

القوى الجزيئية Intermolecular forces :- Intramolecular forces
 القوى الجزيئية (داخل الجزيئية)

القوى الجزيئية هي القوى التي تربط بين الجزيئات والتي تحدث كثير من الخصائص الفيزيائية للمركبات مثل الحالة الفيزيائية ودرجة الغليان والذوبان وغيرها ، وهي على أنواع حسب الجزيئية إذا كانت قطبية أو غير قطبية :-

- (1) قوى فاندر فال (Van der Waals forces) ← توجد بين الجزيئات غير قطبية
- (2) لقوى بين الجزيئات القطبية (Dipole-Dipole forces) وسما أتراعها هي الإزاحة الهيدروجينية (Hydrogen bonding) وهذه القوى توجد في الجزيئات القطبية .

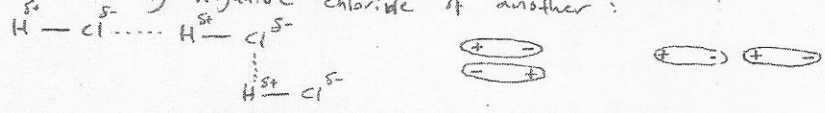
(1) قوى فاندر فال (Van der Waals forces) :- مثل ما قلنا توجد بين الجزيئات ليساهمة غير القطبية حيث في لحظة ما قد يكون التوزيع الإلكتروني في الجزيء غير منتظم نتيجة لحركة الإلكترونات . وبالتالي تكون الشحنة الكهربائية غير منتظمة . بحيث تكون إلكترونية في أحد أطراف الجزيء أعلى قليلاً فتؤدي إما استقطاب بسيط يتكون بصورة مؤقتة (استقطاب لحظي) يؤثر الجزيء المستقطب لحظياً على الجزيء المجاور إلكترونية الجزيء آخر جاور فيكون في الطرف القريب منها شحنة صفادة وإشياء وجود هذه التغيرات القطبية تسبب قوى تجاذب بين الجزيئات غير قطبية . وتؤثر قوى فاندر فال في مسافة قصيرة جداً وتكون على أعظمها عندما تكون الجزيئات في تماس بعضها مع بعض .

* أن قوى فاندر فال بين جزيئية وسما جاورها تعتمد على مساحة السطح الجزيئية ، كلما كانت المساحة السطحية للجزيئية كبيرة كانت قوى فاندر فال أكبر ، ربما أن مساحة السطح الجزيئية ترتبط بالوزن الجزيئي (الجزيئات بوزن جزيئي تأخذ حجم أكبر) ، تأمل نقاط غليان لسلسلة من المركبات تتشابه من حيث التركيب مثل (الكحوليات) فنجد مع زيادة الوزن الجزيئي ، أما في حالة المركبات لها نفس الوزن الجزيئي لكن تختلف في الأيزومرات فأن الأيزومر الذي له مساحة سطحية أكبر يكون له درجة غليان أعلى وذلك لأن الأيزومر المتفرع له مساحة سطحية أقل أي أن قوى فاندر فال بينه تكون أقل فتقل درجة الغليان والذوبان .

Dipole-dipole interaction : توجد في الجزيئات القطبية وتنشأ من ارتباط النهاية

الموجبة أو النهاية الموجبة للجزيئية قطبية مع النهاية سالبة أو النهاية السالبة للجزيئية قطبية أخرى .

the attraction of the positive end of one polar molecule for the negative end of another polar molecule. An hydrogen chloride, for example, the relatively positive hydrogen of one molecule is attracted to the relatively negative chloride of another :



* أن تجاذب Dipole-dipole يجعل من الجزيئات القطبية يكون التجاذب بينها أقوى من التجاذب بين جزيئات المركبات غير قطبية ولها نفس الوزن الجزيئي ، وهذا لا يقتصر على قوة التجاذب انعكاس (reflected) على الخصائص الفيزيائية للمركبات القطبية وغير قطبية .

