valence	C2	1.339			4.393		C30	1.394	1.551
Hill et al. 2007			C4	1.369	1.670	C4	1.506		C9	Valence	C35	1.508	1.106	
	C11	Valence	C	1.390	1.569	C9	1.495		C8	1.378	1.626			4.097
C10	1.383	1.602	O	1.359	1.029		4.087		C10	1.398	1.532		C29	Valence
C12	1.226	2.551			4.268		Valence		O1	1.381	0.951	C28	1.537	1.015
		4.153		C	Valence	C4	1.453			4.109		C30	1.376	1.636
	C12	Valence	C6	1.358	1.725	C6	1.401		C2	Valence	C34	1.400	1.523	
C11	1.226	2.551	C	1.377	1.631	C10	1.399		C3	1.448	1.321			4.174
C13	1.415	1.457	O	1.391	0.917		4.348		O1	1.375	0.971		C34	Valence
		4.008			4.273		Valence		O2	1.211	1.749	C29	1.400	1.523
	C3	Valence		C	Valence	C2	1.573			4.042		C33	1.376	1.636
C4	1.190	2.839	C9	1.355	1.741	C3	1.508		C10	Valence	C35	1.537	1.015	
C31	1.420	1.436	C	1.377	1.631	C11	1.529		C4	1.430	1.394			4.174
		4.274	O	1.384	0.941	O1	1.445		C5	1.406	1.496		C36	Valence
	C4	Valence			4.312		3.813		C9	1.401	1.519	C35	1.526	1.049

Bond Length – Bond Valence Relationships for C-C and C-O Bonds

C37	1.377	1.631	C2	1.407	1.492	C7	Valence	O20	1.220	1.694	C8	1.391	1.564	
C41	1.405	1.501	C9	1.415	1.457	C6	1.497	1.143	O21	1.336	4.232			
		4.180	C10	1.473	1.227	O1	1.314	1.209			C7	Valence		
	C41	Valence			4.176	O2	1.227	1.652		C2	Valence	C2	1.398	1.532
C28	1.529	1.039		C6	Valence			4.003	C3	1.458	1.284	C6	1.382	1.607
C36	1.405	1.501	C7	1.393	1.555	Mattar et al. 2004			O1	1.389	0.923	O	1.407	0.866
C40	1.372	1.655	C7#1	1.393	1.555	C13	Valence		O11	1.214	1.733			4.005
		4.195	C6#2	1.512	1.093	C5	1.394	1.550			3.941		C2	Valence
	C29	Valence			4.203	C9	1.490	1.166		C19	Valence	C1	1.503	1.123
C28	1.390	1.569	Manbeck et al. 2012			C14	1.392	1.559	C3	1.473	1.228	C3	1.396	1.541
C30	1.428	1.402		C2	Valence			4.276	O20A	1.223	1.676	C7	1.398	1.532
C34	1.435	1.373	C1	1.504	1.119		C14	Valence	O21	1.340	1.100			4.196
		4.344	C3	1.396	1.541	C8	1.396	1.543			4.005		C10	Valence
	C34	Valence	C7	1.395	1.546	C10	1.489	1.170	Pandey et al. 2014			C9	1.365	1.690
C29	1.435	1.373			4.207	C13	1.392	1.559		C6	Valence	C11	1.415	1.457
C33	1.418	1.444		C9	Valence			4.272	C7	1.491	1.163	O1	1.382	0.947
C35	1.422	1.427	C8	1.514	1.087	Mehn et al. 2003			O3	1.339	1.105			4.094
		4.244	C10	1.389	1.574		C1	Valence	O4	1.200	1.820		C11	Valence
	C36	Valence	C14	1.393	1.555	C2	1.569	0.923			4.088	C2	1.419	1.440
C35	1.453	1.302			4.216	O1	1.278	1.376		C5	Valence	C6	1.421	1.431
C37	1.405	1.501		C1	Valence	O3	1.194	1.859	C1	1.520	1.067	C10	1.415	1.457
C41	1.408	1.488	C2	1.393	1.555			4.158	O1	1.261	1.462			4.328
		4.290	C6	1.361	1.710		C1	Valence	O2	1.231	1.628		C6	Valence
	C2	Valence	C7	1.511	1.096	C2	1.493	1.156			4.157	C5	1.411	1.474
C1	1.521	1.064			4.361	O1	1.285	1.341		C18	Valence	C7	1.423	1.423
C3	1.414	1.461		C6	Valence	O2	1.240	1.576	C19	1.489	1.170	C11	1.421	1.431
C7	1.366	1.685	C1	1.414	1.461			4.074	O9	1.341	1.097			4.329
		4.210	C5	1.391	1.564		C1	Valence	O10	1.205	1.787		C21	Valence
	C7	Valence	C7	1.497	1.143	C2	1.505	1.116			4.055	C20	1.348	1.777
C2	1.366	1.685			4.169	O1	1.263	1.452		C17	Valence	C22	1.421	1.431
