Interações não covalentes
Non covalent interactions (NCI)

Ignez Caracelli

São Carlos, 21 de agosto de 2019

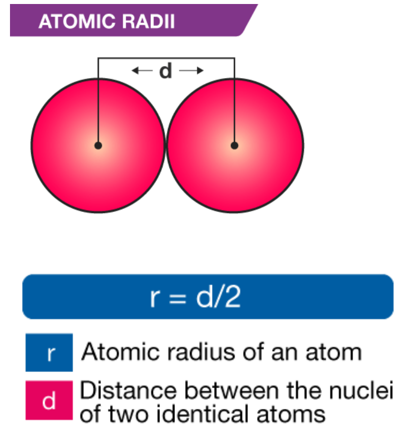
ignez@df.ufscar.br
www.ignez.com

Covalent Interactions?

https://www.youtube.com/watch?v=LkAykOv1foc

Atomic Radii

What is Radius?

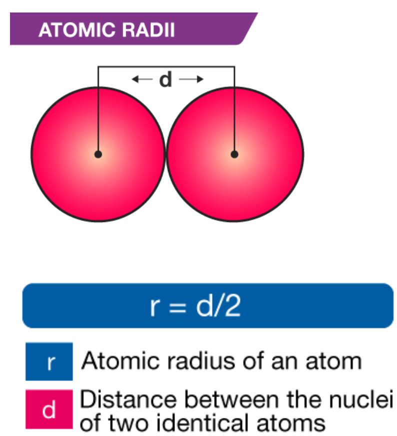


•The radius of a circle is the distance from the center point to the edge of the circle.

•It's the same distance anywhere on the circle, because the circle has radial symmetry.

Atomic Radii

What is Radius?



r → van der Waals (vdw) radius

The van der Waals radius is the radius of an imaginary solid sphere that represents a solid atom.

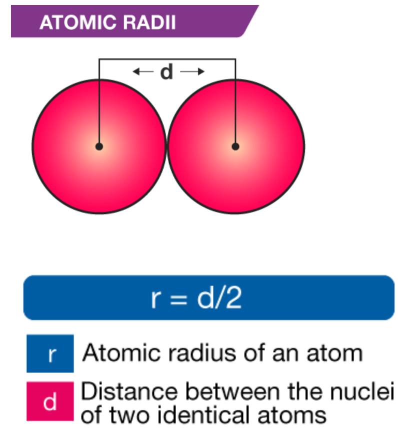
We know that from Quantum Chemistry that the atom is not a rigid sphere

Atomic Radii

What is Radius?

r → van der Waals (vdw) radius $\mathbf{r}_{vdw}$

- $\mathbf{r}_{vdw}$ are determined from the contact distances of non-connected atoms
- $\mathbf{r}_{vdw}$ defines the volume and surface of an atom or molecule

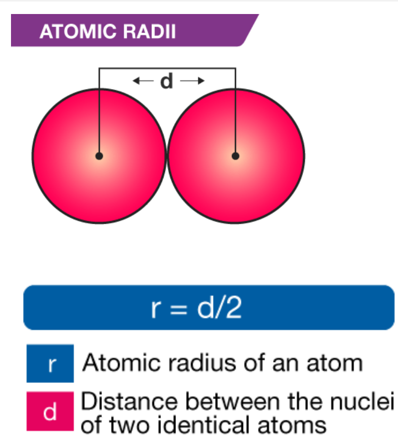


Atomic Radii

What is Covalent Radius?

When a covalent bond is present between two atoms, the covalent radius can be determined.

When two atoms of the same element are covalently bonded, the radius of each atom will be half the distance between the two nuclei because they equally attract the electrons.



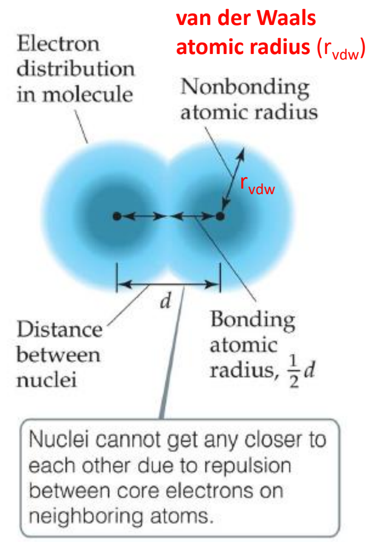
r → van der Waals (vdw) radius $\mathbf{r}_{vdw}$

How close do the atoms have to be to form a bond?

The **van der Waals radius** (r_{vdw}) of an atom X is measured as half of the distance of closest approach of 2 **non-bonded** atoms of X

The **covalent radius** (r_{cov}) of an atom X is taken as half of the internuclear distance (r) in a homonuclear X–X bond.

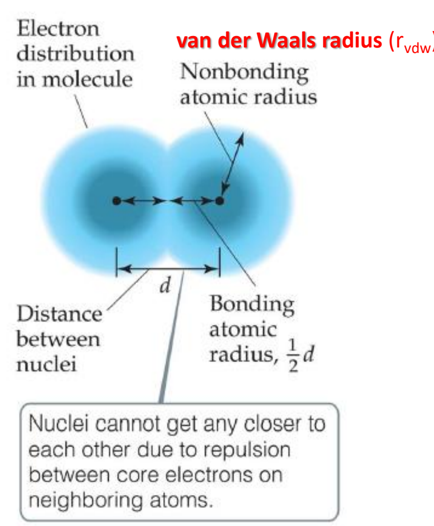
The internuclear distance (r) in a bonded pair of atoms is called the **bond length**



How close do the atoms have to be to form a bond?

The ***nonbonding atomic radius***, or van der Waals radius, is half of the shortest distance separating two nuclei during a collision of atoms.

The ***bonding atomic radius*** is defined as onehalf of the distance between covalently bonded nuclei.



