Topic 2D - The Properties of Bonds

Electronegativity

Quantitative measure of an element's ability to attract electron density in a chemical bond.

Pauling Scale

Based on experimentally measured bond strengths in homo- (A-A) and heteronuclear (A-B) diatomic molecules.

The <u>covalent</u> contribution to the A-B bond is the geometric mean of the dissociation energies (ΔE) of the purely covalent A-A and B-B bonds, i.e., $\sqrt{E_{AA}E_{BB}}$. The "Excess Bond Energy" (Δ), which is taken to be a measure of the <u>ionic</u> contribution to the A-B bond, is then defined as:

$$\Delta = E_{AB} - \sqrt{E_{AA}E_{BB}}$$

where E is the bond dissociation energy in kJ/mol.

The <u>difference</u> in electronegativity (χ, in eV) between elements A and B is then given by:

$$|\chi_A - \chi_B| = 0.102\,\Delta^{\frac{1}{2}} = 0.102\sqrt{E_{AB} - (E_{AA}E_{BB})^{1/2}}$$

where the constant 0.102 converts kJ/mol into eV.

Since Pauling's method gives only <u>differences</u> in electronegativity, an absolute numerical scale is established by defining a value for the most electronegative element, viz., fluorine, i.e., $\chi_{Fluorine} = 4.0$

Mullikan Scale

Defined as being proportional to the average of the first ionization energy (IE_1) and the electron affinity (EA):

$$\chi \text{ (Mullikan)} \propto \tfrac{1}{2}(IE_1 + EA) = 0.187(IE_1 + EA) + 0.17$$

where the R.H.S. of the above equation converts Mullikan E.N. values (in eV) into dimensionless Pauling E.N. values.

The Pauling scale of electronegativity is much more widely utilized than the Mullikan scale.

Example for HCl

Bond Strengths: H–H   424 kJ/mol

                  Cl–Cl   230   "

                  H–Cl   419   "

$$\Delta = E_{AB} - \sqrt{E_{AA}E_{BB}} = 419 - \sqrt{424 \times 230} = 312 \, kJ/mol$$

$$|\chi_A - \chi_B| = 0.102 \, \Delta^{\frac{1}{2}} = 0.102 \sqrt{419 - (424 \times 230)^{1/2}} = 1.05$$

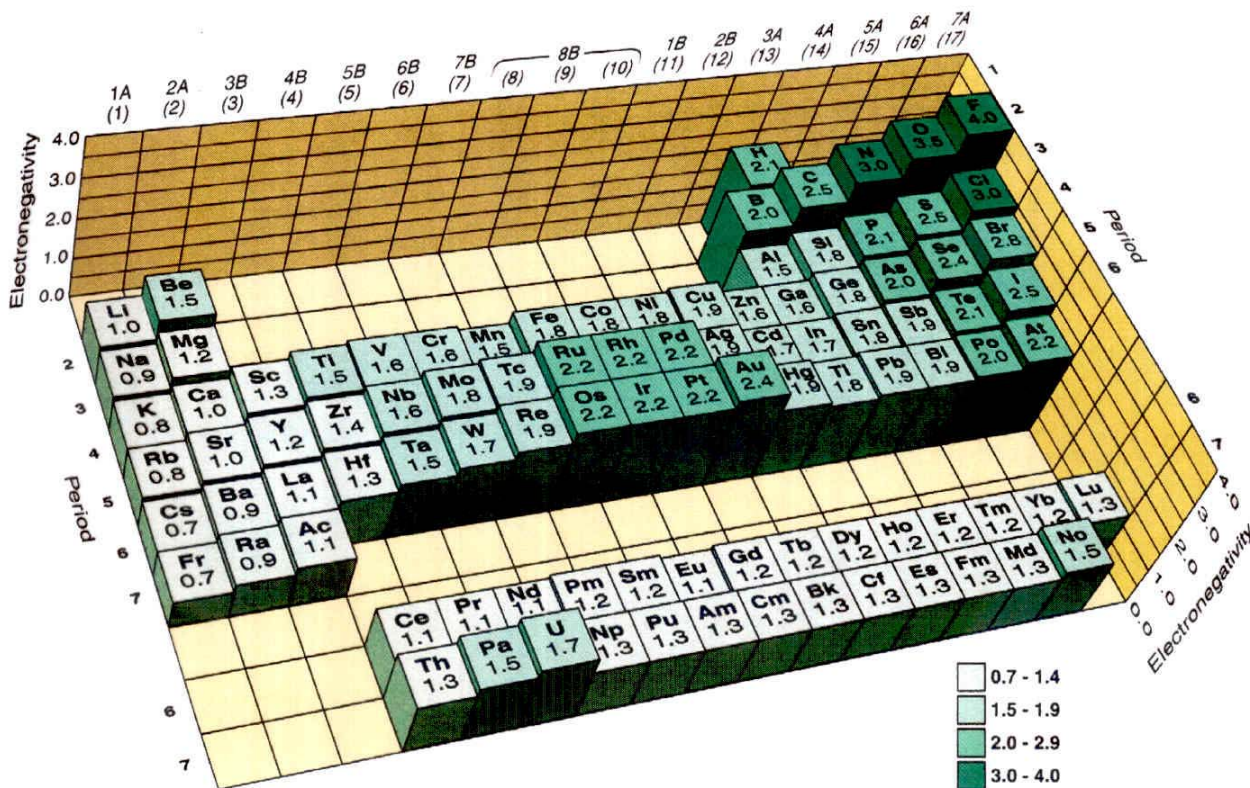The "accepted" Pauling Electronegativities for H and Cl are