C6	1.374	1.645		C3	Valence	O2	1.237	1.593	C13	1.524	1.055	O2	1.404	0.875
C8	1.539	1.009	C4	1.530	1.036			4.161	O7	1.264	1.446			4.084
		4.339	O3	1.281	1.361		C1	Valence	O8	1.237	1.593		C22	Valence
	C14	Valence	O4	1.227	1.652	C2	1.528	1.042			4.095	C13	1.426	1.410
C1	1.530	1.036			4.049	O1	1.201	1.813	Reddy et al. 2014			C17	1.411	1.474
C9	1.382	1.607		C1	Valence	O2	1.251	1.515		C1	Valence	C21	1.421	1.431
C13	1.390	1.569	C2	1.517	1.077			4.371	C2	1.487	1.177			4.316
		4.212	O1	1.261	1.462	Munshi et al. 2010			O1	1.297	1.285		C17	Valence
	C21	Valence	O2	1.237	1.593		C3	Valence	O2	1.203	1.800	C16	1.406	1.496
C16	1.317	1.948			4.132	C2	1.454	1.299			4.262	C18	1.425	1.414
C20	1.425	1.414		C8	Valence	C4	1.379	1.620	Saeed et al. 2012			C22	1.411	1.474
C22	1.552	0.971	C9	1.514	1.087	C19	1.480	1.204		C11	Valence			4.385
		4.333	O3	1.291	1.313			4.122	C1	1.455	1.293		C11	Valence
	C16	Valence	O4	1.225	1.663		C8	Valence	C15	1.355	1.742	C10	1.361	1.710
C15	1.623	0.787			4.063	C7	1.437	1.364	O12	1.362	1.017	C12	1.425	1.414
C17	1.371	1.660		C1	Valence	C9	1.505	1.116			4.052	O1	1.391	0.917
C21	1.317	1.948	C2	1.504	1.119	C18	1.423	1.423		C31	Valence			4.042
		4.395	O1	1.278	1.376			3.903	C2	1.459	1.280		C12	Valence
	C23	Valence	O2	1.242	1.565		C3	Valence	C35	1.357	1.730	C3	1.420	1.436
C22	1.543	0.997			4.060	C2	1.458	1.284	O32	1.371	0.985	C7	1.417	1.448
C24	1.346	1.788		C1	Valence	C4	1.382	1.607			3.994	C11	1.425	1.414
C28	1.401	1.519	C2	1.501	1.129	C19	1.473	1.228	Schumann et al. 2003					4.299
		4.304	O1	1.291	1.313			4.119		C14	Valence		C7	Valence
	C28	Valence	O2	1.228	1.646		C8	Valence	C9	1.376	1.636	C6	1.406	1.496
C15	1.524	1.055			4.088	C7	1.438	1.361	C13	1.381	1.612	C8	1.418	1.444
C23	1.401	1.519		C3	Valence	C9	1.506	1.112	O	1.435	0.783	C12	1.417	1.448
C27	1.367	1.680	C4	1.506	1.113	C18	1.419	1.438			4.030			4.389
		4.253	O1	1.336	1.117			3.911		C8	Valence		C22	Valence
Maher et al. 2010			O2	1.203	1.800		C2	Valence	C3	1.391	1.564	C21	1.361	1.710
	C10	Valence			4.030	C3	1.454	1.299	C7	1.378	1.626	C23	1.420	1.436
C1	1.473	1.227		C7	Valence	O1	1.392	0.915	O	1.404	0.875	O2	1.390	0.920
O1	1.348	1.070	C1	1.511	1.096			4.066			4.066			4.066
O2	1.211	1.749	O1	1.280	1.366	O11	1.211	1.747		C3	Valence		C23	Valence
		4.046	O2	1.221	1.688			3.960	C2	1.502	1.126	C14	1.429	1.398
	C1	Valence			4.149		C19	Valence	C4	1.396	1.541	C18	1.412	1.470
						C3	1.480	1.204						

C22	1.420	1.436			3.921	O2	Valence		O11	Valence	C2	1.151	2.169			
		4.304				C2	1.145	2.216	C2	1.211	1.747		2.169			
	C18	Valence		C25	Valence			2.216			1.747	O1	Valence			
C17	1.438	1.361		C26	1.522	1.061		O3	Valence		O20	Valence	C1	1.115	2.468	
C19	1.424	1.419		C27	1.523	1.058		C3	1.170	2.026	C19	1.220	1.694	2.468		
C23	1.412	1.470		C28	1.515	1.083			2.026			1.694	O2	Valence		
		4.250		O3	1.444	0.758		Krawczuk and Stadnicka 2012			O11	Valence	C2	1.145	2.216	
	C9	Valence				3.961				C2	1.214	1.733		2.216		
C8	1.327	1.891		C21	Valence			O1	Valence			1.733	O1	Valence		
C10	1.435	1.373		C22	1.531	1.033		C2	1.347	1.074		O20A	Valence	C1	1.146	2.208
