

Intermolecular Forces: Van der Waals Interaction

"[There were] only two fundamental forces to account for all natural phenomena. One was Love, the other was Hate. The first brought things together while the second caused them to part."

Empedocles ~450 BC

Torsak Luanphaisarnnont

Evans Group Meeting

September 21, 2009

Outline

- I. Johannes Diderik van der Waals
- II. Introduction: Fundamental Forces
- III. Van der Waals Force
 - Definition
 - Attraction vs Repulsion
 - Lennard Jones Potential
- IV. Van der Waals Molecules
- V. Van der Waals Interaction in Organic Chemistry (Selected Cases)

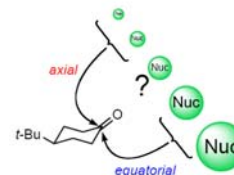
Related Evans group meetings:

Facial Selectivity within the t-Butylcyclohexyl Scaffold: Qualitative Insight into Reagent Size?

Joseph Wzorek (3/20/09)

Evans Group Literature Seminar

Facial Selectivity within the t-Butylcyclohexyl Scaffold:
Qualitative Insight into Reagent Size?



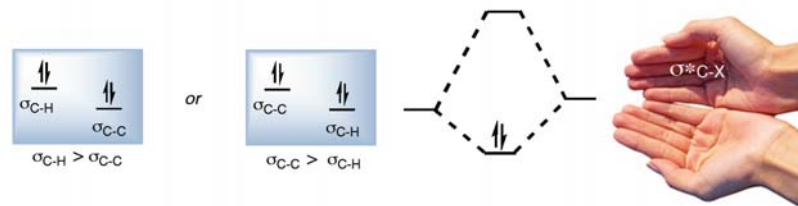
Presented by: Andrew Weiss and Joseph Wzorek
Friday, 3/20/09

Relative Hyperconjugative Electron Release from σ_{C-H} and σ_{C-C} Bonds: Experimental and Theoretical Approaches

Andrew Weiss (3/20/09)

Evans Literature Group Meeting

Relative Hyperconjugative Electron Release From σ_{C-H} and σ_{C-C} Bonds:
Experimental and Theoretical Approaches



Andrew Weiss and Joe Wzorek
Evans Group Meeting
19 March 2009

Johannes Diderik van der Waals

born: November 23, 1837 (Leyden, Netherlands)

died: March 8, 1923 (Amsterdam, Netherlands)

Nobel Prize: Physics in 1910 "for his work on the equation of states for gases and liquid"

education: Doctor's degree with Peiter Reijke at University of Leiden (1873)
Thesis: "On the continuity of gases and liquid states"

career: University of Amsterdam (1876)

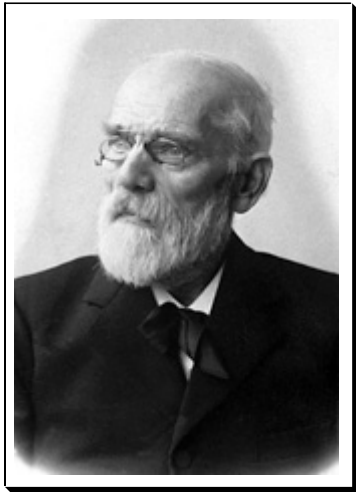
key research:

- **Equation of State** (1873) -- gaseous and liquid states not only merged into each other in a continuous manner, but they are in fact similar in nature. **Volumes of molecules** and **the intermolecular forces** are necessary in establishing the relationship between pressure, volume, and temperature of gases and liquids.

$$\left(p + \frac{a'}{v^2}\right)(v - b') = kT$$

"that there can be no doubt that the name of Van der Waals will soon be among the foremost in molecular science"

James Clerk Maxwell



Johannes Diderik van der Waals

key research (cont.):

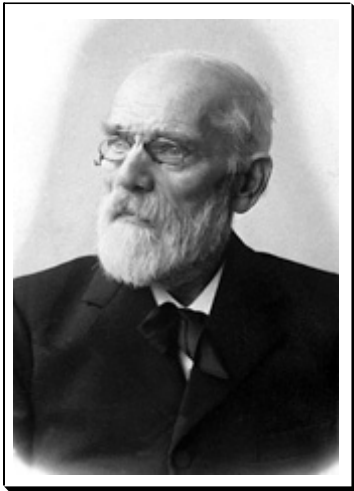
- **Law of Corresponding States** (1880) -- equation of state can be reduced if pressure, volume, and temperature are expressed as a simple function of critical pressure, critical volume, and critical temperature.