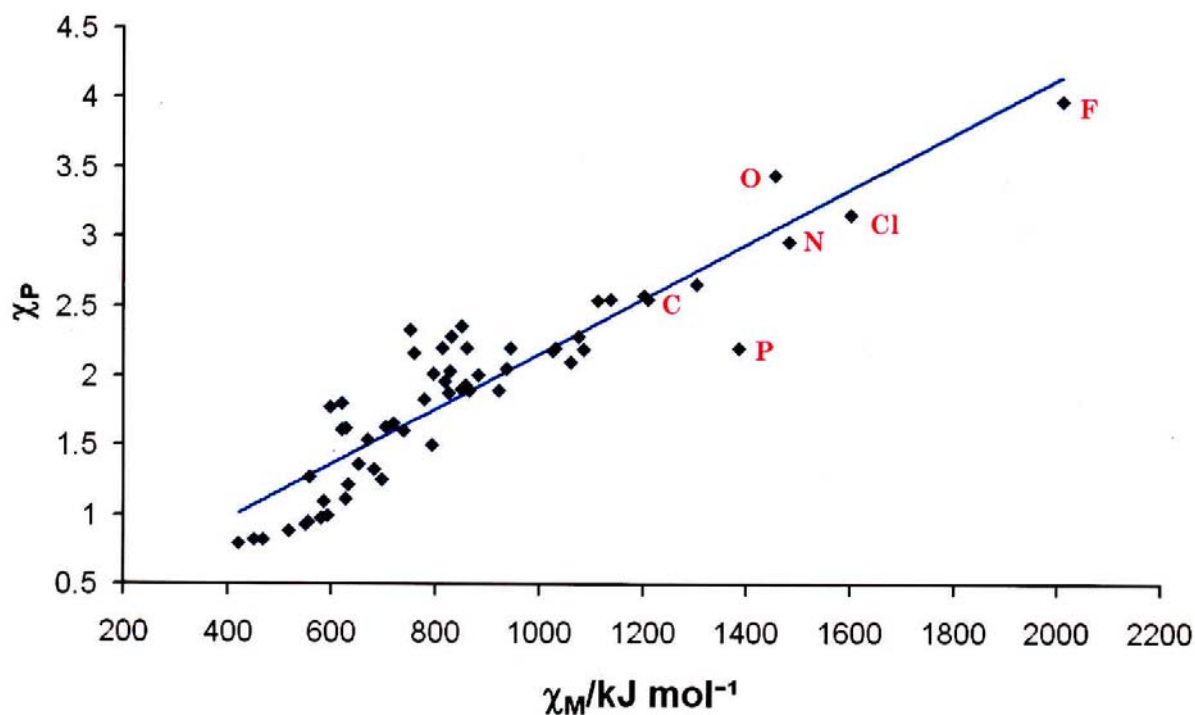$$\chi_H = 2.20 \qquad\qquad \chi_{Cl} = 3.16$$

for which

$$|\chi_A - \chi_B| = 3.16 - 2.20 = 0.96$$

which agrees reasonably well with the value of 1.05 calculated above for the specific case of HCl.