O	1.389	0.924		C23	1.526	1.049		C6	1.360	1.026	C19	1.223	1.676	2.208		
		4.188		C24	1.527	1.045			2.100			1.676	O2	Valence		
	C10	Valence		O1	1.414	0.845					O1	Valence	C2	1.144	2.224	
C1	1.435	1.373				3.972		C4	1.248	1.532	C2	1.392	0.915	2.224		
C5	1.413	1.466		Oxygen Environments					1.532		C9	1.369	0.992	O1	Valence	
C9	1.435	1.373		Bleeke et al. 2010			Liu et al. 2013					1.907	C1	1.140	2.256	
		4.212		O1	Valence		O1	Valence		O21	Valence		2.256			
	C5	Valence		C4	1.385	0.937	C2	1.373	0.978	C19	1.336	1.117	O2	Valence		
C4	1.416	1.453		C5	1.428	0.802	C9	1.386	0.934	C22	1.445	0.757	C2	1.160	2.100	
C6	1.406	1.496			1.740			1.912			1.874		2.100			
C10	1.413	1.466		O1	Valence		O1	Valence		O1	Valence	Reddy et al. 2014				
		4.415		C1	1.148	2.197	C2	1.395	0.906	C2	1.389	0.923	O2	Valence		
Song et al. 2007					2.197		C9	1.372	0.980	C9	1.372	0.982	C1	1.203	1.800	
	C5	Valence			2.197			1.886			1.905		1.800			
C4	1.340	1.820		O2	Valence		O1	Valence		O21	Valence	O3	Valence			
C6	1.406	1.496		C2	1.149	2.189	C2	1.382	0.946	C19	1.340	1.100	C3	1.229	1.640	
C13	1.479	1.205			2.189		C9	1.379	0.956	C22	1.443	0.762		1.640		
		4.522		Bleeke and Anutrasakda 2012				1.902		Pandian et al. 2010		Saeed et al. 2012				
	C1	Valence		O1	Valence		O1	Valence		O1	Valence	O12	Valence			
O1	1.172	2.012		C9	1.156	2.133	C2	1.375	0.971	C9	1.361	1.021	C11	1.362	1.017	
O2	1.362	1.018			2.133		C9	1.377	0.964	C25	1.436	0.780	C13	1.359	1.030	
O3	1.303	1.258		O5	Valence			1.936			1.802		2.047			
		4.287		C59	1.156	2.131	O1	Valence		O2	Valence	O11	Valence			
	C2	Valence			2.131		C2	1.380	0.954	C16	1.381	0.951	C1	1.210	1.754	
O2	1.341	1.097		O1	Valence		C9	1.377	0.964	C29	1.455	0.729	1.754			
O4	1.337	1.113		C9	1.116	2.459		1.919			1.680	O21	Valence			
C6	1.319	1.937			2.459		Lu and Peters 2006			O3	Valence	C2	1.218	1.708		
		4.147		Draskovic et al 2010			O1	Valence		C17	1.331	1.137	1.708			
Varga et al. 2009				O1	Valence		C28	1.073	2.869	C33	1.444	0.758	Schumann et al. 2003			
	C29	Valence		C1	1.427	0.806		2.869			1.896	O	Valence			
C30	1.515	1.083		C2	1.364	1.010	O2	Valence			1.896	C14	1.435	0.783		
C31	1.521	1.064			1.817		C29	1.146	2.208		0.992	C15	1.446	0.753		
C32	1.521	1.064		Esteruelas et al. 2000				2.208		O4	Valence		1.536			
O4	1.440	0.769		O3	Valence			2.200		C24	1.369	0.698	Song et al. 2007			
		3.981		C9	1.156	2.131	C30	1.147	2.200	C37	1.467	1.691	O1	Valence		
	C21	Valence			2.131			2.200		Pierce et al. 2009		C1	1.325	1.162		
C22	1.526	1.049		Huynh et al. 2005			O4	Valence		O1	Valence	C5	1.414	0.845		
C23	1.524	1.055		O1	Valence		C31	1.139	2.265	C1	1.151	2.169	2.007			
C24	1.525	1.052		C1	1.162	2.085		2.265			2.169					
O2	1.441	0.766			2.085		Munshi et al. 2010			O2	Valence					

Literature Cited

- Alonso M, R Chicharro, C Miranda, VJ Arán, MA Maestro, and B Herradón.** 2009. X-ray Diffraction, Solution Structure, and Computational Studies on Derivatives of (3-*sec*-Butyl-2,3-dihydro-1*H*-isoquinolin-4-ylidene)acetic Acid: Compounds with Activity as Calpain Inhibitors. *Journal of Organic Chemistry* 75:342-52.