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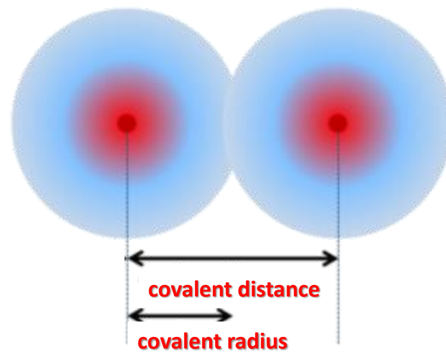


Superposition: the atoms share electrons

vdw & covalent radii

	non-bonded atoms	bonded atoms
element	van der Waals (Å)	covalent (Å)
H	1.09	0.23
C	1.70	0.68
N	1.55	0.68
O	1.52	0.68
F	1.47	0.64
P	1.80	1.06
S	1.80	1.02
Cl	1.75	0.96

Covalent Bond Order

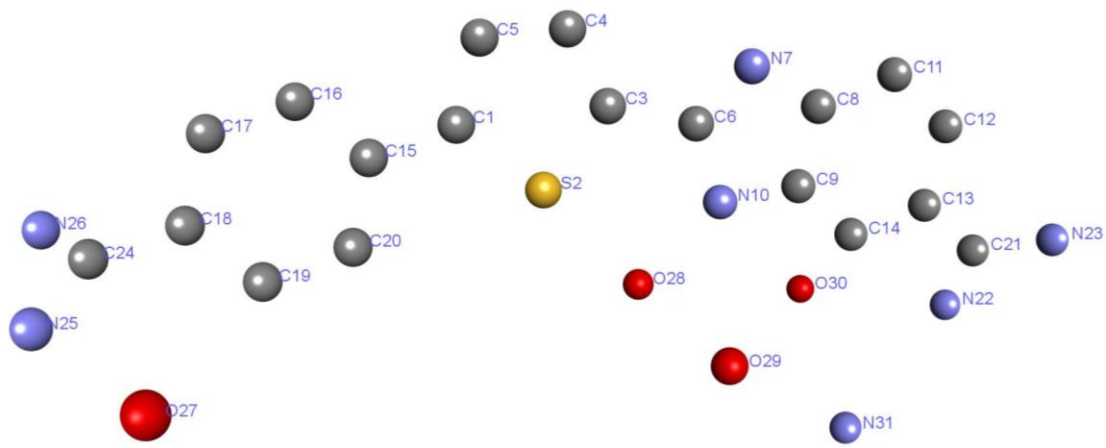
bond	name of bond	bond order
X–X	single	1
X=X	double	2
X≡X	triple	3

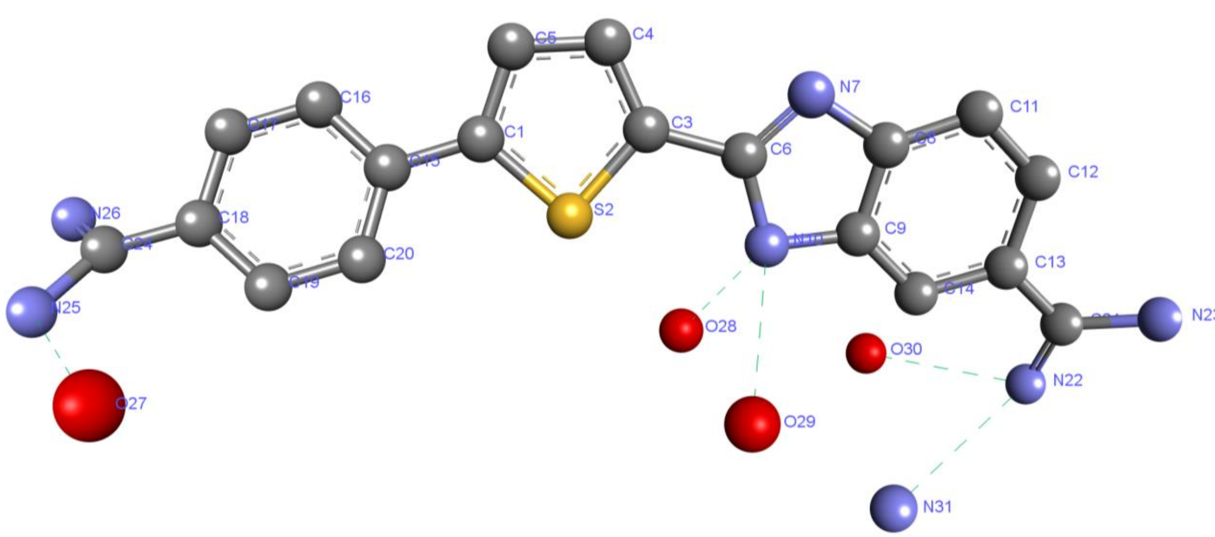
The larger the bond order, the STRONGER the bond

Covalent Bond Order

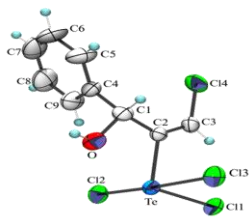
átomos	ordem de ligação	comprimento(Å)
C–C	simples	1.54
C=C	dupla	1.34
C≡C	tripla	1.21

The larger the bond order, the STRONGER the bond

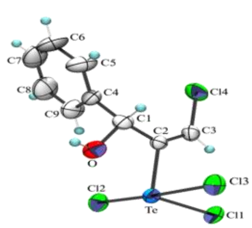

C5
C4
N7
C11
C16
C17
C1
C3
C6
C8
C12
C15
S2
N10
C9
C13
N26
C18
C24
C20
C14
C21
N23
C19
O28
O30
N22
N25
O29
O27
N31

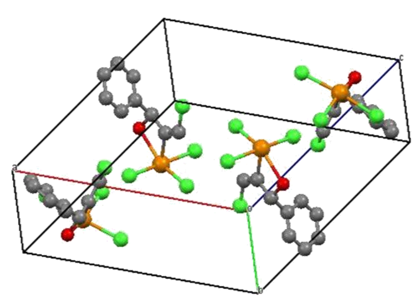

C5
C4
C16
N7
C11
C1
C3
C6
C12
N26
C18
S2
C9
C20
C13
N25
O28
O30
N23
N22
O27
O29
N31

Synthesis (organic)