Pauling Electronegativities

Comparison of Pauling and Mullikan Electronegativity Scales:
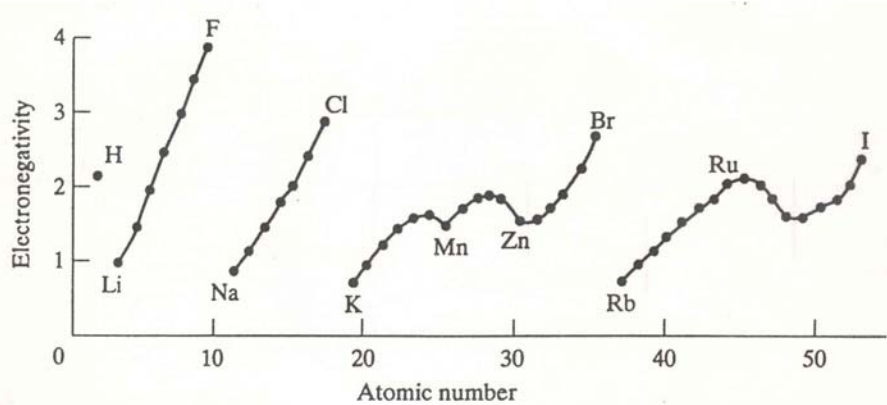

Electronegativities of the Elements (Pauling scale)

Periodic table of electronegativity using the Pauling scale

FIGURE 9.8

The electronegativities of the elements. (Ref. 24.)

Difference in electronegativity ($\Delta\chi$) between two elements is indicative of the **% ionic character (% I.C.)** of a chemical bond between atoms of those elements. **Approximate** relationship between $\Delta\chi$ and % ionic character is given by:

$\Delta\chi$	% I.C.
0.0	0
1.0	20
1.5	40
1.75	50
2.0	60
2.5	80

The differing natures of chemical bonds are often loosely categorized according to their % I.C.:

% I.C.	Bond Type
0	Covalent
> 0, < 50	Polar Covalent
> 50	Ionic

Electron Density Progression .om Covalent to Ionic Bonding
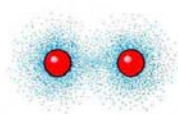
H−H (nonpolar covalent bond)
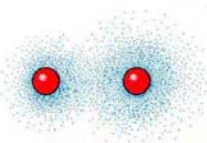
H−F (polar covalent bond)
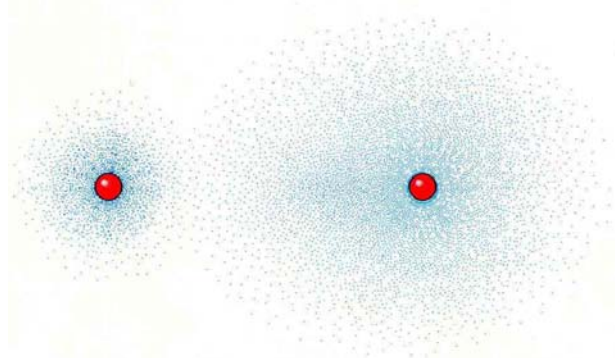
NaF (ionic bond)

NaI (ionic bond with some covalent character)
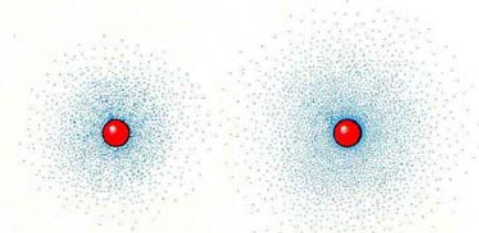
Dipole Moment

A measure of the separation of charge in a molecule. Two unlike charges that are separated by a finite distance constitute an **electric dipole**.
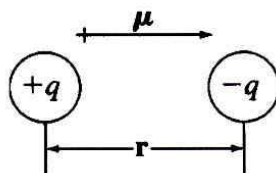
A molecule that has such a charge separation possesses a **dipole moment, μ:**

$$\mu = qr$$

where q is the magnitude of the charge separation, and r is the distance between the charges +q and -q. The dipole moment is a vector quantity, pointing toward the <u>negative</u> charge.