- Allen FH, O Kennard, DG Watson, L Brammer, AG Orpen, and R Taylor.** 1987. Tables of Bond Lengths determined by X-Ray and Neutron Diffraction. Part 1. Bond Lengths in Organic Compounds. *Journal of the Chemical Society Perkin Transactions II* S1-S19.
- Andreu R, L Carrasquer, S Franco, J Garín, J Orduna, NM de Baroja, R Alicante, et al.** 2009. 4*H*-Pyrans-4-ylidenes: Strong Proaromatic Donors for Organic Nonlinear Optical Chromophores. *Journal of Organic Chemistry* 74:6647-57.
- Basuli F, J Tomaszewski, JC Huffman, and DJ Mindiola.** 2003. Carbon-Oxygen Bond Cleavage Promoted by a Scandium Borohydride Complex. *Organometallics* 22: 4705-14.
- Bleeke JR, BL Lutes, M Lipschutz, D Sakellariou-Thompson, and JS Lee.** 2010 Synthesis, Structure, Spectroscopy, and Reactivity of Oxapentadienyl-Cobalt-Phosphine Complexes. *Organometallics* 29:5057-67.
- Bleeke JR and W Anutrasakda.** 2012. Synthesis, Structure, Spectroscopy, and Reactivity of Azapentadienyl-Cobalt-Phosphine Complexes. *Organometallics* 31:2219-30.
- Borbulevych OY, OV Shishkin, and MY Antipin.** 2002. X-ray Diffraction and Ab Initio Quantum-Chemical Study of the Charge Density in the Crystals of Meisenheimer Complexes – Derivatives of 2,4,6-Trinitrobenzene and 5,7-Dinitroquinoline. *Journal of Physical Chemistry* 106:8109-16.
- Breese NE and M O’Keeffe.** 1991. Bond-Valence Parameters for Solids. *Acta Crystallographica* B47:192-7.
- Brown ID.** 2002. *The Chemical Bond in Inorganic Chemistry*. Oxford University Press (New York). Chapter 9, Physical properties of bonds: bond lengths and bond angles; 106-9.
- Brown ID and D Altermatt.** 1985. Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallographica*. B41: 244-247.
- Burlakov VV, VS Bogdanov, P Arndt, W Baumann, A Spannenberg, KA Lyssenko, IV Ananyev, et al.** 2015. Thermal Isomerization of the Buchwald Seven-Membered Zirconacyclocumulene and Its Interaction with Acetylenes. Synthesis and Structures of Novel Seven-Membered Zirconacyclocumulene Complexes. *Organometallics* 34:2471-80.
- Chen G, L Dawe, L Wang, and Y Zhao.** 2009. Planar Acetylene-Expanded TTFAQ Analogues. *Organic Letters* 11:2736-9.
- Chiang RK, CC Huang, and CS Wur.** 2001. Hydrothermal Synthesis and Structural Characterization of a Coordination Polymer Containing Heptanuclear Co₇(μ₃-OH)₈ Clusters. *Inorganic Chemistry* 40:3237-9.
- Clementi E and DL Raimondi.** 1963. Atomic screening constants from SCF functions. *Journal of Chemical Physics* 38:2686-9.
