Theoret. Chim Acta (Berl.) 66, 365–373 (1985)

THEORETICA CHIMICA ACTA

An empirical scheme for evaluating *in situ* bond energy from MNDO data

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The *in situ* bond energy is evaluated from the resonance integral contribution to energy with a correction term of monatomic energy obtained from MNDO calculation. The sum of the *in situ* bond energies in a molecule is expected to be equal to its atomization energy. Root-mean-square error of heat of formation calculated from *in situ* bond energy for seventy nine molecules containing hydrogen, carbon, nitrogen, oxygen, and fluorine amounts to 5.5 kcal/mol. Correlations of *in situ* bond energy with contributional bond energy, bond dissociation energy, isolated stretching frequency, and bond length are performed and discussed.

Key words: Bond energy, *in situ*, from MNDO—bond strength, general measure of—heat of formation, calculation of ~—*in situ* bond energy

1. Introduction

A general measure of bond strength is of great importance for interpreting the chemical behavior of molecules. There have been structural, thermodynamical, and quantum chemical measures of bond strength. Bond length is a good measure of bond strength in the structural view. Stretching frequency can also serve as a measure of bond strength [1]. In the thermodynamical view, bond dissociation energy and contributional bond energy are the most common measures of bond strength. In the quantum chemical view, various measures of bond strength, such as the Mulliken overlap population [2], the diatomic contribution to energy [3], the resonance integral contribution [4], etc., are available.

The structural and quantum chemical measures can be used to compare bonds between two specified kinds of atom, e.g. to compare various CN bonds, but cannot be used to compare bonds of various kinds of atom, e.g. to compare CH bonds with CN bonds. Bond dissociation energy can be used to compare various kinds of bond. However, it depends on the redistribution of the electrons after breaking of the bond, so it is not an *in situ* measure of bond strength. Contributional bond energy, although not depending on the species after breaking, is only an average for a kind of bond, so it cannot characterize individual bonds. Chung-Phillips [5] proposed a scheme for calculating bond energy from CNDO data, but its application seems rather restricted. Therefore, it is necessary to find a general measure of bond strength.

2. Scheme

The MNDO resonance integral contribution to energy, E^R, turned out to be a good measure of bond strength, but not very good in correlation with contributional bond energy [6] for the following reasons. On the one hand, the contributional energy is determined on an unreasonable postulate that various CH bonds have the same bond energy. On the other hand, the MNDO resonance integral contribution is not an overall measure of bond strength: Firstly, it is not a measure for comparing various kinds of bond. For example, OH bonds are generally believed to be stronger than NH bonds, whereas it has been found that $-E^R_{\mathrm{OH}} < -E^R_{\mathrm{NH}}$. Secondly, the MNDO monatomic energy also makes some contribution to bond strength [6].

We attempt to find an empirical scheme for evaluating *in situ* bond energy from the MNDO data including resonance integral contribution and monatomic energy, expecting that the sum of the bond energies is equal to the atomization energy. For two specified kinds of atoms, A and B, we assume that the bond energy E^B_{AB} depends quadratically on the resonance integral contribution E^R_{AB} with a correctional term depending on the monatomic energies E_{A} and E_{B}:

$$E^B_{\mathrm{AB}} = k_{\mathrm{AB}} + a_{\mathrm{AB}} E^R_{\mathrm{AB}} + b_{\mathrm{AB}} (E^R_{\mathrm{AB}})^2 - c_{\mathrm{AB}} (F_{\mathrm{A}} + F_{\mathrm{B}}), \tag{1}$$

where k_{AB}, a_{AB}, b_{AB}, and c_{AB} are empirical constants depending on the kinds of atom A and B; F_{A} and F_{B} depend on the monatomic energy E_{A} and E_{B}, respectively.