In SI units, μ is given in Coulomb-meters. The latter is an inconveniently large unit for molecules, so molecular dipole moments are conventionally given in **debyes (D)**, where

$$1 D = 3.336 \times 10^{-30} \text{ C-m}$$

The Debye can also be defined as the dipole moment that arises from two charges ±e that are separated by 0.2082 Å. Thus, if δ is the fractional unit charge on each atom in a diatomic molecule (δ = q/e) and R is the equilibrium bond length, then

$$\mu(D) = \left[\frac{R(A°)}{0.2082\ A°} \right] \delta$$

T A B L E 3.7   **Dipole Moments of Diatomic Molecules**

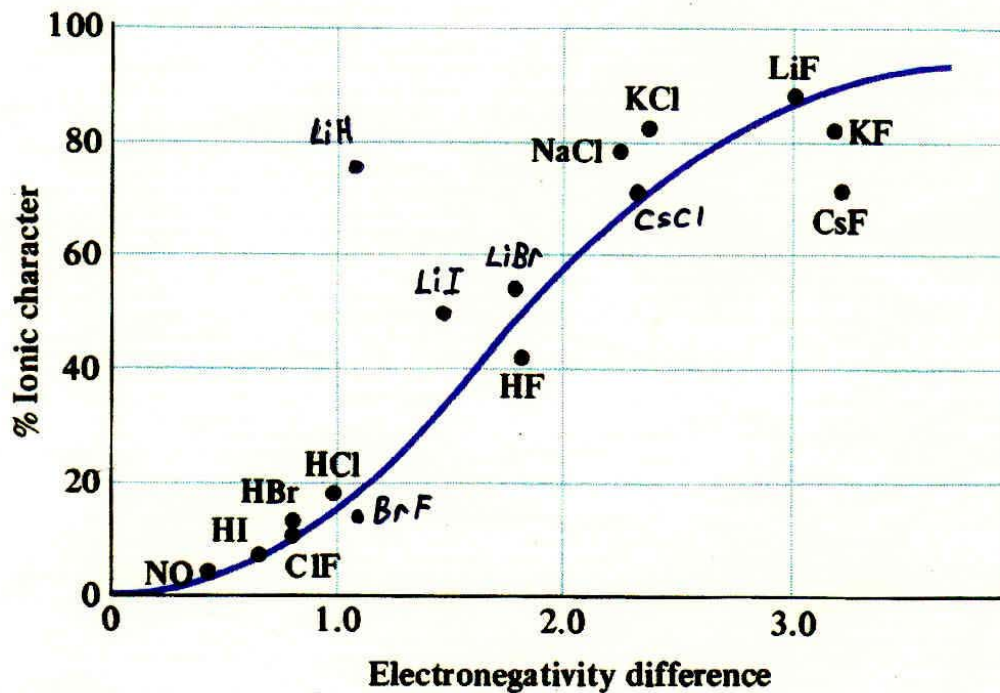| Molecule	Bond Length (Å)	Dipole Moment (D)	Percent Ionic Character (100δ)	Δ(E.N.)
H$_2$, N$_2$, O$_2$, ...	0.751, 1.10, 1.21, ...	0	0	0.0
CO	1.131	0.112	2	1.0
NO	1.154	0.159	3	0.5
HI	1.620	0.448	6	0.5
ClF	1.632	0.888	11	1.0
HBr	1.424	0.828	12	0.7
HCl	1.284	1.109	18	0.9
HF	0.926	1.827	41	1.9
CsF	2.347	7.884	70	3.3
LiCl	2.027	7.129	73	2.0
LiH	1.604	5.882	76	1.1
KBr	2.824	10.628	78	2.0
NaCl	2.365	9.001	79	2.1
KCl	2.671	10.269	82	2.2
KF	2.176	8.593	82	3.2
LiF	1.570	6.327	84	3.0
NaF	1.931	8.156	88	3.1

Figure 14-4

Two measures of ionic character for diatomic molecules are the electronegativity differ-ence (from Fig. 14-1) and the percent ionic character 100δ (calculated from the observed dipole moment and bond length). The curve in this graph shows that the two correlate approximately but that there are many exceptions.

