

A Relation Between Bond Order and Covalent Bond Distance

H. J. Bernstein

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heat-capacity lag, should be used for this adjustment. While the nitrogen is flowing through the apparatus, the alcohol manometer is observed through a microscope and the impact tube is then adjusted for minimum total-head defect. It is important to keep the impact tube carefully centered in the jet, especially when working with gases, such as hydrogen, having a high kinematic viscosity which results in thick nozzle boundary layers.

For the measurements of steam, an ethyl phthalate manometer was used. The manometer was heated to above the boiling point of steam to prevent condensation which

would produce spurious pressure readings. It was necessary to find the zero position of this manometer while a small flow of steam was going through the apparatus, because temperature differences occurred when no steam was flowing. It has been found that this procedure of taking zero readings with a small flow of gas generally gives more consistent results also in measurements of other gases.

When all of these adjustments are properly made, it is possible to reduce the total-head defect to about 0.002 percent of the dynamic pressure, using room temperature nitrogen.

A Relation Between Bond Order and Covalent Bond Distance

H. J. BERNSTEIN

Division of Chemistry, National Research Council Ottawa, Canada

(Received February 26, 1947)

A relation between covalent bond distance and bond order of the form $R = R_1[2/3 + 1/3 \times (n - 1/n + 1)^{p/2}]$ is proposed and tested against the available experimental data. A suitable expression for all covalent bond distances between atoms of the first row of the periodic table of the form $R = Z - A/Z - B[2/3 + 1/3(1/3)^{p/2}]$ is also proposed. The agreement between calculated and observed values is well within the limits of the experimental errors.

A GREAT number of measurements of the CC bond distance¹ in different molecules show that it may have any value intermediate between 1.55Å, the single bond distance, and 1.205Å, the triple bond distance. These intermediate bond distances have been discussed on the basis of a quantum-mechanical treatment by Lennard-Jones,² Penney,³ and Coulson.⁴ These authors have introduced the concept of bond order, designated by p , where p is defined as zero for a single bond, one for a double bond, and two for a triple bond, and may have any intermediate value for bonds of so-called fractional order. In molecules such as benzene and naphthalene, for example, where the electrons are considered to be non-localized or mobile the links have intermediate lengths¹ corresponding to bonds of fractional order. In their papers the above

authors have calculated the bond orders of various links by the method of molecular orbitals and also by the bond pair method; practically identical values are obtained. From their definition of p which depends linearly on the interaction energy, values for the bond energies, and thus for the resonance energy, may be calculated. Also, as Coulson⁴ points out, vibrational frequencies may be estimated.

Lennard-Jones² and Coulson⁴ have derived a relation for the length of a link of order p in the form

$$R_p = R_1 - \frac{R_1 - R_2}{1 + \left(\frac{1-p}{p}\right) \frac{K_1}{K_2}}, \quad (1)$$

where R_p is the length of the link of order p ; R_1 is the length of the link of order $p=0$, i.e., the single bond distance; R_2 is the double bond distance; and K_1 , K_2 are the single and double bond force constants, respectively.

Kavanau⁵ has proposed an empirical relation

⁵ J. L. Kavanau, *J. Chem. Phys.* 12, 467 (1944).

¹ J. M. Robertson, *J. Chem. Soc.* 131 (1938). L. R. Maxwell, *J. Opt. Soc. Am.* 30, 374 (1940).

² J. E. Lennard-Jones, *Proc. Roy. Soc. London* A158, 280 (1937).

³ W. G. Penney, *Proc. Roy. Soc. London* A158, 306 (1937).

⁴ C. A. Coulson, *Proc. Roy. Soc. London* A169, 413 (1939).

between bond distance and bond order of the form

$$R_p = a + b \left(\frac{n_1 + n_2 - 1}{n_1 + n_2 + 1} \right)^{p+1}, \quad (2)$$

where a and b are constants and n_1 and n_2 are the principal quantum numbers of the valence electrons of the bonded atoms. Both of these relations require the knowledge of two data before they can be applied.

