



Single Bond Lengths of Organic Molecules in the Solid State

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Single Bond Lengths of Organic Molecules in the Solid State

Peter F. Lang ^α & Barry C. Smith ^σ

Abstract This paper discusses in detail the calculation of bond lengths of organic molecules in the solid state. It describes briefly the effect of electronegativity in covalent bond length. A set of single bond covalent radii and electronegativity values are proposed. Covalent bond lengths calculated by a modified form of the soft sphere equation (which calculated internuclear separation of different Group 1 and Group 2 crystalline salts to a remarkable degree of accuracy) show very good agreement with observed values. The results also show that electronegativity is a major influence on covalent bond lengths and the soft sphere model described here can be used to calculate covalent bond lengths of other organic/bio-organic molecules in different environments that have not yet been experimentally measured.

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I. INTRODUCTION

Bonding and reactivity form the core in the study of chemistry. How a reaction occurs and the type of bonding that takes place depend on factors such as reaction conditions, electronegativity, covalent or ionic radii of the reacting atoms or ions. There are many different sets/series of ionic and covalent radii in the open literature and it can be confusing to the researcher or student because the values presented in the various sets can be very much different. For example, fairly recently Cordero (Cordero et al, 2008) undertook a large scale statistical exercise and published a set of covalent radii deduced from crystallographic data. Cordero

discussed in detail the need of covalent radii and lack of and limitations of some experimental data. Another recent set of covalent radii (Pyykko and Atsumi, 2009) also produced by straight forward statistical exercise showed values that are completely different. It is also sometimes implied that ionic and covalent radii are additive.

It has been recognised for a long time that there are deviations from additivity of the covalent radii in the bond lengths between atoms of different elements. It was pointed out that the deviations were caused by the differences in electronegativities of the different elements (Schomaker and Stevenson, 1941). As shown in Table 1, the observed bond lengths are usually shorter than the sum of the individual covalent radii, all given in Angstrom units (Å), even for small differences in electronegativity between the two atoms forming the bond. Since experimental uncertainties are usually less than ± 0.002 Å, bond lengths and radii are shown (rounded) to three decimal places of an Angstrom unit. Column 1 of Table 1 shows the particular molecule concerned and the specific bond in question is shown in bold type. Columns 2 and 3 show the covalent of the two individual atoms forming the bond, derivation of the individual covalent radii is briefly described below. Column 4 shows the electronegativity difference between the two atoms, column 6 shows the difference between the observed bond length and the sum of the two covalent radii.

Table 1: Difference between covalent bond lengths and simple sum of covalent radii

(1) Molecule A-B (bond)	(2) Covalent A	(3) radii B	(4) Electronegativity difference	(5) Observed bond length in (Å)	(6) Difference in (Å)
H-I	0.371	1.333	0.317	1.609	0.095
H ₂ -S	0.371	1.072	0.492	1.336	0.107
S-Cl ₂	1.072	0.994	0.459	2.006	0.060
Br-Cl	1.141	0.994	0.284	2.136	0.001
I-Br	1.333	1.141	0.350	2.469	0.005
I-Cl	1.333	0.994	0.634	2.321	0.006
B-H ₃	0.848	0.371	0.186	1.190	0.029
B-I ₃	0.848	1.333	0.503	2.118	0.063
C-H ₄	0.795	0.371	0.295	1.087	0.079
C-Br ₄	0.795	1.141	0.372	1.935	0.001
C-Cl ₄	0.795	0.994	0.656	1.767	0.022
(H ₃ C) ₂ -S	0.795	1.072	0.197	1.802	0.065

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It was also pointed out that observed ionic radii differ from commonly known sets of published ionic radii with few exceptions (Adams, 1974). Our work initially concentrated on the ionic radii of Group 1 and Group 2 binary compounds (Lang and Smith, 2010). In our work we proposed a “soft” or compressible sphere approach to ionic radii and results of internuclear distances calculated by a very simple equation showed remarkable agreement with observed values (with differences between calculated and observed less than 0.01 Å in all cases).