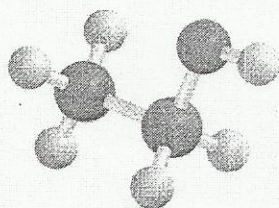
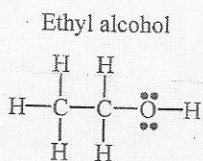
1. **Isomers:** different compounds that have the same molecular formula
2. There are two isomeric compounds with molecular formula C_2H_6O :
 - 1) dimethyl ether: a gas at room temperature, does not react with sodium.
 - 2) ethyl alcohol: a liquid at room temperature, does react with sodium.

Table 1.1 Properties of ethyl alcohol and dimethyl ether

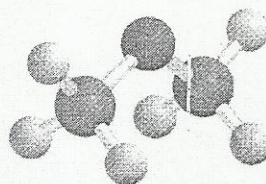
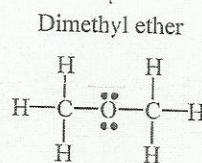
	Ethyl Alcohol C_2H_6O	Dimethyl Ether C_2H_6O
Boiling point, $^{\circ}C^a$	78.5	-24.9
Melting point, $^{\circ}C$	-117.3	-138
Reaction with sodium	Displaces hydrogen	No reaction

^a Unless otherwise stated all temperatures in this text are given in degree Celsius.

- 3.. The two compounds differ in their **connectivity**: $C-O-C$ and $C-C-O$



Ethyl alcohol



Dimethyl ether

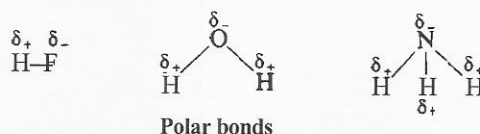
Figure 1.1 Ball-and-stick models and structural formulas for ethyl alcohol and dimethyl ether

السالبية الكهربية (electronegativity) : هي قدرة نواة الذرة على الجذب على إلكترونات التكافؤ (الالكترونات الرابطة) نحوها ، وهي تزداد من اليسار إلى اليمين ، ومن الأعلى إلى الأسفل في الجدول الدوري .

1.15 Polarity of bonds

Besides the properties already described, certain covalent bonds have another property: polarity. Two atoms joined by a covalent bond share electrons; their nuclei are held by the same electron cloud. But in most cases the two nuclei do not share the electrons equally; the electron cloud is denser about one atom than the other. One end of the bond is thus relatively negative and the other end is relatively positive; that is, there is a *negative pole* and a *positive pole*. Such a bond is said to be a **polar bond**, or to *possess polarity*.

We can indicate polarity by using the symbols δ_+ and δ_- , which indicate *partial* $+$ and $-$ charges. (We say "delta plus" and "delta minus".) For example:



We can expect a covalent bond to be polar if it joins atoms that differ in their tendency to attract electrons, that is, atoms that differ in *electronegativity*. Furthermore, the greater the difference in electronegativity, the more polar the bond will be.

The most electronegative elements are those located in the upper right-hand corner of the Periodic Table. Of the elements we are likely to encounter in organic chemistry, fluorine has the highest electronegativity, then oxygen, then nitrogen and chlorine, then bromine, and finally carbon. Hydrogen does not differ very much from carbon in electronegativity; it is not certain whether it is more or less electronegative.

Electronegativity



Bond polarities are intimately concerned with both physical and chemical properties. The polarity of bonds can lead to polarity of molecules and thus profoundly affect melting point, boiling point, and solubility. The polarity of a bond determines the kind of reaction that can take place at that bond, and even affects reactivity at nearby bonds.

1.16 Polarity of molecules

A molecule is polar if the center of negative charge does not coincide with the center of positive charge. Such a molecule constitutes a *dipole*: two equal and opposite charges separated in space. A dipole is often symbolized by \rightarrow , where the arrow points from positive to negative. The molecule possesses a dipole moment, μ , which is equal to the magnitude of the charge, e , multiplied by the distance, d , between the centers of charge:

$$\mu = e \times d$$

in in in
debye e.s.u. cm
units. D

In a way that cannot be gone into here, it is possible to measure the dipole moments of molecules; some of the values obtained are listed in Table 1.4. We shall be interested in the values of dipole moments as indications of the relative polarities of different molecules.