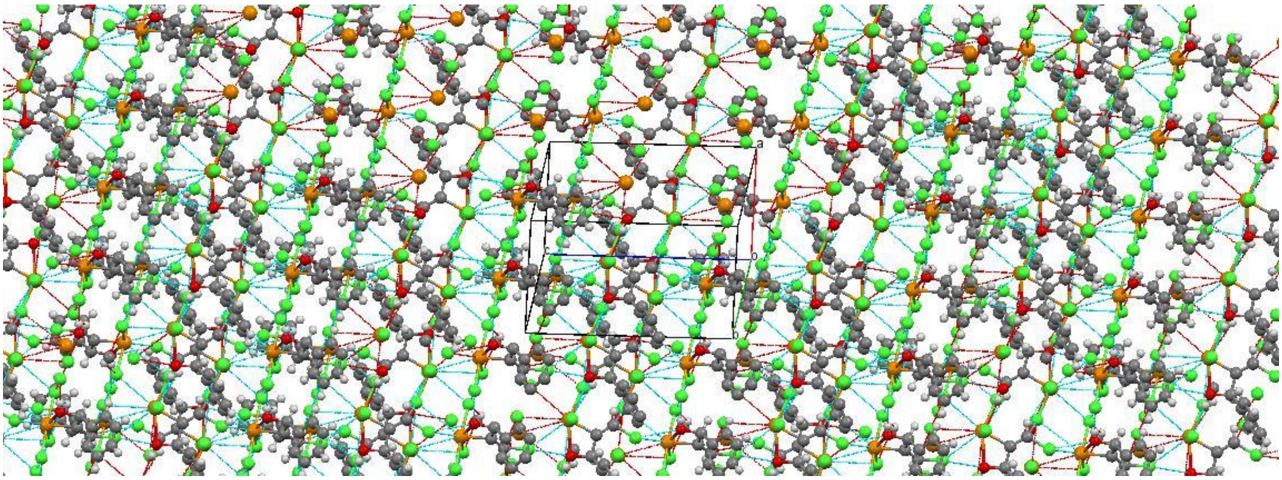


Solid - Crystal

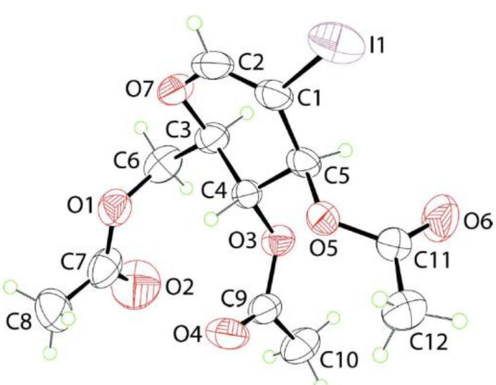


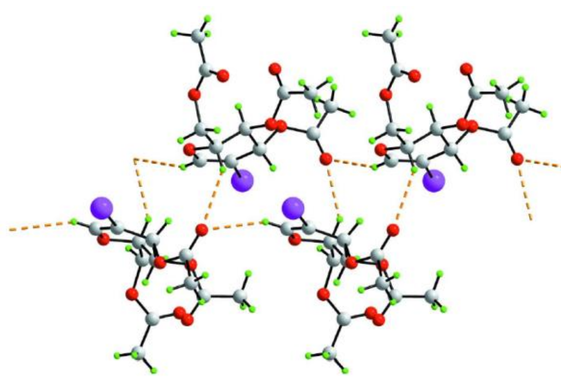


X-ray Crystallography



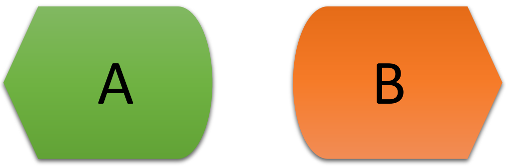
X-ray Crystallography

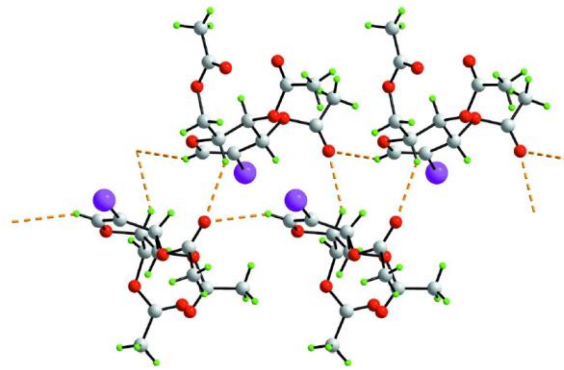




A interacts with B

interactions



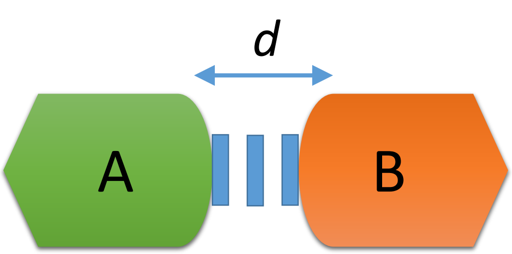


A , B atom, ion, dipoles, ...

Charge, partial charge

A interacts with B

interactions



A , B: atom, ion, dipoles, ...

electrostatic character

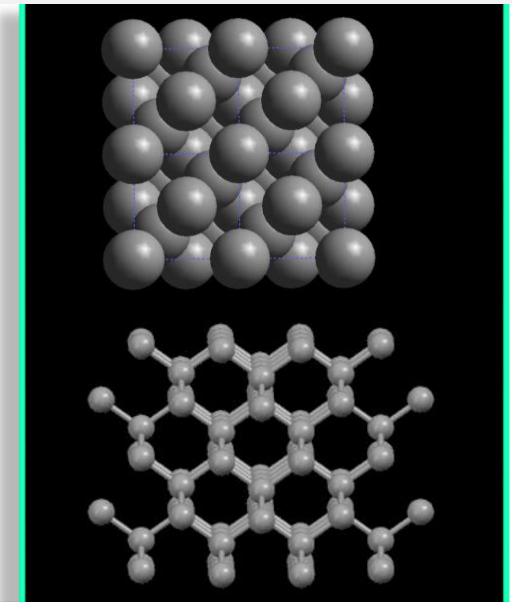
charge, partial charge

A & B interacts

Carbon Diamond

Diamond is a good electrical insulator

Diamond is the hardest naturally occurring material known.



