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# Comparison of Relations between Covalent Bond Order, Energy, and Interatomic Distance for Carbon-Carbon Bonds

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The results given by the relations of Bernstein, Gordy, and the author between interatomic distance and energy and order are compared for carbon-carbon bonds. The predictions of these relations for the benzene and graphite bond orders are compared with the results given by quantum mechanical calculations, while those for the energies are compared with experimental values.

DURING the last several years a number of empirical relations between covalent bond order, energy and interatomic distance have been proposed. It seems desirable to compare the values given by these relations for carbon-carbon bonds.

The author<sup>1</sup> has advanced the relation between bond order  $N$ , and the interatomic distance  $R$ ,

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

where  $n_1$  and  $n_2$  are the principal quantum numbers of the valence electrons of the bonded atoms and  $a$  and  $b$  are constants. Lagemann<sup>2</sup> proposed a generalized modification of (1) by setting  $a = k_1/(Z_1 + Z_2)$ ,  $b = k_2/(Z_1 + Z_2)$ .  $k_1$  and  $k_2$  are constants for atom pairs having the same values of  $n_1$  and  $n_2$ , and  $Z_1$  and  $Z_2$  are the atomic numbers of the bonded atoms. A simplified relation of similar form recently proposed by Bernstein<sup>3</sup> for symmetric bonds is

$$R = R_1 \left[ c + (1 - c) \left( \frac{n - 1}{n + 1} \right)^{(N-1)/2} \right]. \quad (2)$$

$R_1$  is the single bond distance.

Of these equations involving  $N$  as an exponent, (2) with  $c = \frac{2}{3}$  is used to prepare Tables I and II.

A relation recently proposed by Gordy<sup>4</sup> is

$$N = dR^{-2} + e. \quad (3)$$

A least squares determination of  $d$  and  $e$  using the C-C, C=C, and C≡C distances (Table I) gives  $d = 7.475$ ,  $e = -2.179$ .\*

A parabolic relation proposed by the author<sup>5</sup> is

$$(1 - N/4)^2 = f(R - g), \quad (4)$$

where  $f = 1.488$  and  $g = 1.162$ .

<sup>1</sup> J. Lee Kavanau, J. Chem. Phys. 12, 467 (1944).

<sup>2</sup> Robert T. Lagemann, J. Chem. Phys. 14, 743 (1946).

<sup>3</sup> H. J. Bernstein, J. Chem. Phys. 15, 284 (1947).

<sup>4</sup> Walter Gordy, J. Chem. Phys. 15, 305 (1947).

\* All the constants used, except  $c = \frac{2}{3}$ , were evaluated by the author using the method of least squares and the single, double and triple bond data. The calculations are given to four figures for comparative purposes.

<sup>5</sup> J. Lee Kavanau, J. Am. Chem. Soc. 69, 1827 (1947).

In Table I the distances given by (2), (3), and (4) are tabulated together with the percent  $MD$  (mean deviation) of these values from the experimental values.

Using the  $AO$  (atomic orbital) treatment, Penney<sup>6</sup> has calculated the benzene and graphite carbon-carbon bond orders to be 1.623 and 1.45, respectively. Using the  $MO$  (molecular orbital) method Coulson<sup>7</sup> obtained the values 1.667 and 1.53, respectively. In Table II the values predicted by (2), (3), and (4) for these bond orders are compared with the above values ( $R_{\text{benzene}} = 1.39\text{\AA}$ ,  $R_{\text{graphite}} = 1.42\text{\AA}$ ).<sup>8</sup>

The author<sup>9</sup> has proposed the parabolic-type relation

$$(1 - N/4)^m = 1 - (E/q). \quad (5)$$

$E$  is the energy of the bond of order  $N$ . Using the single, double and triple carbon-carbon bond energy values (Table III) calculated by Pitzer<sup>10</sup> upon the basis of the newly determined heat of atomization of carbon,<sup>11,12</sup>  $m = \frac{3}{2}$ ,  $q = 225.8$ . (4) and (5) give

$$(1 - E/225.8)^{4/3} = 1.488(R - 1.162). \quad (6)$$

Bernstein<sup>13</sup> has proposed the relation

$$E = E_1 N \left[ 1 - s \left( \frac{R_1}{R} \right)^2 \left( \frac{R_1 - R}{R_1} \right) \right]. \quad (7)$$

$E_1$  and  $R_1$  are the C-C bond energy and distance and  $s = 0.492$ .

Gordy<sup>4</sup> has proposed the relation

$$E = tR^{-2} + u. \quad (8)$$

$t = 441.9$ ,  $u = -106$ .

In Table III the carbon-carbon single, double and triple bond energies given by (6), (7), and (8) are

<sup>6</sup> W. G. Penney, Proc. Roy. Soc. A158, 306 (1937).

<sup>7</sup> C. A. Coulson, Proc. Roy. Soc. A169, 413 (1939).

<sup>8</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1948).

<sup>9</sup> J. Lee Kavanau, J. Chem. Phys. 15, 77 (1947).

<sup>10</sup> K. S. Pitzer, J. Am. Chem. Soc. 70, 2140 (1948).

<sup>11</sup> L. Brewer, P. W. Gilles, and F. A. Jenkins, J. Chem. Phys. 16, 797 (1948).

<sup>12</sup> L. Gerö, J. Chem. Phys. 16, 1011 (1948).

<sup>13</sup> H. J. Bernstein, J. Chem. Phys. 15, 339 (1947).

given together with those predicted for benzene and graphite.

