

A Relation Between Bond Multiplicity and Interatomic Distance

J. L. Kavanau

Citation: [The Journal of Chemical Physics](#) **12**, 467 (1944); doi: 10.1063/1.1723895

View online: <http://dx.doi.org/10.1063/1.1723895>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/12/11?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Comparison of Relations between Covalent Bond Order, Energy, and Interatomic Distance for Carbon Carbon Bonds](#)

J. Chem. Phys. **17**, 738 (1949); 10.1063/1.1747378

[A Relation Between Bond Order and Covalent Bond Distance](#)

J. Chem. Phys. **15**, 284 (1947); 10.1063/1.1746498

[Relations between CarbonCarbon Bond Energy, Order, and Interatomic Distance](#)

J. Chem. Phys. **15**, 77 (1947); 10.1063/1.1746296

[A Relation Between Bond Multiplicity and Interatomic Distance](#)

J. Chem. Phys. **14**, 743 (1946); 10.1063/1.1724098

[A Relation Between Internuclear Distances and Bond Force Constants](#)

J. Chem. Phys. **2**, 128 (1934); 10.1063/1.1749433



A Relation Between Bond Multiplicity and Interatomic Distance

J. L. KAVANAU

California Institute of Technology, Pasadena, California

November 2, 1944

IN this paper an empirical equation relating the interatomic distances of covalent bonds to the bond multiplicity is advanced.

Pauling, Brockway, and Beach,¹ and Penney,² have treated aspects of this problem using known interatomic distance values for carbon single, double, and triple bonds and for the bonds in graphite and benzene. The former investigators assumed bond-linkage values of 4/3 and 3/2 for graphite and benzene bonds, while Penney by a quantum-mechanical calculation determined bond-order values of 1.45 and 1.623 for these bonds.

Certain simple considerations suggest an equation of the following form, involving the bond multiplicity N for single, double, and triple bonds,

$$D = a + bC^N. \quad (1)$$

D is the interatomic distance in angstrom units, a and b are constants in angstrom units determined by the specific atom pair, and C is a dimensionless constant. The value of the constant C determined by applying this equation suggests that it is equal to the function $(n_1 + n_2 - 1)/(n_1 + n_2 + 1)$, where n_1 and n_2 are the principal quantum numbers of the valence electrons in the bonded atom pair. Thus, I have modified Eq. (1) to

$$D = a + b \left(\frac{n_1 + n_2 - 1}{n_1 + n_2 + 1} \right)^N. \quad (2)$$

By use of the equation

$$\log(D - a) = N \log \left(\frac{n_1 + n_2 - 1}{n_1 + n_2 + 1} \right) + \log b, \quad (3)$$

a linear semilog plot of $(D - a)$ as a function of N may be made. Since $(n_1 + n_2 - 1)/(n_1 + n_2 + 1)$ is a dimensionless constant which determines the slope of the semilog plot, the curves will be of the same slope for all bonds between atoms homomorphic in the principal quantum number of the valence electrons.

For convenience in treating single, double, and triple bonds, the parameters a and b may be eliminated by simultaneous solution of Eq. (2) in $N = 1, 2, 3$ giving

$$\frac{D_2 - D_3}{D_1 - D_2} = \frac{n_1 + n_2 - 1}{n_1 + n_2 + 1}. \quad (4)$$

The principal quantum number for the valence electrons in carbon and nitrogen is 2, so that $(n_1 + n_2 - 1)/(n_1 + n_2 + 1)$ equals 3/5 for such atom pairs.

For carbon bonds the single-bond distance is $1.54 \pm 0.02\text{\AA}$,³ and is known to a high degree of accuracy in diamond, being 1.542\AA .⁴ For the double bond the various determinations of $1.325 \pm 0.005\text{\AA}$ ⁵ and $1.353 \pm 0.01\text{\AA}$ ⁶ in ethylene and $1.330 \pm 0.005\text{\AA}$ ⁵ in allene are known. For the triple bond the value for acetylene is $1.204 \pm 0.005\text{\AA}$.⁷

Using the single- and triple-bond distances, since there is some doubt about the double-bond value, Eq. (4) yields a value of $D_2 = 1.330\text{\AA}$. This checks well with the experimental values for the double-bond distance. The values for the parameters are $a = 1.015$ and $b = 0.875$.

For nitrogen bonds the value for the single bond in hydrazine is $1.47 \pm 0.02\text{\AA}$.⁸ The double-bond value for transazobenzene is $1.23 \pm 0.03\text{\AA}$,⁹ and the value for the triple bond in the nitrogen molecule is $1.094 \pm 0.005\text{\AA}$.⁷ Using the more accurate single- and triple-bond values, Eq. (4) yields $D_2 = 1.235\text{\AA}$ which checks closely with the experimental value. From Eq. (2) the values for the parameters are $a = 0.883$ and $b = 0.979$.

Using the parameters determined for carbon bonds, Eq. (2) becomes

$$D = 1.015 + 0.875(3/5)^N. \quad (5)$$

This equation gives the graphite and benzene interatomic distance values of 1.42\AA and 1.39\AA if N assumes the values 1.508 and 1.659, respectively. These check fairly closely with Penney's values of 1.45 and 1.623 calculated for the bond order. Accordingly, it appears that N in my equation has the same significance for bonds of fractional

TABLE I.

Atom pair	D_1 Exp.	D_3 Exp.	D_2 Covalent radii	D_2 Eq. (4)
C-N	$1.47 \pm 0.02\text{\AA}^a$	$1.154 \pm 0.005\text{\AA}^b$	1.265\AA	1.272\AA
P-P	$2.21 \pm 0.02\text{\AA}^c$	$1.86 \pm 0.005\text{\AA}^d$	2.00\AA	2.006\AA

^a L. O. Brockway and H. O. Jenkins, J. Am. Chem. Soc. **58**, 2036 (1936).

^b See reference 7 of text.

^c L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, J. Chem. Phys. **3**, 698 (1935).

^d G. Herzberg, Ann. d. Physik **15**, 677 (1932).

multiplicity as Penney's bond order. The values 1.508 and 1.659 are only eight-thousandths removed from the fractions 3/2 and 5/3, which are each 1/6 greater than the respective linkage values assigned by Pauling, Brockway, and Beach, this being a contribution of the resonance energy.

I know of no other atom pairs for which the single-, double-, and triple-bond distances are known which would permit further checking of Eq. (2). The single- and triple-bond distances are, however, known for carbon-nitrogen bonds and phosphorus bonds so it is interesting to predict the respective double-bond distances and compare them with the distances indicated in Pauling's table of covalent radii.¹⁰ The results are tabulated in Table I.

¹ L. Pauling, L. O. Brockway, and J. Y. Beach, J. Am. Chem. Soc. **57**, 2705 (1935).

² W. G. Penney, Proc. Roy. Soc. **A158**, 306 (1937).

³ L. Pauling and L. O. Brockway, J. Am. Chem. Soc. **59**, 1223 (1937).

⁴ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), p. 160.

⁵ E. H. Eyster, J. Chem. Phys. **6**, 580 (1938).

⁶ W. S. Gallaway and E. F. Barker, J. Chem. Phys. **10**, 88 (1942).

⁷ G. Herzberg, F. Patat, and J. W. T. Spinks, Zeits. f. Physik **91**, 386 (1934); F. Rasetti, Phys. Rev. **34**, 367 (1929).

⁸ P. A. Giguere and V. Schomaker, J. Am. Chem. Soc. **65**, 2025 (1943).

⁹ J. M. Robertson, J. Chem. Soc. **61**, 1232 (1939).

¹⁰ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), p. 164.