Recently Lagemann⁶ has attempted to extend the applicability of Kavanau's relation by assuming that a and b of Eq. (2) have the form $K_1/(Z_1 + Z_2)$ and $K_2(Z_1 + Z_2)$, respectively. K_1, K_2 are constants for atoms of the same row of the periodic table and Z_1, Z_2 are the atomic numbers of the bonded atoms. Suitable values of K_1, K_2 were found by Lagemann for the first row atoms.

Since the total variation from the single to the triple bond distance is only about 1/4 of the single bond distance, it is apparent that any function which varies slowly enough with its argument is bound to have reasonable success in representing the experimental data. The final choice for the form of the function can be made only by reasons of a fundamental theoretical nature. Lacking these, however, it would not seem worth while to propose yet another relation of this nature unless it succeeded in simplifying the present position of the problem and has sufficiently wide applicability.

A relation which seems to accomplish this for symmetrical linkages is

$$R = R_1 \left[2/3 + 1/3 \left(\frac{n-1}{n+1} \right)^{p/2} \right], \quad (4)$$

where R_1 is the single bond distance; R is the bond distance for a bond of order p ; and n is the principal quantum number of the valence electrons of a bonded atom. (See Appendix for the reasons for proposing this expression.) By use of the additivity rule, *viz.* $R_{AB} = (1/2)R_{AA} + (1/2)R_{BB}$ where R_{AB}, R_{AA} , and R_{BB} are the distances between atoms A-B, A-A, and B-B, respectively, of links AB, AA, BB, the bond distances for non-symmetrical linkages are obtained. Equation (4) then becomes

$$R = R_{AA,1} \left[2/3 + 1/3 \left(\frac{n_A - 1}{n_A + 1} \right)^{p/2} \right] + R_{BB,1} \left[2/3 + 1/3 \left(\frac{n_B - 1}{n_B + 1} \right)^{p/2} \right], \quad (5)$$

where $R_{AA,1}$ and $R_{BB,1}$ are the single bond distances of the links AA and BB, respectively, and n_A, n_B are the principal quantum numbers of the valence electrons of the bonded atoms A and B. Equation (4) requires but one observational datum in order to be applicable as compared with the two data which are required before either of Eqs. (1) or (2) can be used.

TABLE I.

	Calc. Eq. (4)	Pauling	Calc. Eq. (4)	Pauling	Calc. Eq. (4)	Pauling	Calc. Eq. (4)	Pauling	Calc. Eq. (4)	Pauling
	B		C		N		O		F	
Single-bond radius	.88*	.88	.772	.77	.707	.70	.66*	.66	.64*	.64
Double-bond radius	.767	.76	.664	.67	.609	.61	.567	.57	.551	.55
Triple-bond radius	.684	.68	.60*	.60	.55*	.55	.513	.51		
	Si		P		S		Cl			
Single-bond radius			1.17*	1.17	1.11	1.10	1.04*	1.04	.99*	.99
Double-bond radius			1.06	1.07	1.01	1.00	.95	.95	.90	.90
Triple-bond radius			.98	1.00	.93*	.93	.87	.88		
	Ge		As		Se		Br			
Single-bond radius			1.22*	1.22	1.21*	1.21	1.17	1.17	1.14*	1.14
Double-bond radius			1.13	1.12	1.12	1.11	1.08*	1.08	1.05	1.05
	Sn		Sb		Te		I			
Single-bond radius			1.40*	1.40	1.41*	1.41	1.36	1.37	1.33*	1.33
Double-bond radius			1.31	1.30	1.32	1.31	1.28*	1.28	1.25	1.24

⁶ R. T. Lagemann, J. Chem. Phys. 14, 743 (1946).

TABLE II.

Molecule	Bond order p	Bond distance	
		calc. Eq. (4)	obs.
Acetylene	2	1.205	1.205 ⁷
Ethylene	1	1.33	1.33 ⁷
Ethane	0	1.55	1.55 ⁷
Benzene	2/3 ^a	1.39	1.39 ¹
Graphite	.55 ^b	1.417	1.42 ¹
Napthalene	.55 ^b	1.417	1.41 ¹

^a Bond order calculated by Coulson, see reference (4).

