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# The Relation between Bond Lengths and Dissociation Energies of Carbon−Carbon Bonds

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Bond lengths ($r$, Å) of typical carbon−carbon bonds correlate linearly with bond dissociation energies (BDEs) in the full range of single, double, triple, and highly strained bonds, with BDEs ranging from 16 to 230 kcal mol$^{-1}$. The equation is $r = 1.748 - 0.002371(\mathrm{BDE})$, tested with 41 typical carbon−carbon bonds, ranging in length from 1.20 to 1.71 Å. This sets a maximum bond length limit of 1.75 Å for carbon−carbon bonds.

## Introduction

Various correlations have been reported between bond lengths and other properties of chemical bonds and several have been discussed by Pauling.[1] One example is $r_n = r_1 - 0.71 \log(n)$, where $r$ is the bond length and $n$ the multiplicity of the bond. Another example relating bond length to other physical properties is Badger's rule for diatomics,[1,2] relating $r$ to the force constant: $a(r - b) = k^{-1/3}$, where $k$ is the force constant and $a$ and $b$ are constants dependent on the location of the bonded atoms in the rows of the Periodic Table.

## Results

Stronger bonds are shorter and the carbon−carbon bond lengths of ethane, ethene and ethyne are in inverse order of their bond dissociation energies (BDE). We report here a hitherto unnoticed excellent linear relationship between $r$ and BDE for these three molecules: $r = 1.748 - 0.002371(\mathrm{BDE})$, with units of angstroms and kcal mol$^{-1}$ at 298 K. The correlation coefficient is a remarkable 0.9999984. The plot is shown in Figure 1, where the filled triangles are the three compounds and the line is drawn accordingly. The data are given in Table 1, entries 1−3.

Values of $r$ and their corresponding BDEs are available for several other typical carbon−carbon single bonds and we find that they adhere to the line defined by the three prototypical two-carbon compounds. Entries 4−41 of Table 1 provide literature values in order of reported bond length and are denoted by open circles in Figure 1. In symmetrical molecules, the central bond is treated. The BDEs range from 16 to 230 kcal mol$^{-1}$. Table 1 includes archetypal compounds subject to steric strain and all simple, typical combinations of bonds between sp$^3$, sp$^2$, and sp carbons. On the basis of Figure 1 and Table 1 and taking under consideration estimated uncertainties in measurements of bond lengths (at least ±0.005 Å) and of BDEs (±2 kcal mol$^{-1}$) for some of the more complex molecules, we conclude that the line defined by ethane, ethene, and ethyne is valid. A regression of all points in Figure 1, yields $r = 1.746 - 0.002341(\mathrm{BDE})$, correlation coefficient = 0.9973, but this was not used for obtaining calculated $r$ values in Table 1, and neither is it reflected in the line of Figure 1.[3]