Gaseous diatomic molecules are considered as harmonic oscillators and the covalent radii can be reliably measured (Herzberg, 1950). We used covalent radii derived from spectra (Huber and Herzberg, 1979) and radii reported in the Handbook of Chemistry and Physics (Lide, 2009) as a starting point and produced a modified equation as shown below (equation 1) to calculate bond lengths of covalent molecules in the gas phase. The derivation of the equation has been described in detail in previous work and not repeated here (Lang and Smith, 2014).

$$D[AB] = [A]^r + [B]^r - C[\text{abs}(x_a - x_b)] \quad \dots(1)$$

In equation 1 above, $D[AB]$ is the bond length of AB and A and B. C and r are constants, x_a and x_b

are the electronegativity values of A and B. C takes a value of 0.1 and the value of r is 0.5. We discovered that the available electronegativity scales are not completely satisfactory for use in our calculations and the electronegativity values used are taken from a new electronegativity scale (see Appendix 1) we have developed based on “adjusted” ionization energies (Lang and Smith, 2003, 2010). Calculated bond lengths of covalent compounds in the gaseous state were shown to agree very well with observed values.

II. RESULTS

We have now extended our work to include organic compounds in the solid state and particular bond lengths calculated from equation 1 are compared with mean observed bond lengths (of specific bonds) taken from the Handbook of Chemistry and Physics and Crystal Data Determinative Tables (Donnay, Ondik and Mighell, 1973, 1979). The CRC Handbook of Chemistry and Physics provided data on bond lengths in both the gaseous and crystalline state. We have previously shown that radii in the gaseous state may be different from that in the solid state (Lang and Smith, 2014). Therefore, we have used a similar procedure as in prior work to derive covalent radii in the solid state and they are shown in Table 2.

Table 2: Covalent radii of some common atoms/groups and carbon bonded to different groups in Å

Atom/group	radius	electronegativity	Atom/group	radius	electronegativity
(sp ³)C-	0.770	2.30	O ₂ C-	0.820	2.77
H ₃ C-	0.761	2.28	(arene)C-	0.740	2.24
RH ₂ C-	0.764	2.29	-C≡C-	0.750	2.60
R ₂ HC-	0.771	2.29	N≡C-	0.770	2.80
R ₃ C-	0.794	2.31	Cl-	1.108	2.95
-C=C-	0.750	2.32	Br-	1.229	2.67
OHC-	0.760	2.32	I-	1.505	2.32
HO ₂ C-	0.810	2.80	F-	0.759	4.00
HO-	0.779	4.00	O=C-	0.764	2.33
O=C-	0.764	2.33	H ₂ N-	0.760	3.00

Examples of calculated bond lengths between two carbons with at least one of carbon atoms bonded to alkyl groups are shown in Table 3 below.

Table 3: Carbon-carbon bond lengths with calculated compared to observed values in Å

Bond	Observed bond length	Calculated bond length	Abs % difference
H ₃ C-CH ₂ R	1.513	1.515	0.13
H ₃ C-CHR ₂	1.524	1.522	0.13
H ₃ C-CR ₃	1.534	1.538	0.24
RH ₂ C-CH ₂ R	1.524	1.528	0.26
RH ₂ C-CHR ₂	1.531	1.535	0.26
RH ₂ C-CR ₃	1.538	1.544	0.38
R ₂ HC-CR ₃	1.556	1.551	0.33
H ₃ C-C=C	1.503	1.491	0.81
RH ₂ C-C=C	1.502	1.497	0.35
R ₂ HC-C=C	1.510	1.504	0.42
R ₃ C-C=C	1.522	1.534	0.79

The above table shows that there is very good agreement between calculated and observed with agreement of 99% or better in every case. Tables 4 and 5 show the comparison between observed and calculated results for carbon to halogen/hydroxide and other carbon bonds respectively.