^b Average of all bond orders calculated for the CC bonds in napthalene by Penney, see reference (3).

The validity of Eq. (4) may be tested by comparing the covalent bond radii calculated from it with the values given by Pauling⁷ (see Table I). In the table the values marked with an asterisk were considered the most reliable and were used to calculate the other radii. The first, second, and third rows are the single, double, and triple bond covalent radii, respectively. The agreement exclusive of hydrogen is well within the average experimental error of $\pm 0.02\text{\AA}$ in the bond distance determined by x-ray or electron diffraction methods.

In the following subsections the bond distances of particular linkages are discussed in more detail.

C—C BONDS

The CC bonds in ethane, ethylene, and acetylene are considered as usual to be pure single, double, and triple bonds, respectively, with bond orders $p=0, 1, 2$, respectively. The bond orders of benzene, graphite, and napthalene are calculated from quantum-mechanical considerations to be $2/3^4$, $.55^3$ and $.55^3$, respectively.

From the value of the triple bond distance in acetylene (1.205Å) and the above bond orders the following table of calculated [by Eq. (4)] and observed CC bond distances may be drawn up (Table II).

N—N BONDS

The N_2 molecule in the $^1\Sigma_g^+$ ground state is considered to be a pure triple bond with length 1.095Å.⁸ The calculated single and double bond distances are 1.41Å and 1.21Å, respectively. The

⁷ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939).

⁸ G. Herzberg, *Diatomic Molecules* (Prentice-Hall, Inc., New York, 1939).

observed NN distance in H_2N-NH_2 at 1.47Å⁹ corresponds then to a bond of order $p=-0.22$, i.e., 78 percent of a single bond. The fact that the NN bond energy in hydrazine is extremely low¹⁰ may be taken as supporting evidence for this value of the bond order.

O—O BONDS

The O_2 molecule is in a $^3\Sigma_g^-$ ground state and as considered by Pauling⁷ has one single bond and two three electron bonds giving it a fractional order between a single and double bond. Using 1.32Å⁷ as the single bond distance the bond order for O_2 is calculated as $p=0.588$. Here again the observed distance in $HO-OH$ at 1.48Å¹¹ would correspond to a bond of order $p=-0.56$, i.e., 44 percent of a single bond, corresponding to the very low bond energy observed for this bond.¹⁰

C—N, C—O, N—O BONDS

Having obtained the single, double, and triple bond distances for C—C, N—N, O—O bonds, the multiple bond distances for C—N, C—O, N—O are calculated by means of the additivity rule, and in the cases where indicated the appropriate bond orders are calculated.

	p	Calc.	Obs.
C—N	1	1.48	1.47 ¹²
C=N	2	1.27	
C≡N	3	1.15	1.15 ⁷
C—O	1	1.43	1.43 ⁷
C=O	2	1.23	
C≡O	3	1.15	
CO	1.88	1.13 ⁸	1.13 ⁸
N—O	1	1.36	
N=O	2	1.17	
N≡O	3	1.065	
NO	1.16	1.15 ⁸	1.15 ⁸

P—P BONDS

The P_2 molecule in the $^1\Sigma_g^+$ ground state is triply bonded with a bond distance of 1.89Å.⁸ The single and double bond distances are calcu-

⁹ P. A. Giguere and V. Schomaker, J. Am. Chem. Soc. 65, 2025 (1943).

¹⁰ See reference (7) and O. K. Rice, *Electronic Structure and Chemical Binding* (McGraw-Hill Book Company, Inc., New York, 1940).

¹¹ P. A. Giguere, Ann. A. C. F. A. S. 9, 88 (1943).