Carbon Graphite Graphene

Graphite is a good electrical conductor

Graphite is Flexible

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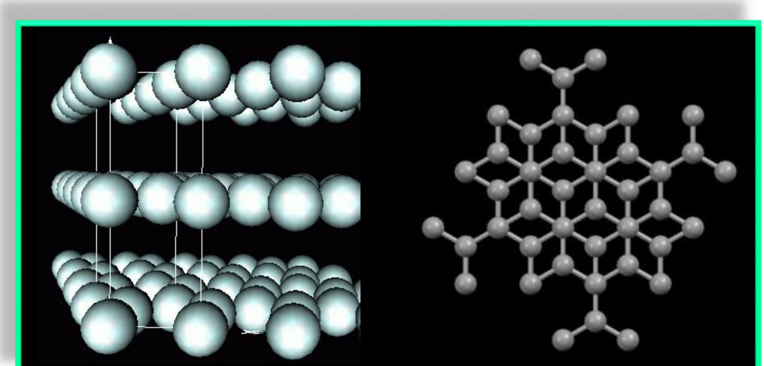
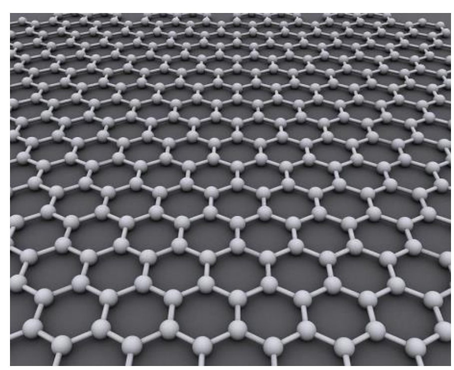
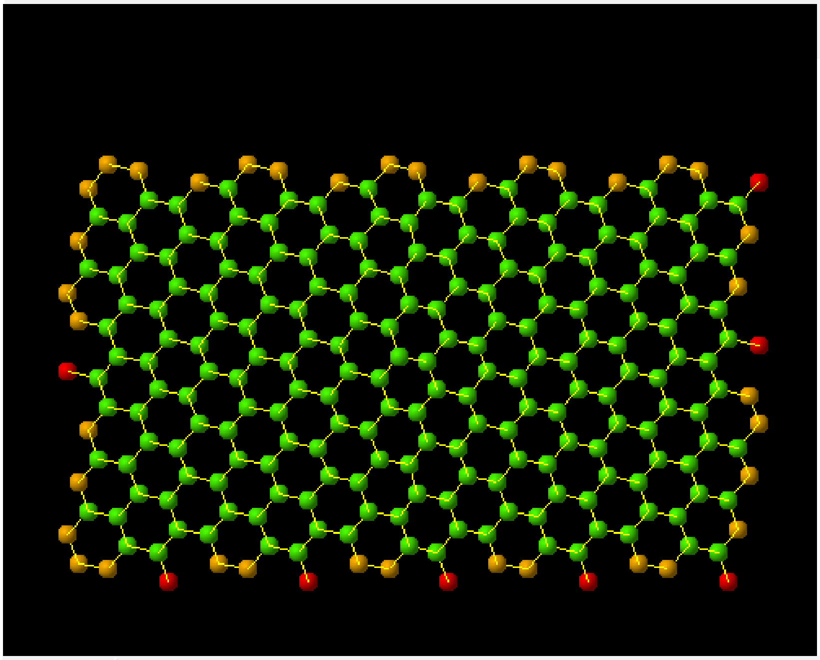
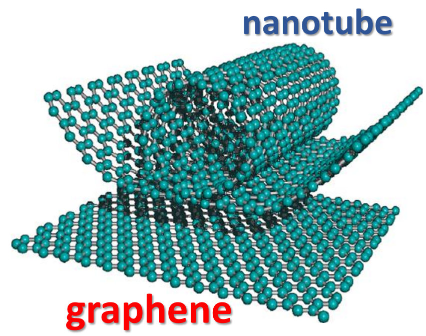




