A Relation Between Bond Multiplicity and Interatomic Distance

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A Relation Between Bond Multiplicity and Interatomic Distance

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IN a note bearing the above title, Kavanau[1] has advanced a most useful relation connecting the interatomic distances of covalent bonds to the bond multiplicity. He suggests that

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

where D is the interatomic distance in angstroms; a and b are constants determined by the specific atom pair; N is the bond multiplicity; and n_1 and n_2 are the principal quantum numbers of the valence electrons in the bonded atoms.

Examination of the constants a and b given by Kavanau shows them to be roughly related to the sum Z of the atomic numbers of the atoms making up the bonded pair. If we set b proportional to Z and a inversely proportional to Z, we have

$$D=\frac{K_1}{Z}+K_2Z\left(\frac{n_1+n_2-1}{n_1+n_2+1}\right)^N, \tag{2}$$

TABLE 1. Observed and calculated bond lengths.

Molecule	Atom pair	Bond order	Bond length in A D obs.	Bond length in A D calc.	Percent deviation
C_2H_6	CC	1.11	1.55[c]	1.50	3.2
CH_3CCH	CC	1.23	1.46[c]	1.47	0.7
C_6H_6	CC	1.78	1.39[c]	1.36	2.2
C_2H_4	CC	2.12	1.33[c]	1.31	1.5
CH_3CCH	CC	2.89	1.21[c]	1.22	0.8
C_2H_2	CC	3.00	1.204[a]	1.21	0.8
CH_3F	CF	1.00	1.396[a]	1.44	2.9
CH_3NH_2	CN	1.00	1.47[a]	1.49	1.4
HCN	CN	3.00	1.154[a]	1.15	0.0
CH_3OH	CO	1.00	1.43[a]	1.46	2.1
H_2CO	CO	2.00	1.21[a]	1.23	1.7
F_2	FF	1.00	1.435[a]	1.42	1.4
NH_2NH_2	NN	1.00	1.47[b]	1.46	0.7
$(C_6H_5N)_2$	NN	2.00	1.23[b]	1.23	0.0
N_2	NN	3.00	1.095[a]	1.09	1.0
OF_2	OF	1.00	1.41[a]	1.42	0.7
				Average percent deviation	1.3

[a] W. Gordy, J. Chem. Phys. **14**, 305 (1946).
[b] J. L. Kavanau, J. Chem. Phys. **12**, 467 (1944).
[c] R. S. Mulliken, C. A. Rieke, and W. G. Brown, J. Am. Chem. Soc. **63**, 41 (1941).

where K_1 and K_2 are considered constant for all pairs of atoms having the same value of n_1 and the same value of n_2. This modification covers more cases with two constants than does Kavanau's original relation, and seems to have considerable merit in empirically correlating bond length and multiplicity. Figure 1 shows the linearity of DZ *versus* $Z^2\,(3/5)^N$ for pairs of atoms for which $n_1=n_2=2$.

Table I gives a list of atom pairs whose valence electrons

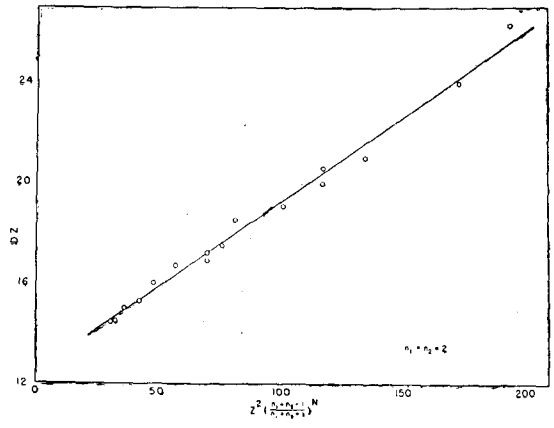

FIG. 1.

possess principal quantum numbers of 2. Included in the table are values of the observed interatomic distances and values of the interatomic distance calculated from Eq. (2) using $K_1=12.45$, and $K_2=0.0676$. The values of K_1 and K_2 were obtained by a least squares treatment of the experimental bond lengths. The combination $n_1=n_2=2$ was selected at random for presentation here, but other combinations of the principal quantum numbers appear on preliminary inspection to yield similar results.

It will be noted that the proposed relation holds for isotopic molecules where Z and D are constant. However, it does not care in a precise way for cases such as CO and N_2 where Z is the same for both molecules but the observed interatomic distance is clearly not.

[1] J. L. Kavanau, J. Chem. Phys. **12**, 467 (1944).