Triangle of Bonding
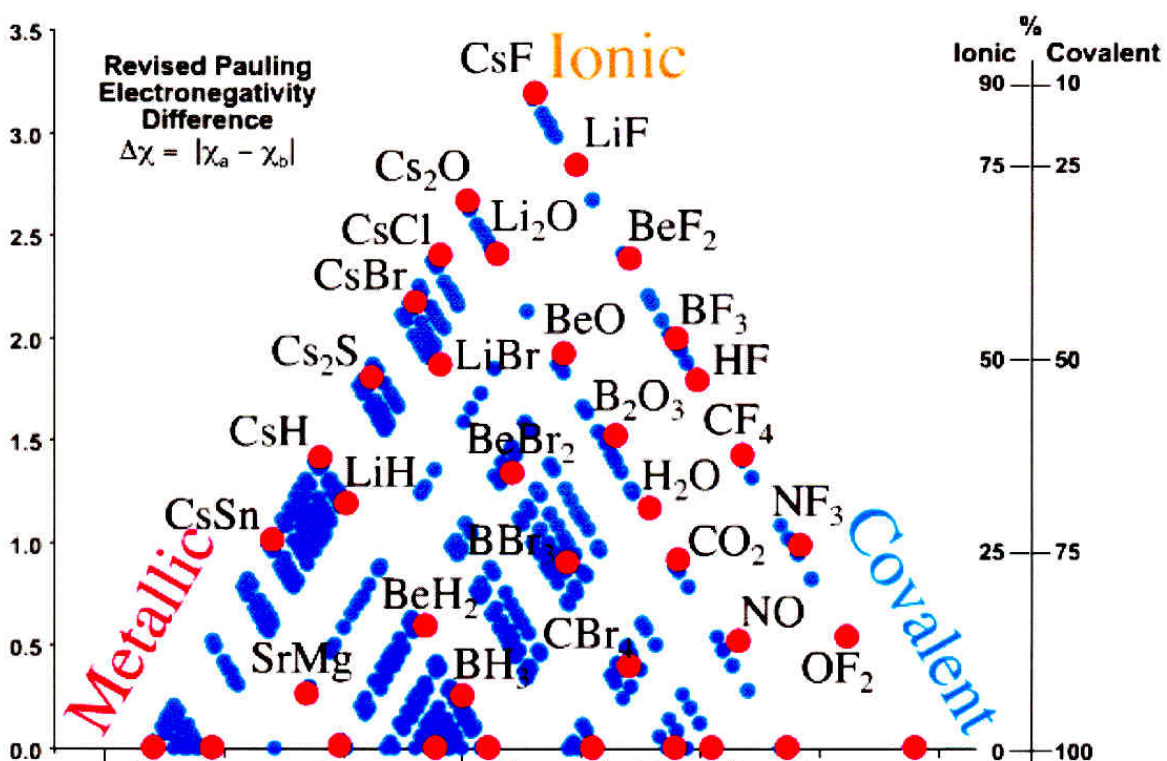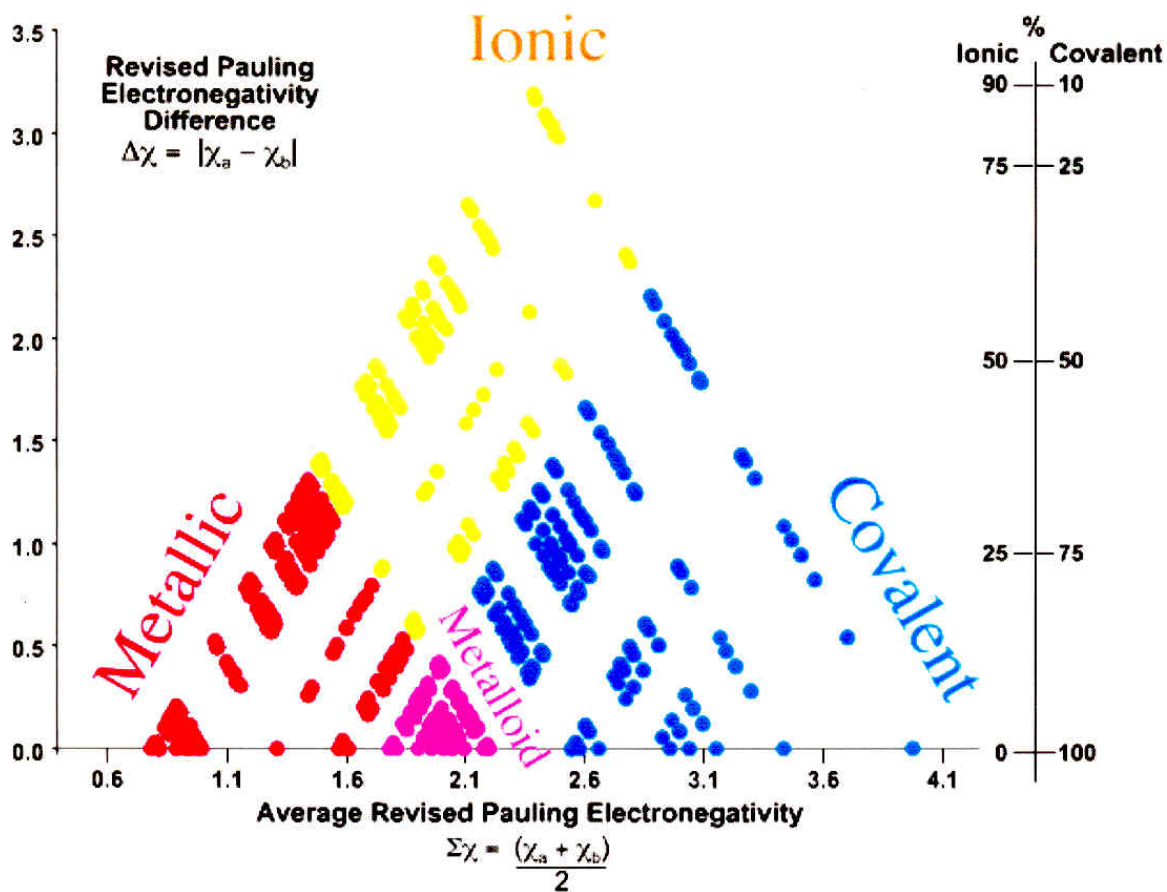
TABLE C-13. Length and Strength of Covalent Bonds