This led to the liquefaction of hydrogen (J. Dewar, 1898) and of helium (H. Kamerlingh Onnes, Nobel Prize in Physics 1913 for his investigations on the properties of matter at low temperatures which led, inter alia, to the production of liquid helium, 1908)

"that Van der Waals' studies have always been considered as a magic wand for carrying out experiments and that the Cryogenic Laboratory at Leiden has developed under the influence of his theories "

H. Kamerlingh Onnes

- **Thermodynamic Theory of Capillarity** (1893) -- a gradual, though very rapid, change of density exists at the boundary layer between liquid and vapour.



"And here I have come to the weak point in the study of the equation of state. I still wonder whether there is a better way. In fact this question continually obsesses me, I can never free myself from it, it is with me even in my dreams."

J. D. van der Waals, Nobel Lecture

Nobel Lectures, Physics 1901-1921, Elsevier Publishing Company, Amsterdam, 1967.

"Cohesion : a scientific history of intermolecular forces" Rowlinson, J. S., Cambridge University Press, 2002. (history of intermolecular forces from Newton period to Van der Waals period)

Fundamental Forces

Gravitation (Isaac Newton, 1687)

shapes the structure and evolution of stars, galaxy and the whole universe.

- weakest of all
- infinite range
- only attractive
- permanent (cannot be absorbed or transformed)

Electromagnetism (James Clerk Maxwell, 1864)

responsible for interactions between charged particles and for emission and absorption of photons. (electrostatic, electricity and magnetism)

- 10^{36} times stronger than gravitation
- infinite range
- repulsive for like charges and attractive for unlike charges

Weak Interaction

accounts for certain nuclear phenomena (radiation) and fusion. First proposed by Enrico Fermi, 1934 (Nobel Prize in Physics, 1938). Developed further by Glashow, Salam, and Weinberg (Nobel Prize in Physics, 1979).

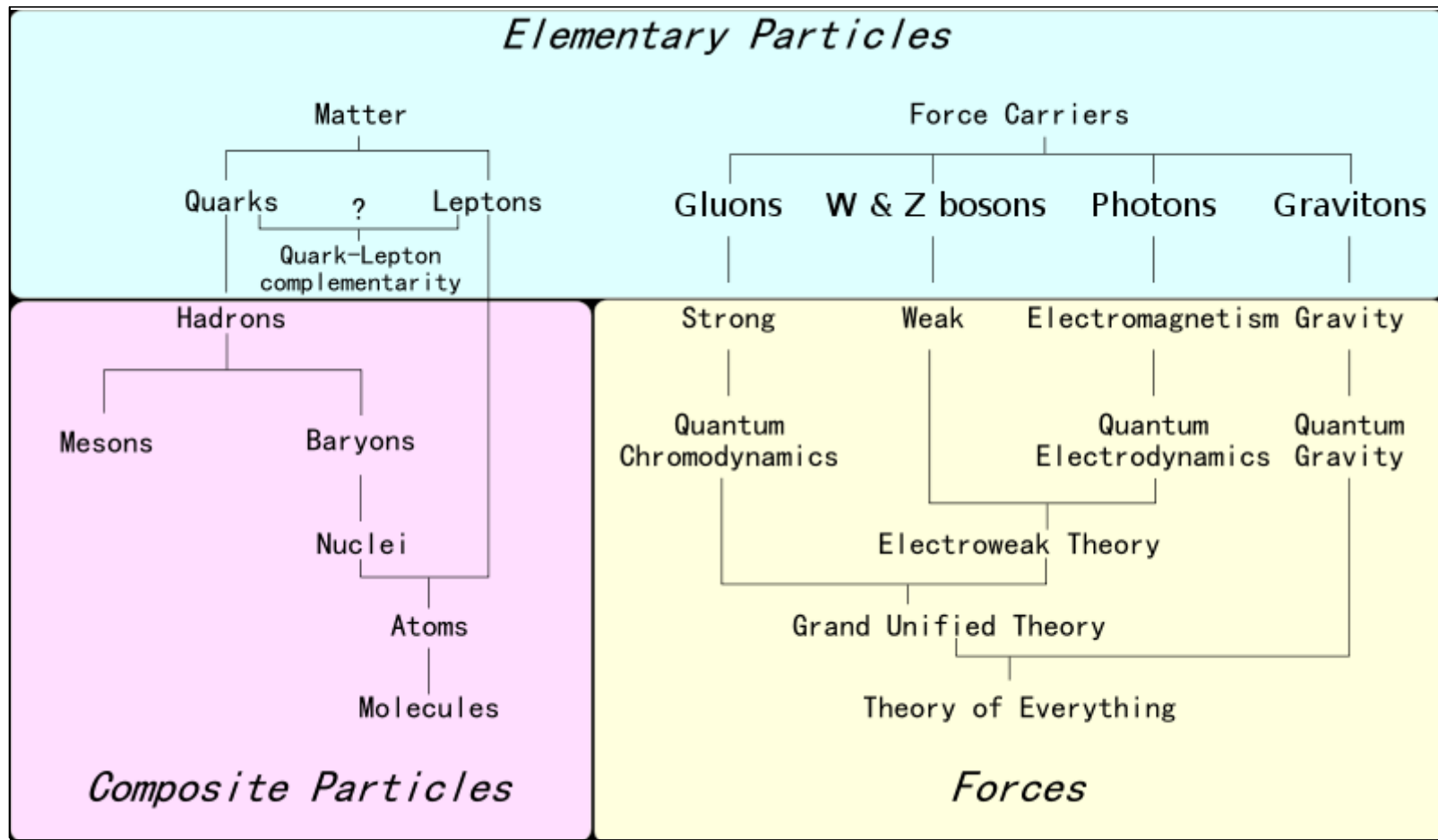
- 10^{25} times stronger than gravitation
- 10^{-18} m range (about 1% of diameter of atomic nucleus)