The meaning of F_{A} is as follows. The monatomic energy of hydrogen depends only on the net charge Q_{H} in the MNDO method:

$$E_H = U_{\mathrm{SS}}(1 - Q_{\mathrm{H}}) + \tfrac{1}{4} g_{\mathrm{SS}} (1 - Q_{\mathrm{H}})^2, \tag{2}$$

where $U_{\mathrm{SS}} = -0.43757$ Hartree, $g_{\mathrm{SS}} = 0.47218$ Hartree [7]. We assume a basic dependence of E_{A} on the net charge Q_{A} for an atom other than hydrogen in the form of $a_{\mathrm{A}} + b_{\mathrm{A}} Q_{\mathrm{A}} + c_{\mathrm{A}} Q_{\mathrm{A}}^2$, while F_{A} is the deviation: $F_{\mathrm{A}} = E_{\mathrm{A}} - (a_{\mathrm{A}} + b_{\mathrm{A}} Q_{\mathrm{A}} + c_{\mathrm{A}} Q_{\mathrm{A}}^2)$. It is obvious that the constant term a_{A} can be combined into k_{AB} in Eq. 1, so we adopt

$$F_{\mathrm{A}} = E_{\mathrm{A}} - (b_{\mathrm{A}} Q_{\mathrm{A}} + c_{\mathrm{A}} Q_{\mathrm{A}}^2). \tag{3}$$

The constants should be determined empirically from the data of atomization energy and the MNDO data. Such a great number of indeterminate constants will lead to instability in their optimization. The number has thus to be reduced as follows:

(1) For CH, NH, OH, and OF bonds there is only a little different strength in different molecules, so that k_{AB}, b_{AB} and c_{AB} for them are set to be zero.

(2) The range of Q_A for fluorine is too narrow to show its effect, so that the coefficients b_A and c_A for fluorine are set to be zero.

As the data of heat of formation at 25°C are much more available than atomization energies, the latter are calculated from the former without regard to the difference of temperature. The adopted atomic heats in this calculation are the same as those in MNDO [7].

3. Results

The optimized constants are listed in Tables 1-2. *In situ* bond energies can then be evaluated by Eq. 1-4 from MNDO data. For example, the MNDO data of acetylene are: $E_C = -3.7651$, $Q_C = -0.155$, $E^R_{CC} = -1.1588$, $E^R_{CH} = -0.4863$, $E^B_{CH} = 236.43 \times 0.4863 = 115.0$ kcal/mol,

$$E^B_{CC} = -1199.0 + 178.20 \times 1.1588 - 24.99 \times 1.1588^2$$
$$-160.61(-3.7651 + 0.312 \times 0.155 - 0.332 \times 0.155^2) \times 2 = 170.4 \text{ kcal/mol.}$$

Table 1. Constants in Eq. 3 in a.u.

A	b_A	c_A
C	0.312	0.332
N	0.294	0.518
O	0.211	0.439

Table 2. Constants in Eq. 1 including a conversion factor from Hartree to kcal/mol

AB	a_{AB}	AB	k_{AB}	a_{AB}	b_{AB}	c_{AB}
CH	−236.43	CC	−1199.0	−178.2	−24.99	160.61
NH	−181.78	CN	−1538.0	−3.3	80.0	149.08
OH	−176.85	CO	−2397.6	54.0	124.8	163.40
		NN	−2127.9	17.1	88.0	156.67
		NO	−1405.5	−400.0	−149.5	69.38
OF	−66.3	CF	−1688.8	−112.5	0	80.90
		NF	−2765.5	−134.5	0	112.49

Table 3. *In situ* bond energy and error of calculated heat of formation (kcal/mol)