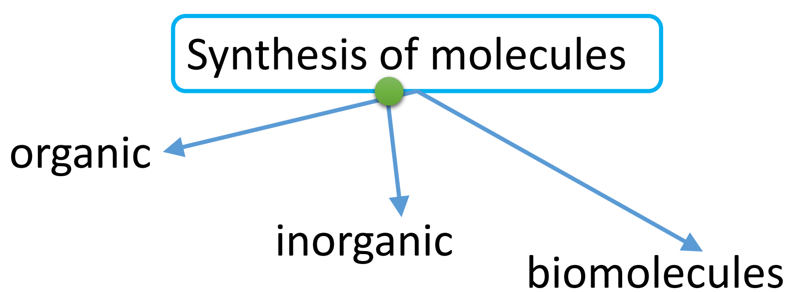
Graphene



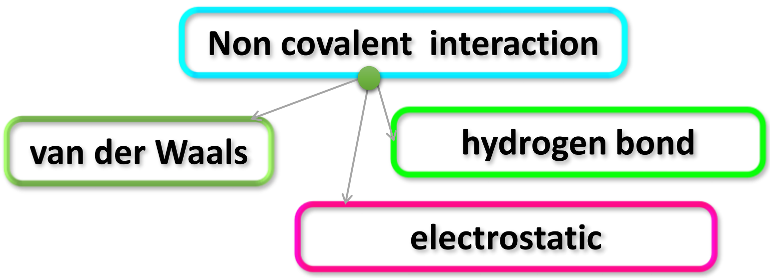


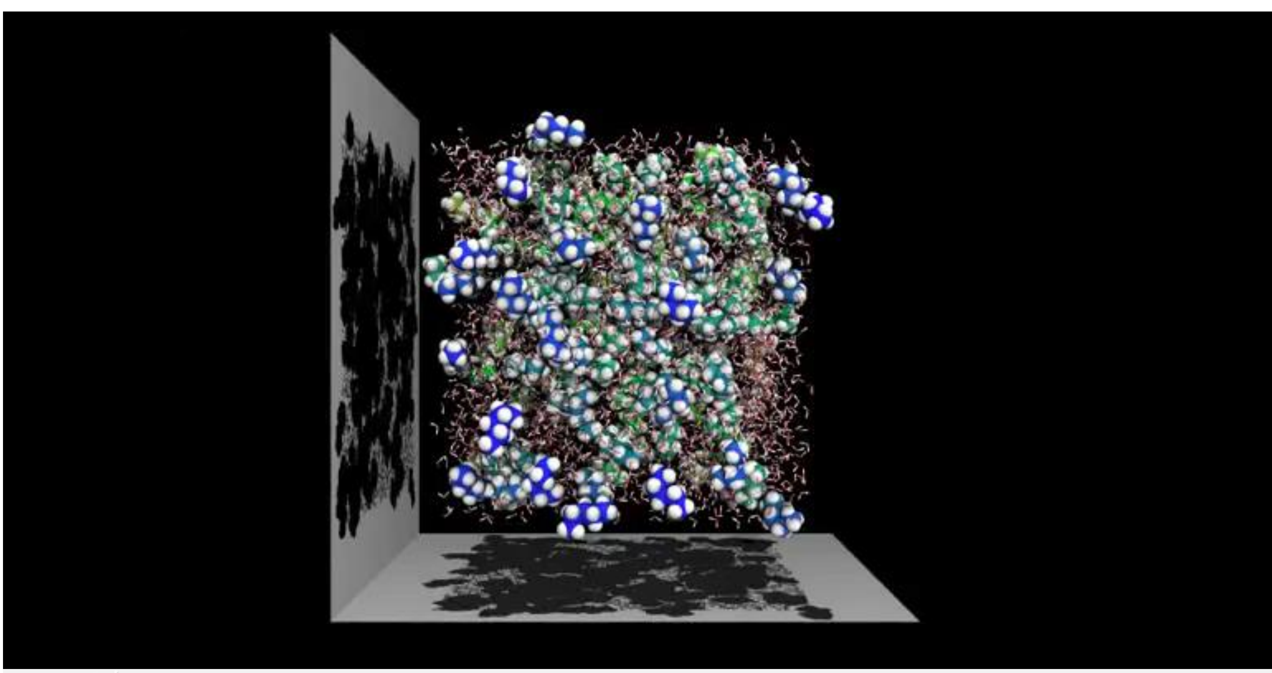
Synthesis

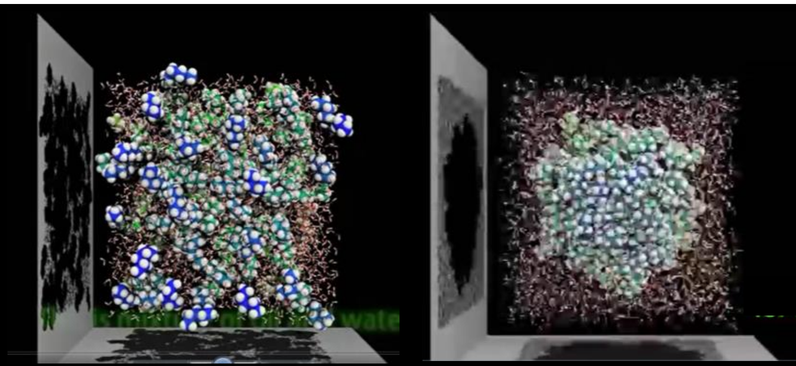
covalent



A interacts with B



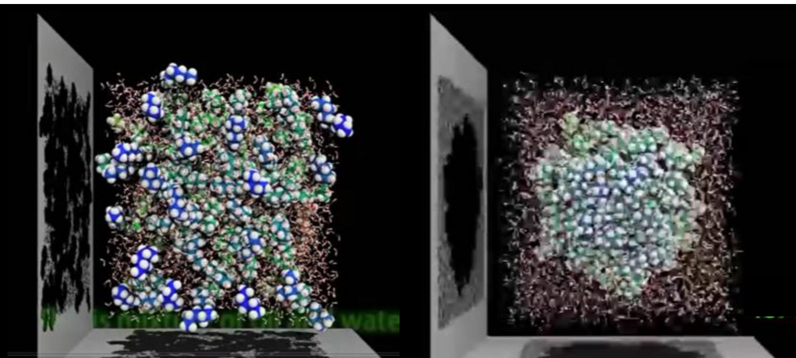




mistura | água + pentano

Molecular dynamics simulation of pentane, (C_5H_{12}) and water separation at 300 K temperature and 1 atm pressure.