Strong interaction (quarks -- Murray Gell-mann, Nobel Prize in Physics 1969)

binds quarks together in cluster to make more familiar particle such as protons and neutrons.

- 10^{38} times stronger than gravitation
- 10^{-15} m range

Fundamental Forces



Chemical Bonding and Intermolecular Forces

can be classified into 3 categories

1. Purely electrostatic (Coulomb Force)

interactions between charges, permanent dipoles, quadrupoles, etc.

2. Polarization forces

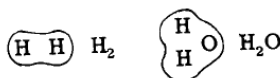
arises from the dipole moments induced in atoms and molecules by the electric fields of nearby charges and permanent dipoles. All interaction in a solvent medium involve polarization effects.

3. Quantum mechanical forces

covalent bonding, charge-transfer interactions, repulsive steric or exchange interactions (Pauli exclusion principle)

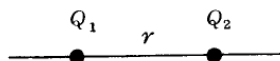
Chemical Bonding and Intermolecular Forces

Covalent, metallic



Complicated, short range

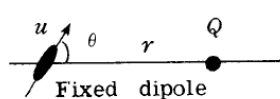
Charge-charge



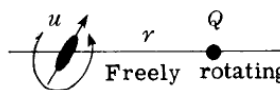
$$Q_1 Q_2 / 4\pi\epsilon_0 r$$

(Coulomb energy)

Charge-dipole

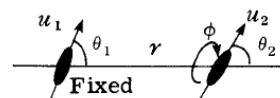


$$-Qu \cos \theta / 4\pi\epsilon_0 r^2$$

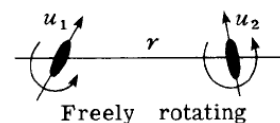


$$-Q^2 u^2 / 6(4\pi\epsilon_0)^2 k T r^4$$

Dipole-dipole



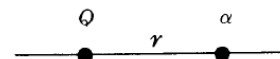
$$-u_1 u_2 [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi] / 4\pi\epsilon_0 r^3$$



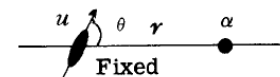
$$-u_1^2 u_2^2 / 3(4\pi\epsilon_0)^2 k T r^6$$

(Keesom energy)

Charge-non-polar

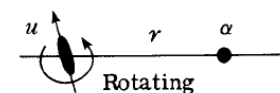


$$-Q^2 \alpha / 2(4\pi\epsilon_0)^2 r^4$$



$$-u^2 \alpha (1 + 3 \cos^2 \theta) / 2(4\pi\epsilon_0)^2 r^6$$

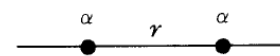
Dipole-non-dipolar



$$-u^2 \alpha / (4\pi\epsilon_0)^2 r^6$$

(Debye energy)