Using the *MO* method and allowing for hyperconjugation, Mulliken *et al.*<sup>14</sup> have found  $N_{\text{benzene}} = 1.77$ ,  $N_{\text{graphite}} = 1.65$ . For a pure single, double and triple bond the distances of Table IV have been proposed. Using the latter values in (2), (3), (4) gives  $c = 0.6466$ ,  $d = 6.93$ ,  $e = -1.777$ ,  $f = 1.330$ ,  $g = 1.159$ , with the results given in Table IV.

Because of the magnitude of the experimental error, (2), (3), (4), (6), (7), (8) may all be said to fit the single-, double-, and triple-bond data quite well. Bernstein's relation (2), since it involves the single bond distance as a parameter, requires the determination of but one constant ( $c$ ). Upon the basis of the model used by Bernstein in arriving at (2) the

whereas the curves of (7) and (5) pass through the point  $(E, N) = (0, 0)$ . This is because Gordy has assumed a linear relation between  $E$  and  $N$  after the linear Coulson-Lennard-Jones relation between  $E$  and  $p$ , the mobile bond order. Such a relation fits the data with the rather large *MD* of 2 percent. Since the plot of the energy values against the bond order indicates a non-linear curve passing through the origin, this is possibly a disadvantage of the Gordy relations.

The author's relations (4), (5), (6) maximize the energy and minimize the interatomic distance for a hypothetical quadruple bond. (4) gives the best agreement with the benzene and graphite *MO* bond orders, and leads to the simple relation  $3R_1 + 5R_3 = 8R_2$  for all bonds. (6) has the possible disad-

TABLE I. Comparison of the interatomic distance-order relations.

	C-C	C=C	C≡C	%MD
Experimental <sup>a</sup> interatomic distance	1.54A	1.33A	1.204A	—
Equation (4)	1.540	1.330	1.2040	0.00
Equation (2)	1.540	1.323	1.198	0.34
Equation (3)	1.533	1.337	1.201	0.41

<sup>a</sup> See Reference 8 of text.

TABLE II. Comparison of the carbon-carbon bond orders predicted for benzene and graphite.

	$N_{\text{benzene}}$	$N_{\text{graphite}}$
Penney	1.623	1.45
Coulson	1.667	1.53
Equation (4)	1.670	1.522
Equation (3)	1.686	1.528
Equation (2)	1.629	1.481

value  $c = \frac{2}{3}$  is taken for all symmetric bonds. The essential significance of this is that in any given row of the periodic table the single, double and triple bond distances bear a constant ratio to one another. (2) has the possible disadvantage of leading to benzene and graphite bond order values somewhat below those of the *MO* treatment (which is probably to be preferred to the *AO* method). Bernstein's relation (7), since it involves the bond order and the single bond distance, also requires the determination of but one constant ( $s$ ). This relation gives values for the benzene and graphite bond energies in good agreement with the experimental values.

Gordy's relations (3) and (8) give good agreement with both the benzene and graphite experimental bond energies and *MO* orders. However, (8)+(3) give a zero order bond an energy of 23 kcal./mole,

<sup>14</sup> R. S. Mulliken, C. A. Rieke, and W. G. Brown, J. Am. Chem. Soc. 63, 41 (1941).

TABLE III. Comparison of the interatomic distance-energy relations.

	$E_1$	$E_2$	$E_3$	%MD	$E_{\text{benzene}}$	$E_{\text{graphite}}$
Experimental ( $\frac{\text{kcal.}}{\text{mole}}$ )	80 <sup>a</sup>	145 <sup>a</sup>	198 <sup>a</sup>	—	120.2 <sup>b</sup>	113.6 <sup>c</sup>
Equation (7)+(2)	80.00	145.6	197.8	0.17	122.6	113.1
Equation (8)	80.33	143.9	198.8	0.52	122.7	113.1
Equation (6)	79.14	146.0	197.6	0.66	125.2	115.7

<sup>a</sup> See reference 10 of text.

<sup>b</sup> Calculated from the energy of formation of benzene from atoms using the new energy values (see references 10 and 11).

<sup>c</sup> Two-thirds of the heat of atomization of graphite (170.39, see reference 11).

TABLE IV. Comparison of the interatomic distance order relations in the Mulliken-Rieke-Brown system.

	Distances				Orders		
	C-C	C=C	C≡C	%MD	Ben- zene	Graph- ite	%MD
Mulliken <i>et al.</i>	1.58A	1.35A	1.204A	—	1.77	1.65	—
Equation (3)	1.578	1.353	1.203	0.14	1.801	1.651	0.91
Equation (4)	1.581	1.347	1.206	0.15	1.780	1.641	0.55
Equation (2)	1.580	1.344	1.208	0.26	1.758	1.616	1.48

vantage of leading to values of the energy of the benzene and graphite bonds which are 4.2 percent and 2 percent greater than the experimental values. It should be pointed out, however, that a second method of calculating the energy of the benzene bonds gives larger values than the method utilizing the energy of formation of benzene from atoms. Thus, the *MO* or *AO* method may be used, after the treatment discussed by Pauling.<sup>8</sup> If  $\alpha$  is the resonance energy associated with the interchange of two electrons between two  $p_z$  orbitals and  $\beta$  is the resonance energy of one electron between two  $p_z$  orbitals, then  $\beta \cong 0.59\alpha$ . If  $\alpha$  is taken to be  $E_{C=C} - E_{C-C} = 65$  kcal./mole, the two treatments give the benzene bond an energy of 125.2 and 124.5 kcal./mole, respectively. If the interchange energy  $\alpha$  is taken to be 80–90 percent of  $E_{C=C} - E_{C-C}$  the values are reduced by 1.3–2.6 kcal./mole.