	In situ bond energy	ΔH_f exptl[a]	Error from E^B	Error from MNDO[a]
CH_4	99.3	−17.9	0.0	6.0
C_2H_6	CC 88.2, CH 98.5	−20.2	−4.8	0.5
C_3H_8	CC 86.0, CH_s 98.5, CH_a 98.6, C^2H 97.5	−24.8	−4.3	−0.1
n-butane	C^1C 86.3, CC 83.7, CH_s 98.5, CH_a 98.7, C^2H 97.6	−30.4	−3.9	0.7
isobutane	CC 84.0, CH_H 98.7, CH_c 98.6, C^2H 96.3	−32.4	−0.4	5.6
n-pentane	C^1C 86.3, CC 84.0, CH_s 98.5, CH_a 98.7, C^2H 97.7, C^3H 97.8	−35.1	−3.7	0.7
neopentane	CC 82.2, CH 98.7	−40.3	6.2	15.7
n-hexane	C^1C 86.3, C^2C^3 84.0, C^3C^4 84.3, CH_s 98.5, CH_a 98.7, C^2H 97.7, C^3H 97.8	−40.0[b]	−3.5	0.9[c]
C_2H_4	CC 128.7, CH 104.0	12.5	−7.1	2.8
$MeCH{=}CH_2$	CC 126.7, 90.6, C^1H 104.1, C^2H 102.8, CH_s 98.7, CH_a 98.1	4.9	−2.9	0.0
trans-butene	CC 91.1, 124.5, CH_s 98.7, CH_a 98.1, C^2H 102.9	−3.0	1.0	−2.1
cis-butene	CC 91.3, 124.6, CH_s 98.9, CH_a 98.0, C^2H 102.4	−1.9	0.3	−2.1
butadiene	CC 125.9, 93.8, CH_c 104.1, CH_H 104.2, C^2H 102.9	26.0	2.2	2.9
C_2H_2	CC 170.4, CH 115.0	54.3	−8.7	3.0
$MeC{\equiv}CH$	CC 168.4, 100.0, CH 115.1, 98.2	44.4	−1.4	−3.5
pentyne-l	CC 168.5, 98.0, 84.4, 86.3, CH 115.2, 97.3, 97.8, CH_s 98.5, CH_a 98.6	34.5[b]	−1.6	−3.7[c]
nitrogen	219.9	0.0	6.1	8.0
NH_3	93.4	−11.0	0.0	4.7
N_2H_4	NN 41.7, NH 90.8	22.8	6.5	−8.5
N_2H_2	NN 115.8, NH 86.9	50.9	−10.3	−17.1
HN_3	NN 156.9, 72.7, NH 89.6	70.3	1.6	2.7
$MeNH_2$	NC 70.8, CH_s 97.5, CH_a 98.9, NH 93.3	−5.5	−2.7	−2.0
$EtNH_2$	NC^1 68.4, CC 87.5, C^1H 98.0, C^2H 98.6, NH 93.4	−11.4	−3.5	−1.5
iso-$PrNH_2$	NC^1 67.1, CC 86.9, C^1H 95.7, C^2H 98.8, 98.5, NH 93.0	−20.0	−0.2	4.0
tert-$BuNH_2$	NC 65.8, CC_s 84.1, CC_a 84.9, CH 98.7, 98.4, 98.3, NH 93.0	−28.9	5.4	13.8
Me_2NH	NC 71.4, CH_c 98.8, CH_{lp} 97.5, CH_H 98.9, NH 93.4	−4.4	−2.8	−2.2
Me_3N	NC 72.6, CH_{lp} 97.6, CH_c 98.8	−5.7	−2.9	2.9
HCN	HC 114.6, CN 192.2	32.3	−3.2	2.6
MeCN	CC 104.1, CN 189.4, CH 98.6	20.9	1.0	−2.0
MeNC	CN 193.9, 72.2, CH 98.7	35.6	13.3	24.4
C_2N_2	CN 187.1, CC 115.9	73.8	3.8	−7.9
$CH_2{=}CHCN$	CC 126.6, 103.4, CN 185.6, CH_c 104.2, CH_H 104.3, C^2H 103.4	44.1	6.5	−0.4
CH_2NN	NN 145.1, NC 77.7, CH 106.4	71	−5.4	−3.9
H_2O	110.8	−57.8	0.0	−3.1
MeOH	OC 84.4, CH_s 99.0, CH_a 97.7, OH 109.5	−48.1	−1.4	−9.3
EtOH	OC^1 81.7, CC 91.1, C^1H 97.1, CH_s 98.6, CH_a 98.9, OH 109.5	−56.2	−2.7	−6.8
iso-PrOH	OC^1 79.2, CC 87.4, C^1H 96.7, CH 98.7, 98.8, OH 109.2	−65.1	1.9	−0.3

Table 3 (*cont.*)