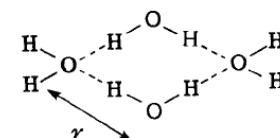
Two non-polar molecules



$$\frac{3}{4} \frac{h\nu \alpha^2}{(4\pi\epsilon_0)^2 r^6}$$

(London dispersion energy)

Hydrogen bond



Complicated, short range,
energy roughly
proportional to $-1/r^2$

Chemical Bonding and Intermolecular Forces

TABLE 1
Typical Interatomic and Intermolecular Forces

Interatomic Bonding:

- Covalent

- Ionic

- Metallic

- Hydrogen

Type	Range (nm)	Energy (kJ/mol)
I. Interatomic bonds		
(a) Ionic	0.15–0.24	335–1050
hydrogen	0.26–0.30 ^a	8.0–42 ^b
(b) Covalent	0.15–0.24	63–920
(c) Metallic	0.26–0.30	110–350
II. Intermolecular bonds (indefinite range)		
(a) Dipole–dipole (excluding hydrogen bonds)		4.0–21
(b) London (dispersion)		4.0–42
(c) Dipole–induced dipole		~2.0

^a 0.186 nm for H₂O and 0.367 nm for crystalline hydrazine.

^b 42 kJ/mol for HF₂⁻.

Intermolecular Force:

- Dipole-dipole

- London (dispersion)

- Dipole-induced dipole

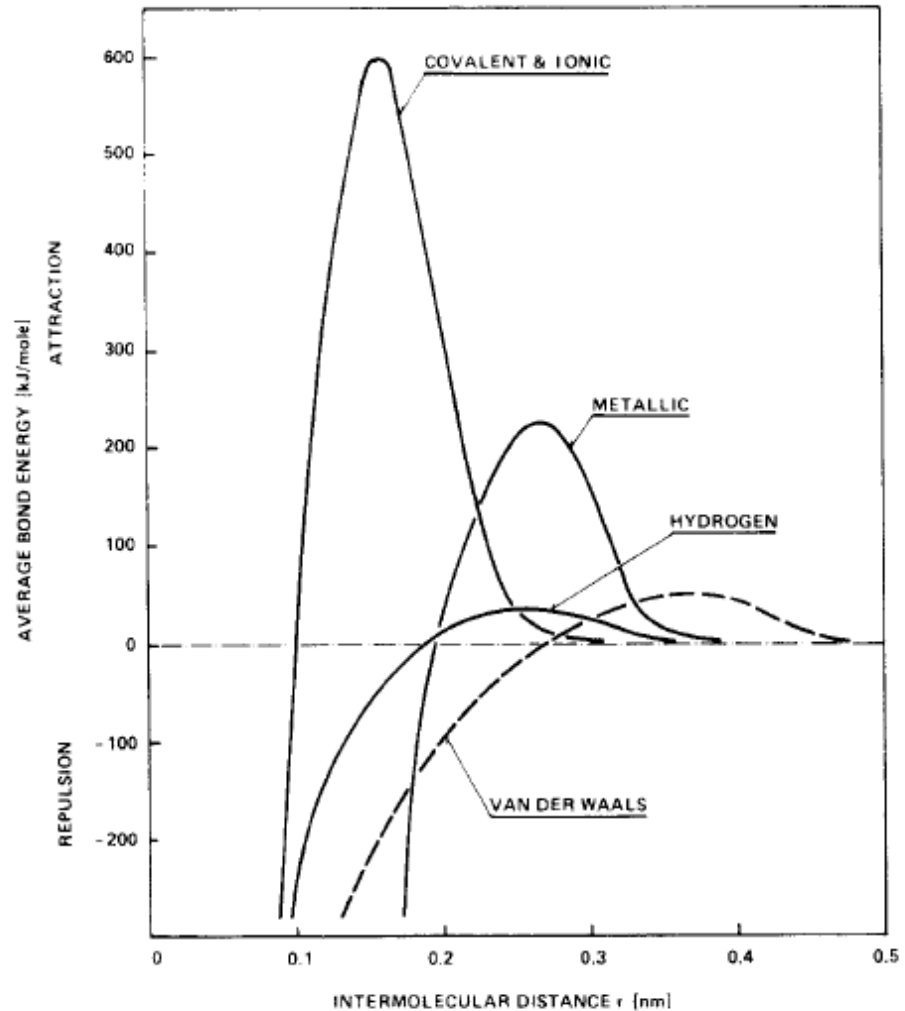
Chemical Bonding and Intermolecular Forces