Atom	Bond	Bond Length (Average) (Å)	Dissociation Enthalpy (Average) (kJ mol^{-1})
H	H—H	0.74	436
	H—F	0.92	565
	H—Cl	1.27	431
	H—Br	1.41	366
	H—I	1.61	299
C	C—C	1.54	348
	C=C	1.34	612
	C≡C	1.20	838
	C—H	1.09	413
	C—N	1.43	305
	C=N	1.38	613
	C≡N	1.16	890
	C—O	1.43	360
	C=O	1.23	743
	C≡O	1.13	1076
	C—F	1.27	484
	C—Cl	1.65	338
	C—Br	1.79	276
	C—I	2.15	238
N	N—N	1.47	163
	N=N	1.24	409
	N≡N	1.10	946
	N—H	1.01	388
	N—O	1.36	157
	N=O	1.22	630
O	O—O	1.48	146
	O=O	1.21	497
	O—H	0.96	463
F	F—F	1.41	155
Cl	Cl—Cl	1.99	242
Br	Br—Br	2.28	193
I	I—I	2.67	151

TABLE 3.3 Properties of Diatomic Molecules

Molecule	Bond Length (Å)	Bond Energy (kJ mol^{-1})
H_2	0.751	433
N_2	1.100	942
O_2	1.211	495
F_2	1.417	155
Cl_2	1.991	240
Br_2	2.286	190
I_2	2.669	148
HF	0.926	565
HCl	1.284	429
HBr	1.424	363
HI	1.620	295
ClF	1.632	252
BrF	1.759	282
BrCl	2.139	216
ICl	2.324	208
NO	1.154	629
CO	1.131	1073

TABLE 3.4 Reproducibility of Bond Lengths

Bond	Molecule	Bond Length (Å)
O—H	H_2O	0.958
	H_2O_2	0.960
	HCOOH	0.95
	CH_3OH	0.956
C—C	Diamond	1.5445
	C_2H_6	1.536
	CH_3CHF_2	1.540
	CH_3CHO	1.50
C—H	CH_4	1.091
	C_2H_6	1.107
	C_2H_4	1.087
	C_6H_6	1.084
	CH_3Cl	1.11
	CH_2O	1.06

T A B L E 3.5   Three Types of Carbon–Carbon Bonds

Bond	Molecule	Bond Length (Å)	Bond Energy (kJ mol^{-1})
C—C	C_2H_6 (or H_3CCH_3)	1.536	345
C=C	C_2H_4 (or H_2CCH_2)	1.337	612
C≡C	C_2H_2 (or HCCH)	1.204	809

T A B L E 3.6   Average Bond Lengths (in Å)

C—C	1.54	N—N	1.45	C—H	1.10
C=C	1.34	N=N	1.25	N—H	1.01
C≡C	1.20	N≡N	1.10	O—H	0.96
C—O	1.43	N—O	1.43	C—N	1.47
C=O	1.20	N=O	1.18	C≡N	1.16