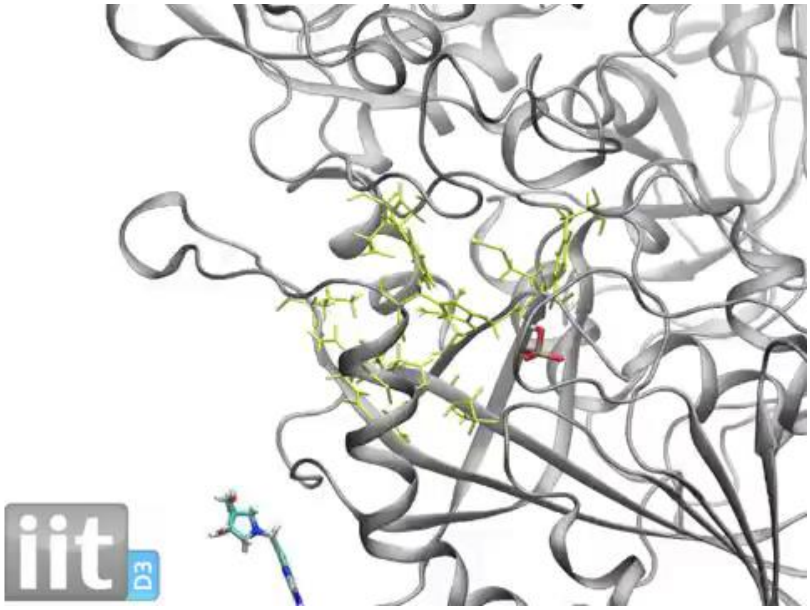
inicio | fim



mistura | água + pentano

sistema atua sobre sistema

https://www.youtube.com/watch?v=xcMSHy3CqXA

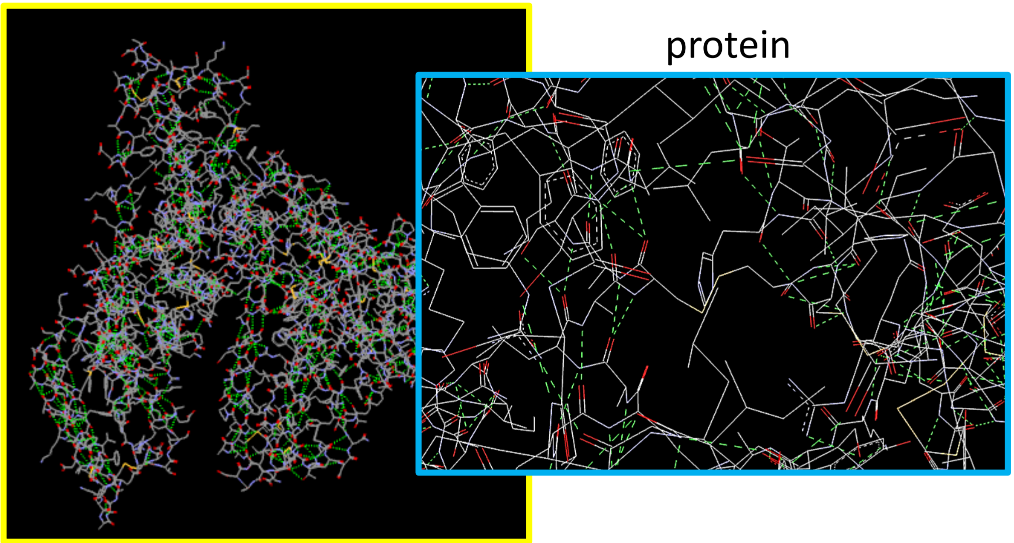


Chemistry

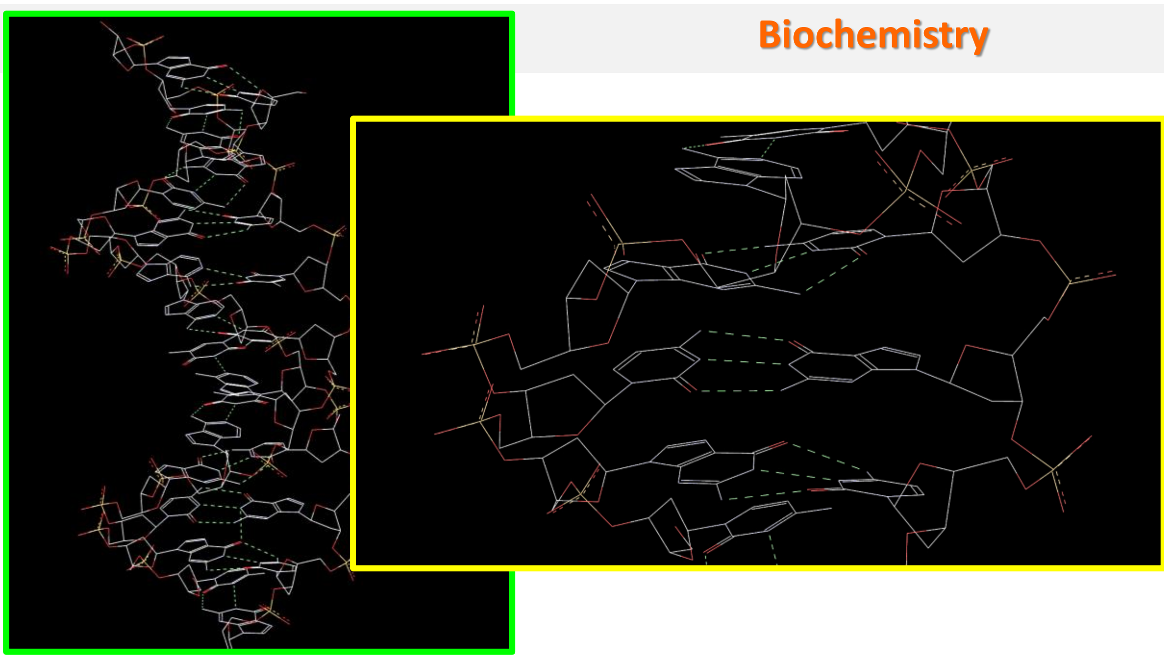
Covalent bonds

Biochemistry

protein



Biochemistry



Chemistry

1990

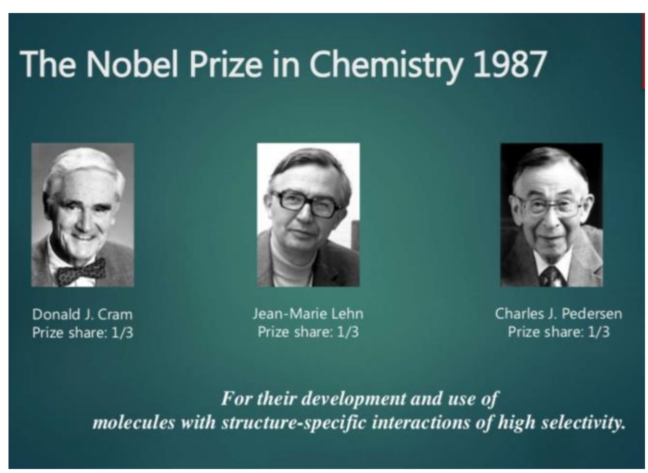
Covalent bonds

non covalent bonds

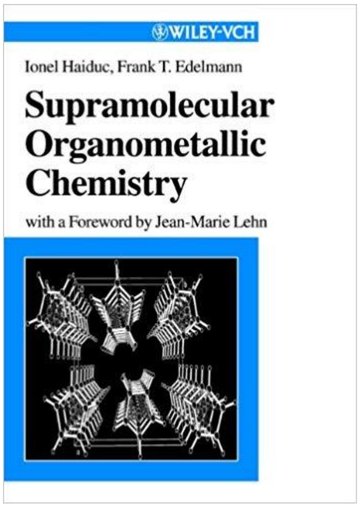
Supramolecular chemistry has proved to be a powerful tool to study nanoscale structures that mimic sophisticated biological systems in living organisms.

Supramolecular Chemistry

The importance of supramolecular chemistry was established by the 1987 Nobel Prize for Chemistry which was awarded to Donald J. Cram, Jean-Marie Lehn, and Charles J. Pedersen in recognition of their work in this area. The development of selective "host–guest" complexes in particular, in which a host molecule recognizes and selectively binds a certain guest, was cited as an important contribution.



