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A CORRELATION OF BOND LENGTH WITH STRETCHING
FREQUENCY FOR CARBON-OXYGEN AND CARBON-NITROGEN
SYSTEMS.

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A CORRELATION OF BOND LENGTH WITH STRETCHING FREQUENCY
FOR CARBON-OXYGEN AND CARBON-NITROGEN SYSTEMS

by

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A CORRELATION OF BOND LENGTH WITH STRETCHING FREQUENCY
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ABSTRACT

Graphical correlations of stretching frequencies with bond lengths for C-O and C-N systems in various compounds are presented. The average deviations of the points from the respective curves are 0.023 and 0.020 Å.

INTRODUCTION

Many investigations are recorded in the literature concerning the interdependence of fundamental and derived molecular parameters, such as bond lengths, bond energies, bond orders, electronegativities, and force constants.¹⁻²⁰ For the most part these discussions

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have been restricted to diatomic molecules and bonds between identical atoms. Recently, Rundle and Parasol¹⁶ and Lord and Merrifield¹⁷ showed that O-H stretching frequencies can be correlated with O-H...O bond distances in hydrogen bonded systems, and Margoshes et al.¹⁸ found that the stretching frequency of carbon-oxygen bonds in carbonyl compounds is similarly related to the bond length. In the present paper the latter correlation is extended to include carbon-oxygen single bond systems. In addition it is shown that the stretching frequency of carbon-nitrogen bonds

in single, double, and triple bond systems can be related to bond lengths by a single curve.

EXPERIMENTAL

The bond length values were taken from rotational spectra data (both in the microwave and lower wave length regions), and from electron-diffraction and x-ray structure determinations. The references for the stretching frequencies are either to an assignment in the literature or a recorded spectrum from which our assignment was made. The absence of a specific reference indicates that the frequency was taken from a spectrum run on a Baird Associates model B double beam recording infrared spectrophotometer.

DISCUSSION

The bond length-frequency correlations are presented graphically in Figures 1 and 2. The points are identified in Tables I and II. The vertical lines on the graphs represent theoretically estimated bond length errors as recorded in the literature for the specific compound. The deviations (δ) listed in the tables refer to the distance from the particular point to the curve. Care was taken to obtain spectra of the compounds in the same physical states as that on which the structural determinations were made.

The shapes of the curves were determined by using bond lengths obtained from three dimensional x-ray, spectroscopic

Fig. 1 - Relation between bond length and stretching frequency for carbon-oxygen systems. $\odot$ --Three dimensional x-ray, electron diffraction and spectroscopic bond lengths; $\triangle$ --Two dimensional x-ray bond lengths.

Fig. 2 - Relation between bond length and stretching frequency for carbon-nitrogen systems. $\odot$ --Three dimensional x-ray, electron diffraction and spectroscopic bond lengths; $\triangle$ --Two dimensional x-ray bond lengths; $\square$ --Dicyandiamide bond lengths.

and electron-diffraction structure studies. Bond lengths obtained from two dimensional x-ray structure studies were then plotted on the resulting curves. Because of the order of magnitude of the error inherent in a crystallographic structure analysis, a least mean squares adjustment of the data to a curve was not considered practical. However, approximately one-half of all the points, for both groups under study, do fall on the curves within the respective limits of error. It should be noted, in passing, that an extraordinarily large number of C-N bond lengths were given in the literature as 1.47 Å. The frequencies obtained for these bond lengths varied in such a fashion as to indicate a possible maximum bond length for the C-N group and a corresponding independence of stretching frequency on bond length below a frequency of approximately 1100 cm^{-1} . The linear plot shown, however, was found to fit better statistically than a smooth curve which became frequency independent at 1.47 Å. A statistical analysis of the curves is given in Table III.

The extension of the carbon-oxygen data to include single bonds produces a curve with a slightly different curvature than the more restricted version previously reported.¹⁸ The carbon-nitrogen plot is essentially linear.

Vibrational coupling may cause marked variations in correlations of this type (when natural vibrational frequencies of neighboring bonds are similar), but no consistent deviations of this nature have been observed. The several combinations of the C-N group with oxygen atoms, sulfur atoms, or the methyl radical are an example of this. In Table II, the deviations of these various groups are seen to be of a random nature.

An application of these relations occurs in the case of the molecule dicyandiamide, which has five different C-N bonds. The infrared spectrum exhibits four probable C-N absorption bands. Since two of the bonds have similar lengths (1.36 and 1.37 Å), a reasonable interpretation is that their respective stretching frequencies are close enough to be either unresolvable or degenerate. This leads to a satisfactory fit of the dicyandiamide points to the curve.

An extension of these correlations to other simple systems does not appear to be feasible. Sufficient bond length data are available for boron-hydrogen, carbon-hydrogen, carbon-sulfur, and nitrogen-oxygen systems, but multiple stretching modes are encountered and it is not possible to unequivocally decide which single frequency or combination of frequencies is comparable to a pure valence stretching frequency.