Table 4: Comparison of carbon to halogen/hydroxide bond lengths in Å

Bond	Observed bond length	Calculated bond length	Abs % difference
RH ₂ C-Cl	1.790	1.791	0.04
R ₂ HC-Cl	1.803	1.798	0.29
R ₃ C-Cl	1.849	1.822	1.46
(arene)C-Cl	1.739	1.764	1.42
(sp ³)C-Br	1.966	1.939	1.36
(arene)C-Br	1.899	1.904	0.29
-C=C-Br	1.883	1.920	1.96
R ₂ HC-F	1.399	1.399	0.0
R ₃ C-F	1.428	1.423	0.35
(arene)C-F	1.363	1.366	0.24
(arene)C-I	2.095	2.112	0.83
(sp ³)C-I	2.162	2.145	0.80
H ₃ C-OH	1.413	1.409	0.29
RH ₂ C-OH	1.426	1.412	0.97
R ₂ HC-OH	1.432	1.419	0.89
R ₃ C-OH	1.440	1.443	0.21
(arene)C-OH	1.362	1.380	1.79

Table 5: Comparison of other carbon bond lengths in organic molecules (in Å)

Bond	Observed bond length	Calculated bond length	Abs % difference
(sp ³)C-CHO	1.510	1.516	0.39
(sp ³)C-C=O	1.511	1.517	0.38
(sp ³)C-COOH	1.502	1.509	0.49
(sp ³)C-COO ⁻	1.520	1.521	0.09
(arene)C-CH ₃	1.506	1.481	1.66
(arene)C-CH ₂ R	1.510	1.482	1.88
(arene)C-CHR ₂	1.515	1.49	1.74
(arene)C-CR ₃	1.527	1.508	1.27
(sp ³)C-C≡C-	1.466	1.465	0.05
(sp ³)C-C≡N	1.470	1.469	0.05
(sp ³)C-NH ₂ *	1.469	1.446	1.54
(arene)C-C=C-	1.488	1.462	1.77
(arene)C-C=O	1.488	1.474	0.94
(arene)C-COOH	1.480	1.475	0.33
(arene)C-COO ⁻	1.484	1.487	0.22
(arene)C-C≡C-	1.434	1.430	0.28
(arene)C-C≡N	1.443	1.435	0.54
(arene)C-NH ₂ *	1.394	1.413	1.35

*(pyramidal not planer)

Again, the comparisons as shown in Tables 4 and 5 show good agreement with the majority of values in agreement to over 99%. In order to maintain our principle of using a simple equation, the exponent r and the constant C are kept the same as the ones used in calculating bond lengths in the gaseous state.

III. DISCUSSION

It was obvious from the start that covalent radii are not additive except for homonuclear bonds and for some bonds between atoms in the same group such as BrCl or where the electronegativity difference is small such as CBr_4 . We suspect that bonds of fluorine, the hydroxyl (OH) or the amino (NH_2) groups with other elements may possess ionic character because they are very electronegative. If that is the case, a modified equation (Lang and Smith, 2015) should be used to calculate the bond length. Our results also demonstrate that covalent bond lengths for the same molecule may be different for the gaseous and solid states.

Research in medical and biological science has advanced by leaps and bounds in the past half a century partly as a consequence of improvements in technology and partly due to the work done and discoveries at the molecular level. For example, investigations down to the molecular level led to better understanding of cell cycle control (Twyman, 2001) may have implications in cancer research, or that hormone activity can be regulated by controlling receptor expression (Johnson and Everitt, 2000). In the study of the physiology of behaviour we know that many of the body's senses are "chemical" senses (Carlson, 2014). The properties and reactivity of biological molecules depend largely on their bonding and structure and the size and structure of molecules are broadly influenced by the length of the various bonds in the molecule. Hence, it is very useful to be able to calculate the lengths of different bonds in organic molecules. As a