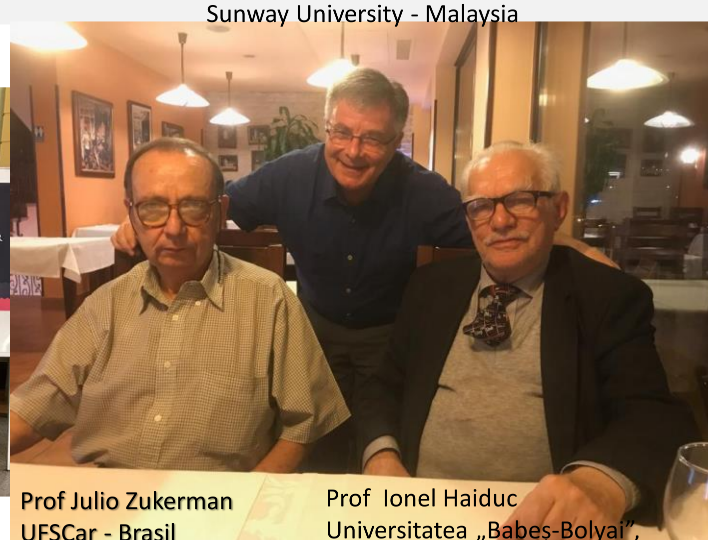
Ionel Haiduc



Ionel Haiduc, Frank T. Edelmann Supramolecular Organometallic Chemistry with a Foreword by Jean-Marie Lehn Supramolecular chemistry has become not only a major field of chemistry, but also a vivid interface between chemistry, biology, physics, and materials science. Although still a relatively young field of research, termini such as molecular recognition, host-guest chemistry, or self-assembly are now common knowledge even for chemistry students, and the research has already been honored with the Nobel prize. This first book on supramolecular organometallic chemistry combines two areas in chemistry that are experiencing the fastest developments. It provides a comprehensive, state-of-the-art review of various organometallic assemblies, and is arranged according to the types of intermolecular bonding. Details on the synthesis, structures, and properties of these compounds will be a valuable asset to the scientific community. The broad spectrum of assemblies containing main group element, transition metal, or f-element metal and a diverse range of ligands, held together by different bonding interactions make this a fascinating compilation. Illustrated extensively, this book is a very easy-to-read, all-you-need-to-know source of information.

Ionel Haiduc

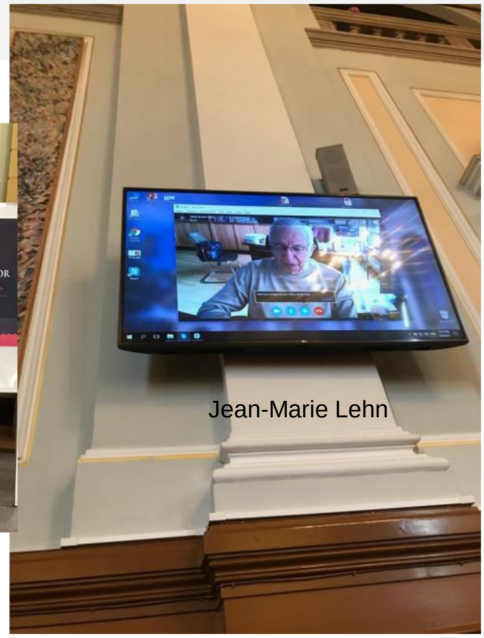
Prof Edward Tiekink
Sunway University - Malaysia



Prof Julio Zukerman
UFSCar - Brasil

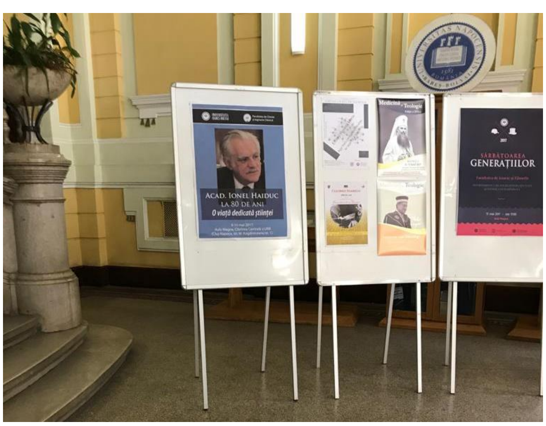
Prof Ionel Haiduc
Universitatea „Babeș-Bolyai",
Cluj-Napoca, Romenia