- Clementi E, DL Raimondi, and WP Reinhardt.** 1967. Atomic screening constants from SCF functions. II Atoms with 37 to 86 electrons. *Journal of Chemical Physics* 47:1300-7.
- DiPasquale AG, DA Hrovat, and JM Mayer.** 2006. Non-Redox-Assisted Oxygen-Oxygen Bond Homolysis in Titanocene Alkylperoxide Complexes: [Cp₂Ti^{IV}(η¹-OO^tBu)L]⁺⁰, L = Cl⁻, OTf⁻, Br⁻, OEt₂, Et₃P. *Organometallics* 25:915-24.
- Drašković BM, GA Bogdanović, MA Neelakantan, AC Chamayou, S Thalamuthu, YS Avadhut, JS auf der Günne, et al.** 2010. N-*o*-Vanillylidene-L-histidine: Experimental Charge Density Analysis of a Double Zwitterionic Amino Acid Schiff-Base Compound. *Crystal Growth & Design* 10:1665-76.
- Esteruelas MA, C García-Yebra, M Oliván, E Oñate, and MA Tajada.** 2000. The Dihydride-Osmium(IV) Complex [OsH₂(κ²-O₂CCH₃)(H₂O)(PⁱPr₃)₂]BF₄ as a Precursor for Carbon-Carbon Coupling Reactions. *Organometallics* 19:5098-106.
- Gavenonis J and TD Tilley.** 2004. Synthesis and Reactivity of Tris(imido)rhenium Complexes Containing Rhenium-Main Group Element Bonds. Silicon-Carbon Bond Activations of PhSiH₃ by Silyl Complexes. *Inorganic Chemistry* 43:4353-62.
- Hardcastle FD.** 2013. Valence-Length Correlations for Chemical Bonds from Atomic Orbital Exponents. *Journal of the Arkansas Academy of Science* 67:53-8.

- Hill AF, AD Rae, M Schultz, and AC Willis.** 2007. Bis(alkynyl), Metallacyclopentadiene, and Diphenylbutadiyne Complexes of Ruthenium. *Organometallics* 26:1325-38.
- Huynh L, Z Wang, J Yang, V Stoeva, A Lough, I Manners, and MA Winnik.** 2005. Evaluation of Phosphorescent Rhenium and Iridium Complexes in Polythionylphosphazene Films for Oxygen Sensor Applications. *Chemistry of Materials* 17:4765-73.
- Krawczuk A and K Stadnicka.** 2012. Experimental and Theoretical Charge Density Study of the Chemical Bonding in Chlorokojic Acid Crystal Structure. *Journal of Physical Chemistry A* 116:9759-68.
- Lee SB, AC Willis, and RD Webster.** 2006. Synthesis of the Phenoxonium Cation of an α -Tocopherol Model Compound Crystallized with Non-Nucleophilic $[B(C_6F_5)_4]^-$ and $(CB_{11}H_6Br_6)^-$ Anions. *Journal of the American Chemical Society* 128:9332-3.
- Leon LA, R Notario, J Quijano, and C Sánchez.** 2002. Structures and Enthalpies of Formation in the Gas Phase of the Most Toxic Polychlorinated Dibenzo-*p*-dioxins. A DFT Study. *Journal of Physical Chemistry A* 106:6618-27.
- Liu JF, SL Huang, YC Lin, YH Liu, and Y Wang.** 2002. New Acetylide Migration and Oxygen Transfer Reactions in Ruthenium Complexes Containing an Acetyl-Substituted Cp Ligand. *Organometallics* 21:1355-61.
- Liu X, JM Cole, PG Waddell, TC Lin, and S McKechnie.** 2013. Molecular Origins of Optoelectronic Properties in Coumarins 343, 314T, 445, and 522B. *Journal of Physical Chemistry C* 117:14130-41.
- Liu X, Z Su, W Ji, S Chen, Q Wei, G Xie, X Yang, and S Gao.** 2014. Structure, Physicochemical Properties, and Density Functional Theory Calculation of High-Energy-Density Materials Constructed with Intermolecular Interaction: Nitro Group Charge Determines Sensitivity. *Journal of Physical Chemistry C* 118:23487-98.
- Lu CC and JC Peters.** 2006. Pseudotetrahedral Manganese Complexes Supported by the Anionic Tris(phosphino)borate Ligand $[PhBP^{iPr}_3]$. *Inorganic Chemistry* 45:8597-607.