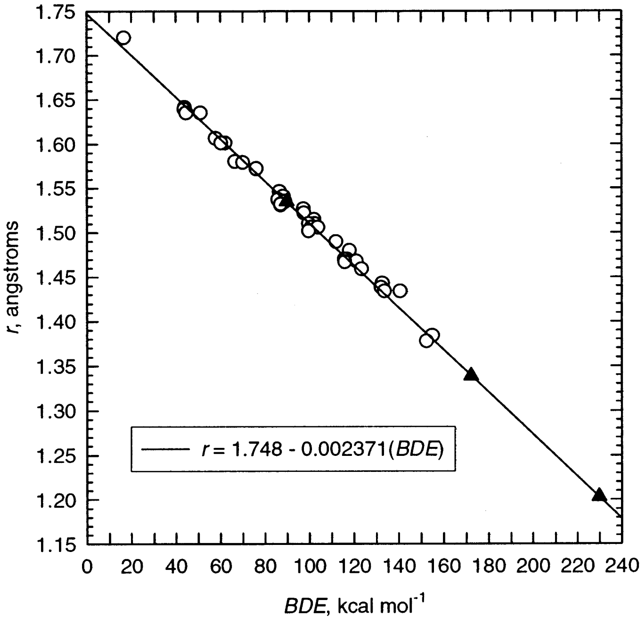

**Figure 1.** Literature values of carbon−carbon bond lengths vs bond dissociation energies.

Data in Table 1 are mostly from commonly available sources: the NIST database for the BDEs and the CRC Handbook for $r$, as specified in the table; for strained compounds, primarily from works of Rüchardt and Beckhaus. The standard deviation between experimental and calculated $r$ in Table 1 is 0.0040 Å, and the average deviation 0.0056. A few specific bonds were found not to fit the correlation well: (a) bonds to carbonyl carbon and to CF$_3$ and (b) the strained molecules 1,1,2,2-tetramethyl-1,2-diphenylethane (dicumyl) and 3,3,4,4-tetramethylhexane. Regarding (a), we note a commonality in that the electronegativities of carbonyl and trifuoromethyl carbons are quite different from those of the carbons involved in the bonds of Table 1. Electronegativity differences are known to lead to bond lengths different from those obtained by simple addition of covalent radii.[1,4] The C−C bonds of acetone and of 1,1,1-trifuoroethane are both shorter by 0.02 Å than those calculated from the respective BDEs. Regarding (b), enthalpies of formation and BDE values for some of the strained molecules are not well-known. An uncertainty of 2 kcal mol$^{-1}$ in BDE leads to ±0.005 Å in the calculated bond length. A typical example of such types of uncertainties is included in Table 1 and Figure 1: phenylacetylene (phenylethyne) is clearly off the line in Figure 1 and shows the largest deviation, 0.019 Å. The

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**TABLE 1: Carbon−Carbon Bond Dissociation Energies (kcal mol$^{-1}$ at 298 K), Literature Values of Bond Lengths and Calculated Values (Å), and Deviation $|\Delta(r)|$**

| entry | compound | BDE | *r* (lit.) | r (calcd ) | $\lvert\Delta(r)\rvert$ | ref, BDE | ref, *r* |
|---|---|---|---|---|---|---|---|
| 1 | Me−Me | 89.68 | 1.5351 | 1.5350 | 0.0001 | 10 | 11a |
| 2 | $H_2C{=}CH_2$ | 172.2 | 1.339 | 1.3394 | 0.000 | 10 | 11a |
| 3 | $HC{\equiv}CH$ | 229.9 | 1.203 | 1.2029 | 0.000 | 10 | 11a |
| 4 | $(Ph_3C)_2$ | 16.6 | 1.72 | 1.7086 | 0.01 | 12 | 12 |
| 5 | $(t\text{BuMe}_2C)_2$ | 44.0[b] | 1.641[c] | 1.6437 | 0.003 | 13 | 13 |
| 6 | $(\text{AdMe}_2C)_2$[a] | 43.7[b] | 1.639[d] | 1.6444 | 0.005 | 14 | 14 |
| 7 | $(\text{PhEt}_2C)_2$ | 44.7[d] | 1.635[d] | 1.6420 | 0.007 | 15 | 6 |
| 8 | $(Et_3C)_2$ | 51.0[b] | 1.635[c] | 1.6271 | 0.008 | 13 | 13 |
| 9 | $(i\text{BuMe}_2C)_2$ | 57.8[b] | 1.606[c] | 1.6110 | 0.005 | 13 | 13 |
| 10 | $(i\text{PrMe}_2C)_2$ | 62.2[b] | 1.601[c] | 1.6005 | 0.001 | 13 | 13 |
| 11 | $(Et_2MeC)_2$ | 60.2 | 1.601[c] | 1.6052 | 0.004 | 13 | 13 |
| 12 | $(PhCH_2)_2$ | 66.6 | 1.58 | 1.5901 | 0.01 | 10 | 16 |
| 13 | $(Cl_3C)_2$ | 70.1 | 1.579 | 1.5818 | 0.003 | 10 | 17 |
| 14 | $(Me_3C)_2$ | 76.0 | 1.572[c] | 1.5678 | 0.004 | 10 | 13 |
| 15 | $(i\text{Pr})_2$ | 86.6 | 1.546[d] | 1.5427 | 0.003 | 10 | 6 |
| 16 | $H_3C{-}CCl_3$ | 88.3 | 1.541 | 1.5386 | 0.002 | 10 | 11a |
| 17 | *t*Bu−Me | 86.0 | 1.537 | 1.5441 | 0.007 | 10 | 11a |
| 18 | *i*Pr−Me | 88.9 | 1.535 | 1.5372 | 0.002 | 10 | 11a |
| 19 | Et−Et | 87.2 | 1.531 | 1.5412 | 0.010 | 10 | 11a |
| 20 | *t*Bu−Ph | 97.4 | 1.527 | 1.5171 | 0.010 | 10 | 11b |
| 21 | Me−Et | 87.2 | 1.532 | 1.5412 | 0.009 | 10 | 11a |
| 22 | $t\text{Bu}{-}CHCH_2$ | 97.5 | 1.522 | 1.5168 | 0.005 | 10 | 11b |
| 23 | *i*Pr−Ph | 102.1 | 1.515 | 1.5059 | 0.009 | 10 | 11b |
| 24 | Et−Ph | 102.3 | 1.510 | 1.5054 | 0.005 | 10 | 11b |
| 25 | $i\text{Pr}{-}CHCH_2$ | 99.7 | 1.510 | 1.5116 | 0.002 | 10 | 11b |
| 26 | $Me{-}CHCH_2$ | 100.9 | 1.506 | 1.5088 | 0.003 | 10 | 11a |
| 27 | Me−Ph | 103.9 | 1.506 | 1.5017 | 0.004 | 10 | 11b |
| 28 | $Et{-}CHCH_2$ | 99.6 | 1.502 | 1.5118 | 0.010 | 10 | 11b |
| 29 | $Ph{-}\text{cyclo}C_3H_5$ | 111.9[f] | 1.490 | 1.483 | 0.007 | 10[f] | 11b |
| 30 | Ph−Ph | 118.0 | 1.48 | 1.4679 | 0.012[g] | 10 | 11b |
| 31 | $Ph{-}CHCH_2$ | 116.9 | 1.470 | 1.4708 | 0.001 | 10 | 11b |
| 32 | *t*Bu−CN | 115.8 | 1.470 | 1.4734 | 0.003 | 10 | 11b |
| 33 | Me−CN | 121.1 | 1.468 | 1.4609 | 0.007 | 10 | 11a |
| 34 | $(CH_2CH)_2$ | 116.0 | 1.467 | 1.4730 | 0.006 | 10 | 11a |
| 35 | Me−CCH | 123.5 | 1.459 | 1.4552 | 0.004 | 10 | 11a |
| 36 | Ph−CN | 132.7 | 1.443 | 1.4334 | 0.010 | 10 | 11a |
| 37 | $CH_2CH{-}CN$ | 132.1 | 1.438 | 1.4348 | 0.003 | 10 | 11a |
| 38 | Ph−CCH | 140.7 | 1.434 | 1.4144 | 0.019 | 10 | 11b |
| 39 | $CH_2CH{-}CCH$ | 133.6 | 1.434 | 1.4312 | 0.003 | 10 | 11a |
| 40 | HCC−CCH | 155.0 | 1.384 | 1.3805 | 0.004 | 10 | 11a |
| 41 | HCC−CN | 152.4 | 1.378 | 1.3867 | 0.009 | 10 | 11a |