		ΔH_f	Error from	
	In situ bond energy	exptl[a]	E^B	MNDO[a]
tert-BuOH	OC 77.9, CC_s 86.8, CC_a 85.8, CH 98.5, 98.6, 98.9, 98.7, OH 109.3	−74.7	4.7	10.4
Me_2O	OC 84.5, CH_s 99.0, CH_a 98.0	−44.0	−0.8	−7.2
H_2CO	OC 171.7, CH 101.3	−26.0	−13.6	−7.0
MeCHO	OC^1 166.0, CC 99.1, C^1H 100.9, CH_a 98.5, CH_s 99.2	−39.7	−12.7	−2.7
HCOOH	CO 169.4, 96.4, CH 105.3, OH 109.0	−90.6	4.7	−2.1
MeCOOH	CO 165.5, 94.0, CC 104.0, CH_s 99.5, CH_a 98.8, OH 109.0	−103.3	3.1	2.1
HCOOMe	OC^1 171.8, 98.1, OC^2 80.4, C^1H 105.1, CH_s 99.1, CH_a 98.6	−83.6	1.3	−2.0
CO	253.1	−26.4	3.7	20.2
CO_2	190.6	−94.1	2.9	18.7
$HCONH_2$	NC 83.0, NH 97.6, 98.3, CO 169.1, CH 103.9	−44.5	−7.6	4.7
$MeCH{=}NOH$	NC^1 110.9, NO 69.5, CC 94.2, OH 107.0, C^1H 103.2, CH_s 99.2, CH_a 98.2	18.2[b]	12.7	0.7[c]
trans-HONO	NO 126.7, 67.3, OH 107.4	−18.8	1.6	−21.8
cis-HONO	NO 128.1, 74.7, OH 105.3	−18.3	−5.5	−20.7
$HONO_2$	NO_{lp} 111.1, NO_H 112.6, NO 51.5, OH 106.0	−32.1	−5.3	14.6
MeONO	NO 124.8, 68.1, CO 86.5, CH_s 99.0, CH_a 98.7	−15.8	−0.8	−20.8
$MeNO_2$	CN 55.7, NO 108.0, NO_H 107.9, CH_s 100.2, CH_a 99.8	−17.9	5.8	21.2
N_2O_5	N—O 35.9, NO_{lp} 113.6, NO_N 113.4	2.7[b]	−4.8	34.4[c]
N_2O_4	NN 10.1, NO 113.1	2.5[b]	−0.8	29.5[c]
N_2O_3	NN 37.8, NO_{lp} 109.0, NO_o 110.0, NO 129.2	19.8[b]	−1.1	−6.1[c]
N_2O	NN 159.8, NO 110.1	19.6	−3.9	11.3
CH_3F	CF 108.1, CH 98.4	−56.8	−0.5	−4.1
CH_2F_2	CF 110.9, CH 98.5	−107.7	1.7	−4.1
CHF_3	CF 114.3, CH 100.5	−166.6	2.9	2.7
EtF	CC 91.2, C^1F 106.0, C^1H 97.7, CH_a 99.0, CH_s 62.9	−62.9	−5.5	−2.2
$MeCHF_2$	CC 96.7, C^1F 109.0, C^1H 97.7, CH_s 99.4, CH_a 99.3	−119.7	−2.8	6.2
$CH_2{=}CHF$	CC 129.2, C^1F 108.7, C^1H 104.7, CH_F 104.8, CH_N 104.7	−32.5	−2.6	−2.1
$CH{\equiv}CF$	CC 167.6, CF 113.6, CH 115.9	5.0	10.6	10.0
NF_3	67.1	−31.4	−0.4	−2.7
cis-FNNF	NN 108.9, NF 68.0	16.4	2.5	−18.6
trans-FNNF	NN 100.2, NF 68.7	19.4	6.7	−16.9
N_2F_4	NN 53.6, NF 64.7	−2.0	−8.9	−16.3
FCN	FC 117.7, CN 188.9	8.6	−12.5	−11.3
HOF	FO 46.4, OH 105.3	−23.5	2.4	4.8
F_2O	45.7	5.9	0.0	12.3
CF_3OF	FO 46.9, OC 97.2, CF_s 118.0, CF_a 117.3	−182.8	−8.1	19.3
F_2CO	CO 175.9, FC 118.3	−152.7	8.3	13.9
CF_3CH_2OH	CC 104.3, CO 84.3, CF_s 112.8, CF_a 112.3, CH 98.7, OH 109.8	−220.6	1.7	12.2
CF_3COOH	CC 122.3, CO 167.7, 92.6, CF_s 114.0, CF_a 112.8, OH 109.6	−255	2.7	16.6
F_3NO	NO 114.2, NF 51.0	−39	1.0	61.8

Table 3 (*cont.*)

		ΔH_f	Error from	
	In situ bond energy	exptl[a]	E^B	MNDO[a]
FNO	NO 129.4, NF 68.0	−15.0	9.0	−9.8
FNO_2	NO 113.9, NF 46.7	−26.0	2.6	26.6
$FONO_2$	OF 47.7, NO 26.8, NO_F 112.7, NO_{lp} 112.6	2.5	8.4	25.5
	Root-mean-square error		5.5	13.7

[a] Ref. [7].
[b] Benson S. W., et al., Chem. Rev. **69** (1969) 279.
[c] This work. Subscript: s = in-plane, a = out-of-plane, lp = *trans* to lone pair, H = *trans* to a hydrogen atom, etc.