Table 1.4 DIPOLE MOMENTS, D

H ₂	0	HF	1.75	CH ₄	0
O ₂	0	H ₂ O	1.84	CH ₃ Cl	1.86
N ₂	0	NH ₃	1.46	CCl ₄	0
Cl ₂	0	NF ₃	0.24	CO	0
Br ₂	0	BF ₃	0		

It is the *fact* that some molecules are polar which has given rise to the *speculation* that some bonds are polar. We have taken up bond polarity first simply because it is convenient to consider that the polarity of a molecule is a composite of the polarities of the individual bonds.

Molecules like H₂, O₂, N₂, Cl₂, and Br₂ have zero dipole moments, that is, are non-polar. The two identical atoms of each of these molecules have, of course, the same electronegativity and share electrons equally; e is zero and hence μ is zero, too.

A molecule like hydrogen fluoride has the large dipole moment of 1.75 D. Although hydrogen fluoride is a small molecule, the very high electronegative fluorine pulls the electrons strongly; although d is small, e is large, and hence μ is large, too.

Methane and carbon tetrachloride, CCl₄, have zero dipole moments. We certainly would expect the individual bonds—of carbon tetrachloride at least—to be polar; because of the very symmetrical tetrahedral arrangement, however, they exactly cancel each other out (Fig. 1.16). In methyl chloride, CH₃Cl, the polarity

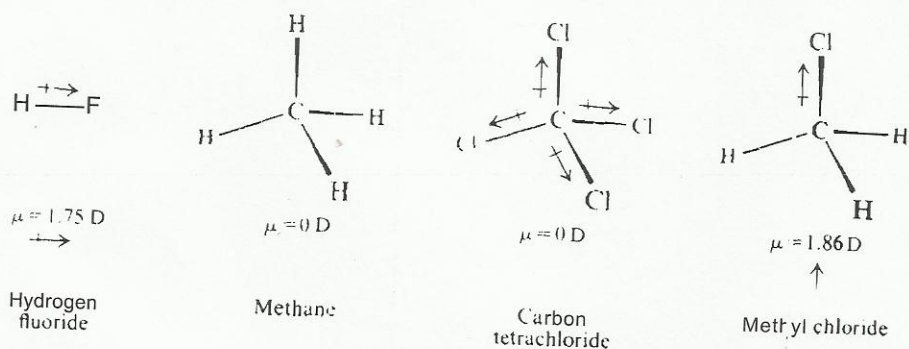
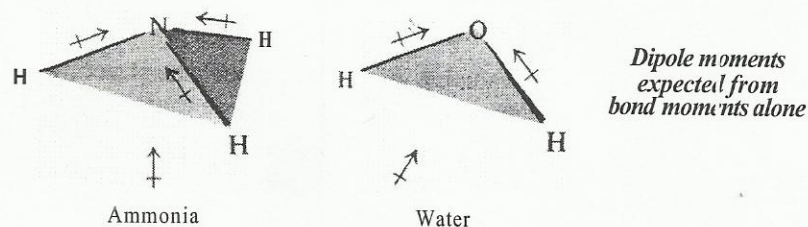


Figure 1.16 Dipole moments of some molecules. Polarity of bonds and of molecules.

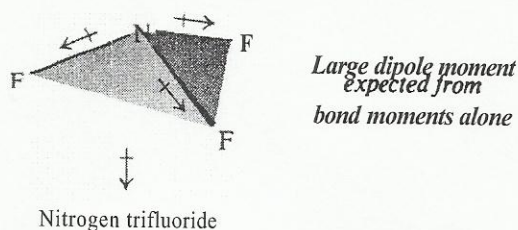
of the carbon-chlorine bond is not canceled, however, and methyl chloride has a dipole moment of 1.86 D. Thus the polarity of a molecule depends not only upon the polarity of its individual bonds but also upon the way the bonds are directed, that is, upon the shape of the molecule.

Ammonia has a dipole moment of 1.46 D. This could be accounted for as a net dipole moment (a *vector sum*) resulting from the three individual bond moments,

and would be in the direction shown in the diagram. In a similar way, we could account for water's dipole moment of 1.84 D.