¹² G. W. Wheland, *The Theory of Resonance* (John Wiley and Sons, Inc., New York, 1945).

lated as 2.27Å and 2.04Å, respectively. Penney³ has shown that four similar atoms at the corners of a regular tetrahedron have bonds between them of order $p=1/3$, so the calculated P—P distance in P_4 for $p=1/3$ is 2.21Å. These calculated values of 2.21Å and 2.27Å agree very well with the observations in P_4 where the P—P distance is found to be $2.21 \pm .02$ Å,¹³ and in amorphous red and black phosphorous where the P—P distance is found to be $2.28 \pm .02$ Å.¹⁴ It seems probable that the difference between these experimental values is real and not to be attributed to experimental error.

S—S BONDS

S_2 is in a $^3\Sigma$ ground state and should be similar to O_2 in its bondings. Since the S—S bond distance has been measured in H_2S_2 , $(CH_3)_2S_2$, and S_8 and found to be $2.04 \pm .02$ Å⁷ in all three molecules, the bond order is apparently the same, but does not necessarily correspond to that of a single bond. Again the bond distance in the S_2 molecule is accurately known to be 1.89Å,⁸ but its bond order is unknown. A plausible set of distances is obtained by assuming the bond order in S_2 to be 0.75. The single bond distance is then calculated to be 2.05, and the double and triple bond distances are 1.85, 1.71, respectively.

As—As BONDS

The As—As distance observed in the crystal is 2.50Å,⁷ and in As_4 it is 2.44Å.⁷ Again the bond order for As_4 as for P_4 is $p=1/3$. Taking 2.44Å as corresponding to a bond of order $p=1/3$ the calculated single, double, and triple bond distances are 2.50Å, 2.32Å, and 2.16Å, respectively. Again the difference between the values of 2.50Å and 2.44Å for the As—As distance would appear to be real and not to be attributed to experimental errors. Since the vibrational frequency and internuclear distance of both Se_2 , Br_2 are known for atoms of this row of the periodic table, Badger's rule⁷ may be employed to estimate the bond distance in As_2 where the vibrational frequency is known.⁸ The value 2.13Å is obtained

for the triply bonded As—As distance which is in as good agreement as can be expected with the value 2.16Å calculated above.

Se—Se AND Te—Te BONDS

Since the ground states of these molecules are $^1\Sigma^8$ it would appear reasonable to suppose that the molecules have double bonds. Using the observed values⁸ of 2.16Å and 2.59Å for the doubly bonded Se_2 and Te_2 molecules, respectively, the single bond distances have been calculated as 2.34Å and 2.76Å. Pauling⁷ gives these distances from x-ray measurements as 2.32Å and 2.76Å, respectively.

Unfortunately there is a lack of known multiple bond distances with which to test Eq. (4) any further but the agreement so far obtained between calculated and observed distances is within 1 percent.

GENERAL EXPRESSION FOR COVALENT BOND DISTANCE OF THE ATOMS OF THE FIRST ROW OF THE PERIODIC TABLE

By assuming a reasonable relation for the single bond distances of the first row atoms in terms of the atomic numbers of the bonded atoms it is possible to express the bond distance in the form

$$R = \left(\frac{Z - 1.50}{Z - 3.10} \right) [2/3 + 1/3(1/3)^{p/2}]$$

for all the symmetrical linkages of the first row atoms. The bond distances for unsymmetrical links may be calculated by means of the additivity rule. This equation fits all the reliable data to within 1 percent. The extensive table which may be drawn up to show this agreement is omitted for the sake of brevity.

DISCUSSION

Substituting the value for R_2 obtained in terms of p for the C—C double bond from Eq. (4) into Eq. (1) and equating Eqs. (4) and (1) it is found that

$$\frac{K_1}{K_2} = \frac{p}{1-p} \cdot \frac{(1/3)^{p/2} - (1/3)^{1/2}}{1 - (1/3)^{p/2}}$$

Evaluating K_1/K_2 for values of p between -1 and 2 it is found that K_1/K_2 has values from

¹³ L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, J. Chem. Phys. **3**, 698 (1935).

¹⁴ C. D. Thomas and N. S. Gingrich, J. Chem. Phys. **6**, 659 (1938). R. Hultgren, N. S. Gingrich, and B. E. Warren, J. Chem. Phys. **3**, 351 (1935).