[a] Ad = 1-adamantyl. [b] Enthalpy of activation for homolytic cleavage. [c] MM2 force field calculation. [d] Crystallographic value. [e] Electron diffraction measurement. [f] The enthalpy of formation of the cyclopropyl radical was obtained from Kerr's compilation (Lide, R. D., Ed. *CRC Handbook of Chemistry and Physics*, 77th ed.; CRC Press: Boca Raton, FL; 1996; pp **9**-64−**9**-73). [g] Kerr's compilation yields BDE = 114.3, which reduces the deviation to 0.003.

enthalpy of formation and the resulting BDE value used here are based on a determination of the enthalpy of hydrogenation ($\Delta H_{\text{hyd}}$) of the compound that has supplanted an older $\Delta H_{\text{hyd}}$ value.[5] Using the older value of $\Delta H_{\text{hyd}}$ for obtaining the enthalpy of formation leads to BDE[Ph-CCH] = 135.9 and reduces the deviation to an acceptable 0.008 Å. In addition, Rüchardt and Beckhaus have pointed out that some steric strain can be relieved in crowded molecules not only by bond elongation, but also by angle distortion.[6] Nevertheless, most of the highly strained molecules for which the needed data exist (entries 4−11) adhere to the correlation.

The correlation indicates that the longest theoretically possible C−C bond length is 1.748 Å, where the BDE reaches zero. The longest C−C bonds measured experimentally appear to be those in substituted benzocyclobutenes, the highest value being 1.720 Å for the $C(sp^3){-}C(sp^3)$ bond in the four-membered ring of 1,1,2,2-tetraphenyl-3,8-dichloronaphthocyclobutene.[7] Reliable BDE values are not available for strained cyclic compounds (e.g., cyclopropane, cyclobutene, etc.) and the correlation has not been tested with such bonds. However, at $r = 1.720$ Å, the above compound must be approaching the limits of thermal stability.

There is also a correlation between observed *uncoupled* infrared stretching frequencies ($\nu$ in cm$^{-1}$) of carbon−carbon bonds and BDE: $\nu = 171.9(\text{BDE}) - 632$ is obtained from ethane, ethene, and ethyne, with observed $\nu$ values assigned by Shimanouchi as 995, 1623, and 1974 cm$^{-1}$, respectively.[8] The correlation coefficient is 0.9999999. Other bonds have been shown to adhere to this type of correlation.[9] Thus, there is a quantitative link between three fundamental bond properties: bond dissociation energy, bond length, and uncoupled stretching frequency (or force constant for the general case, because coupled vibrations are common in complex molecules[9]).

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