Seventy nine acylic molecules are calculated by MNDO with fully geometry optimization. The *in situ* bond energies are then calculated from the obtained resonance integral contributions and monatomic energies. In order to check the accuracy of this scheme, heats of formation are calculated from the *in situ* bond energies, and the errors are listed in Table 3 in comparison with those by the MNDO method. The root-mean-square error of 5.5 kcal/mol is significantly better than that of 13.7 kcal/mol by the MNDO method.

4. Correlations of *in situ* bond energy with various properties

4.1. Contributional bond energy

The correlation of the *in situ* bond energy with the contributional bond energy proposed by Pitzer [8] is shown in Fig. 1. For a part of C—N, C—O, and C—C single bonds, the *in situ* bond energies are greater than Pitzer's for two reasons. The first, conjugation with adjacent double bond makes some contribution of π-bonding to the single bond and strengthens it, while Pitzer's single bond energy

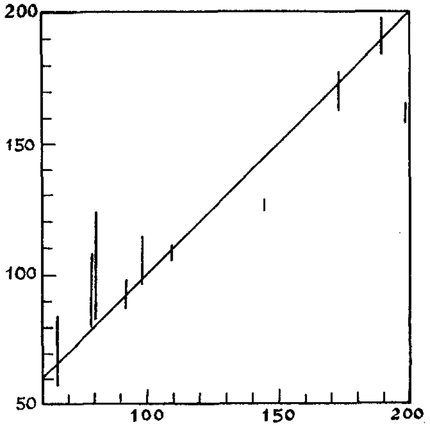

Fig. 1. Correlation of *in situ* bond energy (ordinate) with Pitzer's contributional bond energy (abscissa). From left to right: C—N, C—O, NH, CH, OH, C=C, C=O, C≡N, C≡C

belongs to "pure" single bond. The second, single bonds of the *sp* or sp^2 hybridized carbon are stronger than those of the sp^3 carbon, while Pitzer's bond energy belongs to the latter. Similarly, ethylenic and acetylenic CH bonds are stronger than parafinic ones and have greater *in situ* bond energies. For contributional bond energy, all CH bonds are regarded to be the same, so that Pitzer's CH bond energy is in agreement only with the *in situ* bond energy for parafinic CH bonds. As CH bond energies are underestimated in ethylenic and acetylenic species, the contributional bond energies of C=C and C≡C should be overestimated, as shown in Fig. 1. Excluding these cases, we can regard the correlation to be good.

4.2. *Bond dissociation energy*

The correlation of *in situ* bond energy with bond dissociation energy is less significant, since the latter is not a good measure of bond strength. As is well known, sequent dissociations of equivalent bonds in a molecule, such as methane, show different bond dissociation energies, whereas they should have the same *in situ* bond energy. Generally,bond dissociation energy is not equal to the corresponding *in situ* bond energy, although they are close to each other in most cases. Conjugation stabilizes the dissociation product and lowers the bond dissociation energy. This fact can be illustrated by comparing *in situ* bond energy with bond dissociation energy of CH bonds [1] for some typical examples:

	CH_4	C_2H_6	C_3H_8	C_2H_4	C_2H_2	C_6H_6	Me_3CH	Me_4C	$MeC{\equiv}CH$	PhMe
BDE	98	95	98	108	128	110.5	92	99.3	93.9	88.3
E^B	99.3	98.5	98.6	104.0	115.0	104.6	96.3	98.7	98.2	98.4

The last two examples show lower BDE due to the strengthening of the conjugation in the dissociation product.

Comparison of *in situ* bond energy with bond dissociation energy will be further made in the next paragraph.