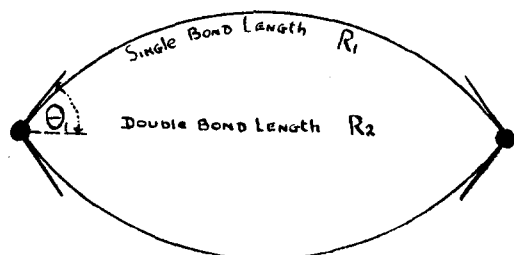


FIG. 1.

.790—.740 with the average value of 0.764, where the average deviation is ± 0.015 and greatest deviation ± 0.025 . In the theoretical development of Eq. (1) the energy was taken as a first approximation to be a parabolic function of the displacement from the equilibrium position, so that K_1/K_2 is the force constant ratio for harmonic oscillators. Pauling⁷ on the basis of Badger's rule employs a value of $1/3$ for the ratio. Lennard-Jones² uses the value 0.507 which was derived from the infra-red vibration spectra values of the fundamental modes of ethane and ethylene, and the use of suitable potential functions for the molecules. Coulson⁴ uses the value 0.765 which is obtained by substituting the value of the observed distance in acetylene in Eq. (1). Coulson justifies his choice of constant on semi-empirical grounds. Whereas Eq. (1) with Pauling's or Lennard-Jones's constants give calculated triple bond distances which are a good deal too high, use of the constant 0.765 fits the data accurately. Since this ratio appears in the part of Eq. (1) which is at most $1/4$ of the total bond distance, the greatest difference between the value of K_1/K_2 obtained above and the value used by Coulson introduces an error of about 0.8 percent in the bond distance calculations. It is difficult to believe that this agreement is entirely fortuitous, in fact the agreement obtained seems to justify in a rather indirect manner both the suitability of Coulson's choice of 0.765 for the K_1/K_2 ratio and our choice for the relationship between bond distance and bond order.

A serious objection to relation (4) exists in as much as it makes the hydrogen—hydrogen bond distances independent of bond order. That the expression is not valid for hydrogen is to be expected, however, since most approximations of this kind become more accurate with increasing atomic number.

APPENDIX

Since the tetrahedral angle is extremely well preserved in a wide variety of substituted methanes and ethanes⁷ it is not unreasonable to assume, as a first approximation, that this angle is also preserved in a double or triple bond. As an *ad hoc* model for double bond formation one may consider two normal single C—C bonds to be bent in circles* with the tetrahedral angles preserved at the nuclei as is shown in the figure. It is readily seen from the geometry of the figure that

$$R_2 = R_1 \frac{\sin \theta_1}{\theta_1} \quad (1)$$

where θ_1 is half the value of the tetrahedral angle. Similarly for the triple bond, for which the angle θ_2 is (π -tetrahedral angle), there is the relation

$$R_3 = R_1 \frac{\sin \theta_2}{\theta_2} \quad (2)$$

The angles θ_1 and θ_2 are related by the expression

$$\sin \theta_2 = [2/3(1 - \cos 2\theta_1)]^{1/2} \quad (3)$$

The general expression

$$R = R_1 \frac{\sin \theta}{\theta} \quad (4)$$

is thus indicated. Now let $\cos \theta = M^p$ where p is the bond order and M is some quantity independent of R . This choice for $\cos \theta$ satisfies Eq. (4) for $p=0$. For $p=1$, $\cos \theta_1 = M$ and for $p=2$, $\cos \theta_2 = M^2$. Substituting these values in (3) it is found that $M = (1/3)^{1/2}$ and thus $\cos \theta = (1/3)^{p/2}$. Expanding $\sin \theta$ and $\cos \theta$ in terms of θ and neglecting powers of θ greater than the second, Eq. (4) becomes

$$R = R_1 [2/3 + 1/3(1/3)^{p/2}]. \quad (5)$$

It would seem that this crude multiple CC bond model has been adequate for evaluating M and the first two coefficients of a very probable general expression for the bond distance which has the form $R = R_1(a_0 + a_1M^p + a_2M^{2p} + \dots)$.