further example in medical science consider the replacement of damaged or diseased bone. Traditionally, it often involves patients donating their own bone tissue, which means two separate surgeries are required. In the past, ivory, which is chemically similar to bone has been used as a replacement. However, more recent work is based on the idea of using degradable material as a temporary support for the bone and enough allow natural bone to regenerate. Biodegradable materials need to be strong enough to support the human body and porous enough to allow bone tissue to regenerate. To produce such material, factors such as toxicity, bond type, activity and the space between atoms forming the bonds, bond-lengths etc. need to be taken into account. A new material that may be suitable have been discovered (Davies et al, 2014) but more research still need to be done.

Technetium complexes have been known for a long time as useful cancer imaging agents (Lang, 1984) and the use of other transition metals such as gold (Martin, 2010) is important as medical treatment. This shows the importance of both traditional organic and transition metal chemistry in bio-medicine. Hence, there is a good case for further research into the soft/compressible spheres methodology to improve agreement between calculated and observed values.

IV. CONCLUSION

The above calculations show that covalent radii are definitely not additive for the majority of covalent bonds in the solid state and covalent radii of atoms in the gaseous state are different from that of the solid state in many cases. Results show that our "soft" sphere approach is sound. Electronegativity differences play an important part in determining bond type and bond length. An understanding of molecular structure will become more important in drug and certain branches of medical research.

APPENDIX 1

Electronegativities & Single Bond Covalent Radii of elements in the gaseous state

Atomic Number	Symbol	Electronegativity	Covalent Radius (Å)
1	H	2.00	0.371
2	He	N/A	N/A
3	Li	1.24	1.292
4	Be	2.14	0.930
5	B	1.81	0.848
6	C	2.30	0.795*
7	N	2.82	0.759
8	O	3.39	0.732
9	F	4.00	0.706
10	Ne	N/A	N/A
11	Na	1.18	1.613
12	Mg	1.76	1.450
13	Al	1.31	1.200
14	Si	1.66	1.124
15	P	2.05	1.080

16	S	2.49	1.072
17	Cl	2.95	0.994
18	Ar	N/A	N/A
19	K	1.00	1.952
20	Ca	1.40	1.723
21	Sc	1.51	1.395
22	Ti	1.57	1.294
23	V	1.62	1.260
24	Cr	1.65	1.250
25	Mn	1.71	1.310
26	Fe	1.77	1.235
27	Co	1.84	1.225
28	Ni	1.92	1.187
29	Cu	2.02	1.140
30	Zn	2.16	1.199
31	Ga	1.31	1.233
32	Ge	1.62	1.234
33	As	1.95	1.230
34	Se	2.30	1.170
35	Br	2.67	1.141
36	Kr	N/A	N/A
37	Rb	0.96	2.077
38	Sr	1.31	1.880
39	Y	1.54	1.520
40	Zr	1.57	1.430
41	Nb	1.61	1.490
42	Mo	1.66	1.380
43	Tc	1.71	1.310
44	Ru	1.76	1.300
45	Rh	1.84	1.260
46	Pd	1.91	1.200
47	Ag	1.92	1.350
48	Cd	2.06	1.340
49	In	1.26	1.450
50	Sn	1.49	1.432
51	Sb	1.73	1.425
52	Te	2.01	1.340
53	I	2.32	1.333
54	Xe	N/A	N/A
55	Cs	0.89	2.200
56	Ba	1.20	2.000
57	La	1.28	1.720
72	Hf	1.57	1.428
73	Ta	1.73	1.37
74	W	1.81	1.355
75	Re	1.80	1.345
76	Os	1.94	1.350
77	Ir	2.06	1.300
78	Pt	2.06	1.220
79	Au	2.12	1.200
80	Hg	2.40	1.316
81	Tl	1.34	1.580
82	Pb	1.51	1.565
83	Bi	1.68	1.535
84	Po	1.90	1.450
85	At	2.12	1.440

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