4.3. *Isolated stretching frequency*

The isolated stretching frequency of CH bond is a good measure of bond strength. Details have been reviewed by McKean [1]. Correlation of *in situ* bond energies for CH bond with forty four data of isolated stretching frequency cited in McKean's review is shown in Fig. 2. The upper two points in the figure stand for acetylenic CH bonds (C_2H_2 and C_3H_4), whose *in situ* bond energies are 115.0 and 115.1 kcal/mol, respectively. The middle five points stand for ethylenic (C_2H_4 and C_3H_6) and aromatic (C_6H_6) CH bonds, whose *in situ* bond energies are from 102.8 to 104.6 kcal/mol. The lower points stand for paraffinic CH bonds, whose *in situ* bond energies are mainly 98–99 kcal/mol in agreement with Pitzer's contributional bond energy of 98.2 kcal/mol. The isolated stretching frequency shows some overlap region of ethylenic and paraffinic CH bonds. Nevertheless, the correlation is still fairly good: the correlation coefficient is 0.9315, and the root-mean-square deviation amounts to 1.4 kcal/mol.

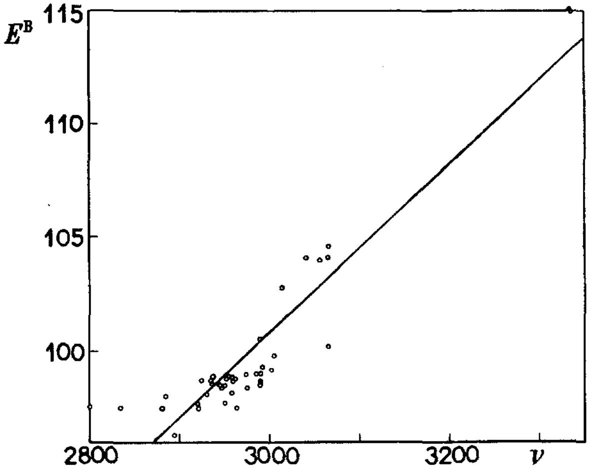

Fig. 2. Correlation of *in situ* bond energy (kcal/mol) for CH bond with isolated stretching frequency (cm^{-1})

Note that bond dissociation energy shows much worse correlation with isolated stretching frequency. The correlation of the ten data mentioned in the last paragraph with isolated stretching frequency shows a root-mean-square deviation of 3.6 kcal/mol. This emphasizes that bond dissociation energy is not a good measure of bond strength.

4.4. Bond length

As CH, NH, and OH *in situ* bond energies are assumed simply proportional to the resonance integral energy contribution E^R, the correlation of the former with bond lengths is similar to that of the latter. Correlation of E^R for CH, NH, and OH bonds with bond length has been reported [6] and need not be discussed here. The *in situ* bond energies of other bonds of the molecules in Table 3 are correlated with bond lengths R_{AB} by using the relation

$$E^B_{AB} = B_{AB}/(R_{AB} - C_{AB}), \tag{4}$$

where B_{AB} and C_{AB} are empirical constants depending only on the kinds of atom A and B. The data of bond length are mainly cited from *LB II/7* [9]. The mean value is accepted when there are more than one datum for a bond of a molecule. Some data are cited from Dewar and coworker's papers [7] when they are not available in *LB II/7*. For a specified kind of bond AB, B_{AB} and C_{AB} are optimized to give least square sum of deviation $B_{AB}/(R_{AB} - C_{AB}) - E^B_{AB}$.

The results are listed in Table 4. As the available data of OF bond length are not enough, the result of correlation for OF bonds is not listed. The overall root-mean-square deviation amounts to 7.0 kcal/mol. The deviation due to the error of bond length seems as important as the uncertainty of the *in situ* bond energy. For example, as a CO bond length changes from 1.20 Å to 1.21 Å, the calculated E^B (equation 4) changes from 168.6 kcal/mol to 161.5 kcal/mol.

Table 4. Correlation of *in situ* bond energy with bond length

AB	B_{AB} Å · kcal/mol	C_{AB} Å	Range of R_{AB} Å	Number of data	Standard deviation kcal/mol
CC	62.14	0.8389	1.20–1.54	26	4.3
CN	29.22	1.0006	1.16–1.49	13	8.1
CO	38.31	0.9728	1.13–1.44	17	8.0
NN	20.86	0.9990	1.09–1.75	10	9.7
NO	39.47	0.8419	1.14–1.41	16	7.2
CF	96.77	0.4636	1.26–1.40	11	4.7
NF	49.13	0.6243	1.36–1.51	7	7.9

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Received April 6, 1984