Now, what kind of dipole moment would we expect for nitrogen trifluoride, NF_3 , which, like ammonia, is pyramidal? Fluorine is the most electronegative element of all and should certainly pull electrons strongly from nitrogen; the N—F bonds should be highly polar, and their vector sum should be large—far larger than for ammonia with its modestly polar N—H bonds.



What are the facts? Nitrogen trifluoride has a dipole moment of only 0.24 D. It is not larger than the moment for ammonia, but rather is *much smaller*.

How are we to account for this? We have forgotten the *unshared pair of electrons*. In NF_3 (as in NH_3) this pair occupies an sp^3 orbital and must contribute a dipole moment in the direction opposite to that of the net moment of the N—F bonds (Fig. 1.17); these opposing moments are evidently of about the same size,

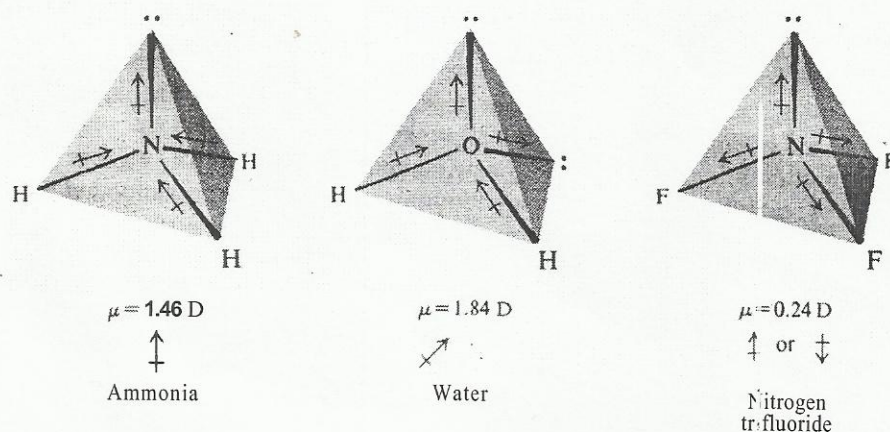
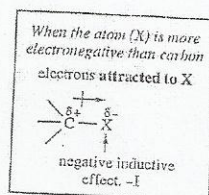


Figure 1.17 Dipole moments of some molecules. Contribution from unshared pairs. In NF_3 , the moment due to the unshared pair opposes the vector sum of the bond moments.

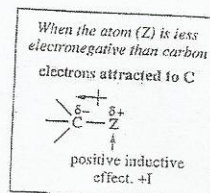
1.6.1 Inductive effects

In a covalent bond between two different atoms, the electrons in the σ -bond are not shared equally. The electrons are attracted towards the most electronegative atom. An arrow drawn above the line representing the covalent bond can show this. (Sometimes an arrow is drawn on the line.) Electrons are pulled in the direction of the arrow.



-I groups
X = Br, Cl, NO₂, OH, OR, SH, SR, NH₂, NHR, NR₂, CN, CO₂H, CHO, C(O)R

The more electronegative the atom (X), the stronger the -I effect



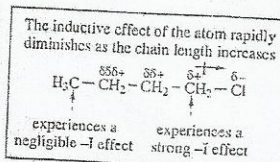
+I groups
Z = R (alkyl or aryl), metals (e.g. Li or Mg)

The more electropositive the atom (Z), the stronger the +I effect

Pauling electronegativity scale

K = 0.8	I = 2.5
C = 2.5	Br = 2.8
N = 3.0	Cl = 3.0
O = 3.5	F = 4.0

The higher the value, the more electronegative the atom

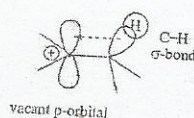


The overall polarity of a molecule is determined by the individual bond polarities, formal charges and lone pair contributions, and this can be measured by the dipole moment (μ). The higher the dipole moment (measured in debyes (D)), the more polar the compound.

1.6.2 Hyperconjugation

A σ -bond can stabilise a neighbouring carbocation (or positively charged carbon) by donating electrons to the vacant p-orbital. The positive charge

is delocalised or 'spread out', and this stabilising effect is known as *resonance*.



The electrons in the σ -bond spend some of the time in the vacant p-orbital