Table I

Bond Length-Frequency Data for Carbon-Oxygen Bond Systems

Compound	Bond Length (Å)		Frequency (cm ⁻¹)	δ (Å)
Hydroxy-L-proline	1.26±0.03	(1)	1580 + 1640 +	-0.002 +0.013
L-Threonine	1.25±0.02	(2)	1620	-0.002
Salicylic acid	1.24±0.01	(3)	1665	+0.000
	1.33±0.01	(3)	1440	+0.031
Urea	1.26±0.01	(5)	1665	+0.020
Formaldehyde	1.21±0.01	(6)	1744	-0.009
Phosgene	1.166±0.002	(8)	1827	-0.034
Ketene	1.16±0.01	(10)	2153	+0.004
Nickel carbonyl	1.15±0.03	(12)	2045	-0.014
Carbonyl sulfide	1.16±0.05	(14)	2050.5	-0.004
Carbon monoxide	1.128	(16)	2169.8	-0.027
Borine carbonyl	1.13±0.01	(18)	2164	-0.025
Methanol	1.434	(20)	1033	+0.007
Trioxane	1.42±0.02	(22)	1074	+0.008
Methyl acetate	1.36±0.04	(24)	1246	+0.005
	1.22±0.03	(24)	1738	+0.000
Methyl formate	1.47±0.04	(24)	910	+0.000
	1.37±0.04	(24)	1212	+0.004
Uracil	1.230	(25)	1719	+0.004
	1.241	(25)	1665	+0.000
Formic acid	1.23	(27)	1794	+0.023
	1.36	(27)	1105	-0.042
Oxalic acid dihydrate	1.254±0.008	(29)	1666	+0.015
	1.299±0.014	(29)	1241	-0.058
1,4-Dioxane	1.42±0.02	(22)	880	-0.061
Carbon suboxide	1.19	(31)	2190(s) 2258(as)	+0.036 +0.038
DL-Serine	1.42±0.02	(33)	1032	-0.007
	1.265±0.02	(33)	1570	+0.000
β -Succinic acid	1.25±0.02	(35)	1641	+0.004
Acetyl chloride	1.22±0.04	(37)	1802	+0.015
Acetone	1.22±0.03	(38)	1709	-0.008
Carbon dioxide	1.1632	(40)	2349.3(as)	+0.012
Anthraquinone	1.15±0.02	(41)	1673	-0.088
Adipic acid	1.23±0.04	(43)	1700	+0.000
	1.29±0.04	(43)	1425	-0.013
Maleic acid	1.20±0.02	(44)	1705	-0.029
	1.27±0.02	(44)	1437	-0.030
p-Chlorobenzoic acid	1.22±0.05	(45)	1685	-0.015
	1.24±0.05	(45)	1425	-0.063

Table I. (Continued)

Compound	Bond Length (Å)	Frequency (cm ⁻¹)	(A)
p-Benzoquinone	1.23±0.04 (46)	1664 (42)	-0.010
Ethanol	1.40 (47)	1067 (21)	-0.015
Nicotinic acid	1.18±0.02 (48)	1700 (4)	-0.051
Thioacetic acid	1.24±0.04 (49)	1696 (50)	+0.008
Furoic acid	1.16±0.05 (51)	1663	-0.081
p-Aminophenol	1.47 (52)	1083	+0.061
Acetic acid dimer	1.36±0.04 (53)	1412 (54)	+0.053
	1.25±0.03 (53)	1704 (54)	+0.021
Two Dimensional Crystallographic Data			
Calcite	1.31±0.01 (55)	1430	+0.008
Glycylglycine	1.23±0.02 (56)	1570	-0.035
	1.21±0.02 (56)	1650	-0.034
DL-Alanine	1.20±0.02 (57)	1597	-0.058
Sodium formate	1.27±0.04 (58)	1352 (s) (59)	-0.053
		1584 (as) (59)	+0.009
Glycine	1.26±0.02 (60)	1587 (34)	+0.000
Acetaldehyde	1.22±0.01 (61)	1740 (62)	+0.000
Glyoxal	1.20±0.01 (63)	1730 (64)	-0.023
Methyl nitrite	1.44±0.02 (65)	1019 (66)	+0.008
Methyl nitrate	1.44±0.03 (65)	984 (67)	-0.004
Oxalyl chloride	1.20 (68)	1757 (69)	-0.016
Tetrahydrofuran	1.43±0.03 (70)	1068	+0.015
Acetamide	1.28 (71)	1694 (26)	+0.048
Acetyl bromide	1.13± (72)	1813 (26)	-0.073

*Assignment uncertain.

The two symbols (s) and (as) refer to symmetric and antisymmetric stretching frequencies, respectively. In general the antisymmetric frequency fits the curve best.