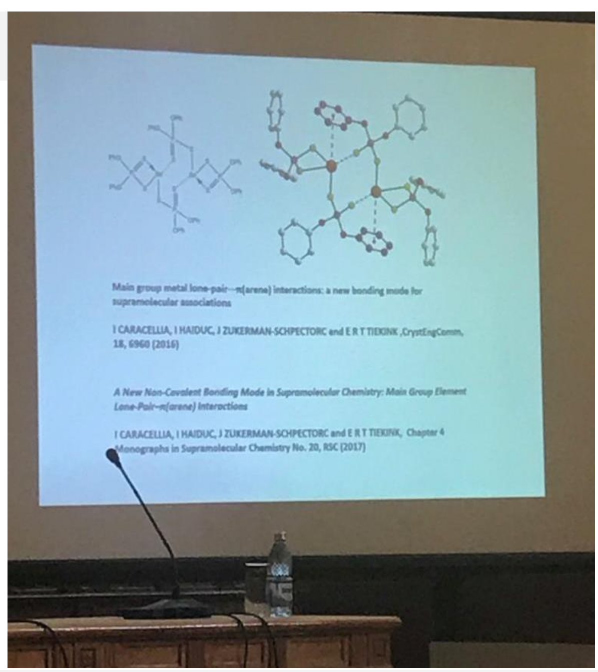
Ionel Haiduc



Jean-Marie Lehn

Ionel Haiduc



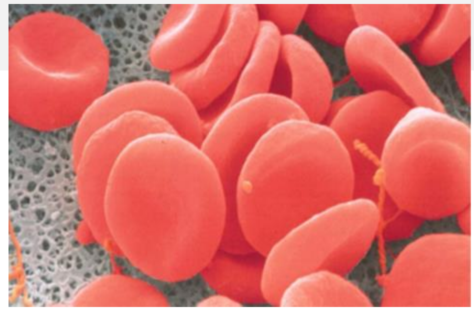


Ionel Haiduc

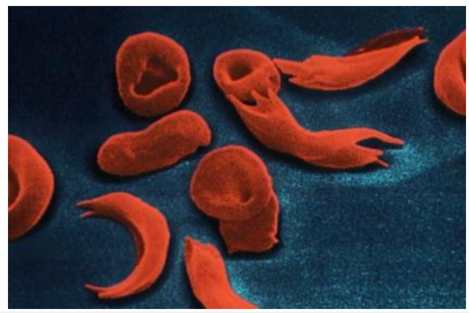
Ionel Haiduc

Red cells

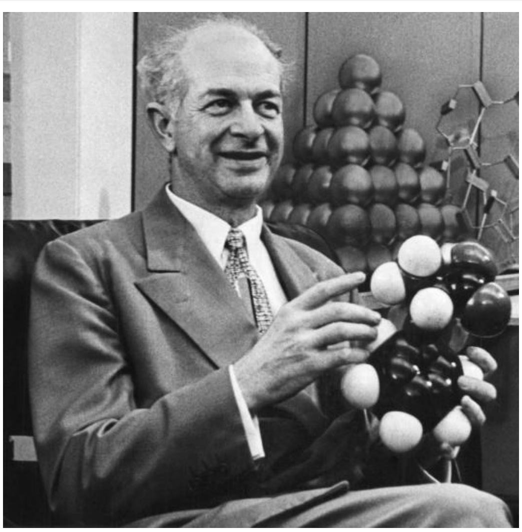
normal



sickle cell anemia
anemia falciforme



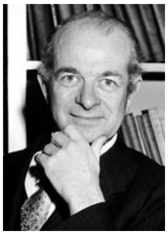
Linus Pauling



Research on **the nature of chemical bonds and the molecular structure**

Interações não covalentes (NCI) Julio Zukerman Ignez Caracelli

Nobelprize.org



1949 – Linus Pauling showed that sickle cell anemia is a molecular disease, resulting from a mutation in the protein Hemoglobin molecule

Reprinted from SCIENCE, November 25, 1949, Vol. 110, No. 2865, pages 543–548.

Sickle Cell Anemia, a Molecular Disease[1]

Linus Pauling, Harvey A. Itano,[2] S. J. Singer,[2] and Ibert C. Wells[3]

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California[4]

THE ERYTHROCYTES of certain individuals possess the capacity to undergo reversible changes in shape in response to changes in the partial pressure of oxygen. When the oxygen pressure is lowered, these cells change their forms from the normal biconcave disk to crescent, holly wreath, and other forms. This process is known as sickling. About 8 percent of American Negroes possess this characteristic; usually they exhibit no pathological consequences ascribable to it. These people are said to have sicklemia, or sickle cell trait. However, about 1 in 40 (*4*) of these individuals whose cells are capable of sickling suffer from a severe chronic anemia resulting from excessive destruction of their erythrocytes; the term sickle cell anemia is applied to their condition.

The main observable difference between the erythrocytes of sickle cell trait and sickle cell anemia has been that a considerably greater reduction in the partial pressure of oxygen is required for a major fraction of the trait cells to sickle than for the anemia cells (*11*). Tests *in vivo* have demonstrated that between 30 and 60 percent of the erythrocytes in the venous circulation of sickle cell anemic individuals, but less than 1 percent of those in the venous circulation of sicklemic individuals, are normally sickled. Experiments *in vitro* indicate that under sufficiently low oxygen pressure, however, all the cells of both types assume the sickled form.

The evidence available at the time that our investigation was begun indicated that the process of sickling might be intimately associated with the state and the nature of the hemoglobin within the erythrocyte. Sickle cell erythrocytes in which the hemoglobin is combined with oxygen or carbon monoxide have the biconcave disk contour and are indistinguishable in that form from normal erythrocytes. In this condition they are termed promeniscocytes. The hemoglobin appears to be uniformly distributed and randomly oriented within normal cells and promeniscocytes, and no birefringence is observed. Both types of cells are very flexible. If the oxygen or carbon monoxide is removed, however, transforming the hemoglobin to the uncombined state, the promeniscocytes undergo sickling. The hemoglobin within the sickled cells appears to aggregate into one or more foci, and the cell membranes collapse. The cells become birefringent (*11*) and quite rigid. The addition of oxygen or carbon monoxide to these cells reverses these phenomena. Thus the physical effects just described depend on the state of combination of the hemoglobin, and only secondarily, if at all, on the cell membrane. This conclusion is supported by the observation that sickled cells when lysed with water produce discoidal, rather than sickle-shaped, ghosts (*10*).

It was decided, therefore, to examine the physical and chemical properties of the hemoglobins of individuals with sicklemia and sickle cell anemia, and to compare them with the hemoglobin of normal individuals to determine whether any significant differences might be observed.

EXPERIMENTAL METHODS

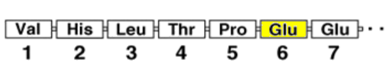
The experimental work reported in this paper deals largely with an electrophoretic study of these hemoglobins. In the first phase of the investigation, which concerned the comparison of normal and sickle cell anemia hemoglobins, three types of experiments were performed: 1) with carbonmonoxyhemoglobins; 2) with uncombined ferrohemoglobins in the presence of dithionite ion, to prevent oxidation to methemoglobins; and 3) with carbonmonoxyhemoglobins in the presence of dithionite ion. The experiments of type 3 were performed and compared with those of type 1 in order to ascertain whether the dithionite ion itself causes any specific electrophoretic effect.

Samples of blood were obtained from sickle cell anemic individuals who had not been transfused within three months prior to the time of sampling. Stroma-

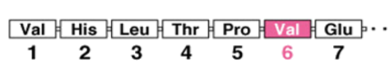
[1] This research was carried out with the aid of a grant from the United States Public Health Service. The authors are grateful to Professor Ray D. Owen, of the Biology Division of this Institute, for his helpful suggestions. We are indebted to Dr. Edward R. Evans, of Pasadena, Dr. Travis Winsor, of Los Angeles, and Dr. G. E. Burch, of the Tulane University School of Medicine, New Orleans, for their aid in obtaining the blood used in these experiments.

[2] U. S. Public Health Service postdoctoral fellow of the

Hemoglobin & Sickle cell anemia

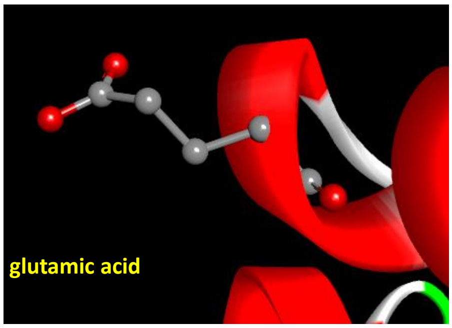


normal hemoglobin

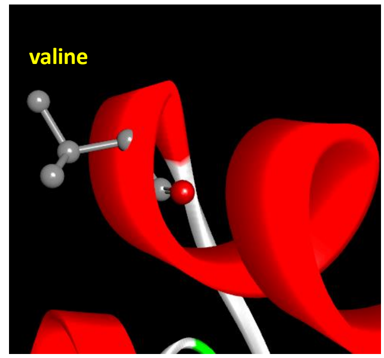


hemoglobin S

Mutation



normal hemoglobin



hemoglobin S

Hemoglobin S

Hemoglobin normal