Equation (5) may be tested for CC bonds by assuming the accurately known triple bond distance 1.205\AA ⁷ and calculating the double and

* A rod or spring having stretching and bending force constants is reasonably approximated by a circle when equal bending movements are applied at its ends.

single CC bond distances. The calculated values are 1.33Å and 1.55Å for the double and single bond distances, respectively. The experimental values are also 1.33Å⁷ and 1.55Å,⁷ respectively.

This very good agreement makes it of interest to attempt a more general expression for M which would then provide an expression suitable for all multiple bond distances. The form of Kavanau's relation [Eq. (2) of the text] indicates the choice $M = (n-1/n+1)^{1/2}$ which is satisfied for CC bonds where $n=2$. The relation $R = R_1[2/3 + 1/3(n-1/n+1)^{1/2}]$ is thus obtained.

Another relation which may be derived from this crude model is that between force constants of multiple CC bonds.

The potential energy of the double bond may be written as $(K_2/2)\Delta R_2^2$ for small displacements from the equilibrium position, where K_2 is the force constant of the double bond. From the figure, the energy can also be written as $(2K_1/2)\Delta R_1^2$ (since the tetrahedral angles are preserved) where K_1 is the single bond force

constant. From (1) $\Delta R_1/\Delta R_2 = \theta_1/\sin\theta_1$ whence $K_2 = 2K_1(\theta_1/\sin\theta_1)^2$. Similarly for triple bonds $K_3 = 3K_1(\theta_2/\sin\theta_2)^2$, where K_3 is the triple bond force constant. Putting in the values of θ_2 and θ_1 of 70.5° and 54.75° one obtains $K_3:K_2:K_1 = 5:2.7:1$ which is of the same order of accuracy as the ratio derived from Badger's rule,⁷ viz: $K_3:K_2:K_1 = 5:2.5:1$.

That the circular bond notion with preserved tetrahedral angles is internally consistent is further demonstrated by the bond energy/bond distance relation which can be derived from it. (See Letter to the Editor, this Journal.)

Though this model was useful in obtaining relations which apparently represent the data, its success is totally unwarranted on the basis of present day valence theory. The author can suggest no reason for the apparent physical significance of this model.

The author takes pleasure in acknowledging the helpful discussions with members of the Yerkes Observatory of the University of Chicago.

The Mechanism of the Luminescence of Solids*

FERD E. WILLIAMS**

RCA Laboratories, Princeton, New Jersey

AND

HENRY EYRING***

Princeton University, Princeton, New Jersey

(Received March 3, 1947)

In this paper, effort is directed toward explaining various diverse luminescent properties of solids in terms of a simple model of potential energy *versus* configuration coordinate. Three states of different multiplicities—a normal, metastable and an emitting state—are involved. The luminescent process consists of the excitation of an electron to the metastable level, the activated release of the electron to the emitting level, and a forbidden transition between the emitting and the ground state. With high excitation energy, the metastable state is bypassed. At high temperatures, the electron in the metastable state surmounts a

larger potential barrier to undergo radiationless recombination with the activator atom.

Among those significant phenomena that have been measured experimentally and treated quantitatively by calculations based on this model are the temperature dependence of luminescent efficiency and the effect of type and wave-length of excitation on this temperature dependence; the three types of phosphorescence—spontaneous, metastable, and recombination phosphorescence; the phenomena of two-stage afterglow and the effect of type of excitation and temperature on the two stages; the

* Part of a dissertation submitted by Ferd E. Williams to Princeton University in partial fulfillment for the degree of Doctor of Philosophy. Portions of this article are based upon work performed for the Office of Scientific Research and Development under Contract NDCrc-150 and Contract OEMsr-440. Presented in part at the American Physical Society Meeting in New York in January, 1946.

** Now Assistant Professor of Chemistry, University of North Carolina, Chapel Hill, North Carolina.

*** Now Dean of the Graduate School, University of Utah, Salt Lake City, Utah.