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Table II

Bond Length-Frequency Data for Carbon-Nitrogen Bond Systems

Compound	Bond Length (Å)	Frequency (cm ⁻¹)	δ (Å)
Cyanogen bromide	1.158 (1)	2187 (2)	+0.000
Cyanogen chloride	1.163 (1)	2213 (3)	+0.012
Cyanogen iodide	1.159 (1)	2158 (2)	-0.007
Cyanuric acid	1.345 (4)	1460 (5)	-0.012
Urea	1.34 $\pm$ 0.01 (4)	1477 (6)	-0.010
Methyl amine	1.48 (7)	1041 (8)	+0.009
Methyl isocyanide	1.426 (9)	1130 (10)	-0.022
	1.167 (9)	2166 (10)	+0.003
Dimethylamine	1.47 $\pm$ 0.02 (7)	1082 (6)	+0.011
Ethyl amine	1.47 $\pm$ 0.02 (7)	893 (6)	-0.042
Dimethylhydrazine	1.47 $\pm$ 0.03 (11)	961 (12)	-0.023
Diethylamine	1.47 $\pm$ 0.02 (7)	1049 (6)	+0.001
Hexamethylenetetramine	1.48 $\pm$ 0.01 (13)	1048 (14)	+0.010
Triethylamine	1.47 $\pm$ 0.02 (7)	994	-0.014
p-Dinitrobenzene	1.48 $\pm$ 0.03 (15)	1105	+0.026
Isatin	1.38 $\pm$ 0.03 (16)	1327	-0.013
	1.35 $\pm$ 0.03 (16)	1573	+0.024
p-Aminophenol	1.39 (17)	1487	+0.042
Hydrogen cyanide	1.1574 (2)	2110 (18)	-0.022
Acetoxime	1.29 $\pm$ 0.03 (19)	1683 (6)	-0.006
Acetamide	1.38 (20)	1399 (6)	+0.006
Dimethylglyoxime	1.27 $\pm$ 0.02 (21)	1628	-0.041
Uracil	1.375 $\pm$ 0.01 (22)	1408 (6)	+0.004
	1.34 $\pm$ 0.01 (22)	1510 (6)	-0.003
Methylammonium chloride	1.465 $\pm$ 0.01 (23)	1003 (24)	-0.017
1,5-Dinitronaphthalene	1.35 $\pm$ 0.03 (25)	1542	+0.016
Aniline hydrochloride	1.35 (26)	1493	+0.002
Methyl isothiocyanate	1.47 (27)	1087 (28)	+0.011
	1.22 (27)	2106 (28)	+0.040
Methyl thiocyanate	1.21 (27)	2153 (28)	+0.043
Alanine	1.42 $\pm$ 0.03 (29)	1237 (6)	+0.002
Glycine	1.39 (29)	1330 (30)	-0.003
syn-p-Chlorobenzaldoxime	1.31 (31)	1650 (32)	+0.005
Isothiocyanic acid	1.21 $\pm$ 0.01 (33)	1963 (34)	-0.009
Nicotinic acid	1.34 $\pm$ 0.01 (35)	1571	+0.014
Dicyanoacetylene	1.14 (36)	2287 (37)	+0.010
Oxamide	1.315 $\pm$ 0.004 (38)	1613 (39)	+0.000
Thiocyanate ion	1.15 (2)	2066	-0.041
DL-Serine	1.49 $\pm$ 0.02 (40)	1032 (41)	+0.016

Table II (Continued)

Compound	Bond Length (Å)	Frequency (cm ⁻¹)	δ (Å)
Two Dimensional Crystallographic Data			
Nitromethane	1.47±0.02 (42)	1090 (6)	+0.012
Methyl azide	1.47±0.02 (43)	914 (6)	-0.036
Tetranitromethane	1.47±0.02 (44)	862 (45)	-0.050
Methyl cyanide	1.16±0.03 (46)	2267.3 (10)	+0.024
Methyl isocyanate	1.47±0.03 (47)	870 (48)	-0.047
	1.19±0.03 (47)	2232 (48)	+0.045
Cyanogen	1.16±0.02 (46)	2235 (2)	+0.015
Pyrrole	1.42±0.02 (49)	1018 (6)	-0.057
Pyridine	1.37±0.03 (49)	1581 (6)	+0.046
Diketopiperazine	1.33±0.03 (50)	1470 (51)	-0.024
	1.41±0.03 (50)	1260 (51)	-0.001
Melamine	1.35±0.02 (52)	1481 (53)	-0.001
Dicyandiamide	1.22±0.02 (54)	2156	+0.054
	1.28±0.02 (54)	1628	-0.031
	1.36±0.02 (54)	1530	+0.032
	1.37±0.02 (54)		+0.022
	1.34±0.02 (54)	1568	+0.013
Cyanic acid	1.19±0.03 (47)	2180 (55)	+0.030
Azomethane	1.47±0.06 (56)	1110 (57)	+0.016

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Table III

Statistical Analysis of the Curves

System	Number of Points	Maximum Deviation (A)	Average Deviation (A)	Number of Deviations Less Than 0.02 A	Number of Points on Curve Within Experimental Error
C-O	64	0.088	0.023	38	32
C-N	58	0.057	0.020	34	26