- Maher TR, AD Spaeth, BM Neal, CL Berrie, WH Thompson, VW Day, and MV Barybin.** 2010. Linear 6,6'-Biazulenyl Framework Featuring Isocyanide Termini: Synthesis, Structure, Redox Behavior, Complexation, and Self-Assembly on Au(111). *Journal of the American Chemical Society* 132:15924-6.
- Manbeck KA, S Kundu, AP Walsh, WW Brennessel, and WD Jones.** 2012. Carbon-Oxygen Bond Activation in Esters by Platinum(0): Cleavage of the Less Reactive Bond. *Organometallics* 31:5018-24.
- Mattar SM, AH Emwas, and LA Calhoun.** 2014. Spectroscopic Studies of the Intermediates in the Conversion of 1,4,11,12-Tetrahydro-9,10-anthraquinone to 9,10-Anthraquinone by Reaction with Oxygen under Basic Conditions. *Journal of Physical Chemistry A* 108:11545-53.
- Mehn MP, K Fujisawa, EL Hegg, and L Que, Jr.** 2003. Oxygen Activation by Nonheme Iron(II) Complexes: α -Keto Carboxylate versus Carboxylate. *Journal of the American Chemical Society* 125:7828-42.
- Munshi P, C Jelsch, VR Hathwar, and TNG Row.** 2010. Experimental and Theoretical Charge Density Analysis of Polymorphic Structures: The Case of Coumarin 314 Dye. *Crystal Growth & Design* 10:1516-26.
- Pandey AK, GPA Yap, and NJ Zondlo.** 2014. (2*S*,4*R*)-4-Hydroxyproline(4-nitrobenzoate): Strong Induction of Stereoelectronic Effects via a Readily Synthesized Proline Derivative. Crystallographic Observation of a Correlation between Torsion Angle and Bond Length in a Hyperconjugative Interaction. *Journal of Organic Chemistry* 79:4174-9.
- Pandian RP, NP Raju, JC Gallucci, PM Woodward, AJ Epstein, and P Kuppasamy.** 2010. A New Tetragonal Crystalline Polymorph of Lithium Octa-*n*-Butoxy-Naphthalocyanine (LiNc-BuO) Radical: Structural, Magnetic and Oxygen-Sensing Properties. *Chemistry of Materials* 22:6254-62.
- Pauling L.** 1929. The principles determining the structure of complex ionic crystals. *Journal of the American Chemical Society* 51:1010-26.
- Pauling L.** 1947. Atomic radii and interatomic distances in metals. *Journal of the American Chemical Society* 69:542-53.

- Pierce GA, D Vidovic, DL Kays, ND Coombs, AL Thompson, ED Jemmis, S De, and S Aldridge.** 2009. Half-Sandwich Group 8 Borylene Complexes: Synthetic and Structural Studies and Oxygen Atom Abstraction Chemistry. *Organometallics* 28:2947-60.
- Reddy ST, KP Krovi, and MJ Swamy.** 2014. Structure and Thermotropic Phase Behavior of a Homologous Series of *N*-Acylglycines: Neuroactive and Antinociceptive Constituents of Biomembranes. *Crystal Growth & Design* 14:4944-54.
- Saeed A, MF Erben, and M Bolte.** 2012. Twisted Imide Bond in Noncyclic Imides. Synthesis and Structural and Vibrational Properties of *N,N*-Bis(furan-2-carbonyl)-4-chloroaniline. *Journal of Organic Chemistry* 77:4688-95.
- Schomaker VS and DP Stevenson.** 1941. Some Revisions of the Covalent Radii and the Additivity Rule for the Lengths of Partially Ionic Single Covalent Bonds. *Journal of the American Chemical Society* 63:37-40.
- Schumann H, S Dechert, S Schutte, JY Hyeon, M Hummert, and BC Wassermann.** 2003. Oxygen-Stabilized Organoaluminum Compounds as Highly Active Cocatalysts for Ziegler-Natta Olefin Polymerization. *Organometallics* 22:1391-401.
- Song J, YX Lei, and Z Rappoport.** 2007. The First Solid Enols of Anhydrides. Structure, Properties, and Enol/Anhydride Equilibria. *Journal of Organic Chemistry* 72:9152-62.
- Varga V, I Císařová, R Gyepes, M Horáček, J Kubišta, and K Mach.** 2009. Evaluation of the Oxygen π -Donation in Permethyltitanocene Silanolates and Alcoholates. *Organometallics* 28:1748-57