Interatomic Bonding:

- Covalent
- Ionic
- Metallic
- Hydrogen

Intermolecular Force:

- Dipole-dipole
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- Dipole-induced dipole

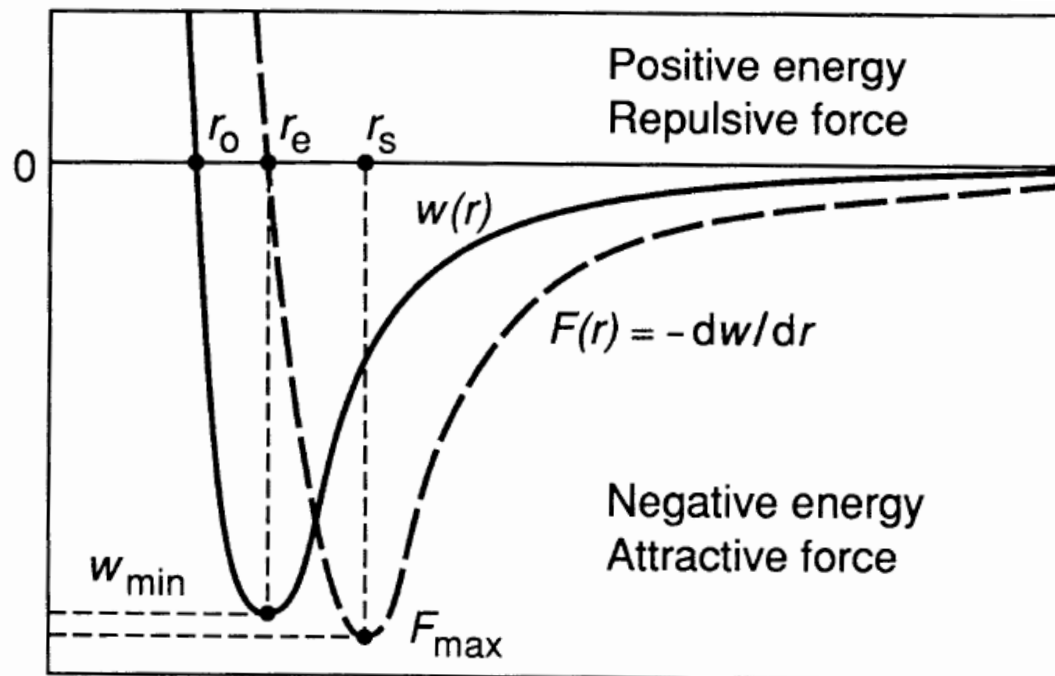


Van der Waals Interaction

Definition:

The attractive or repulsive forces between molecular entities (or between groups within the same molecular entity) other than those due to bond formation or to the electrostatic interaction of ions or of ionic groups with one another or with neutral molecules. **The term includes: dipole–dipole, dipole-induced dipole and London (instantaneous induced dipole-induced dipole) forces.** The term is sometimes used loosely for the totality of nonspecific attractive or repulsive intermolecular forces

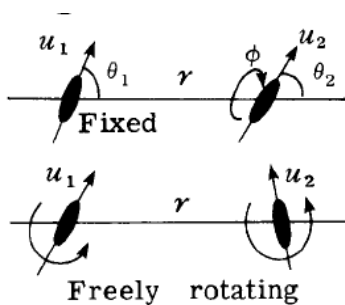
IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). <http://goldbook.iupac.org> (2006-).



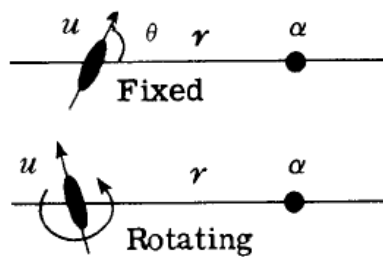
Attraction

Attractions considered in Van der Waals force:

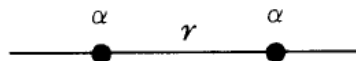
1. Dipole-dipole interaction



2. Dipole-induced dipole interaction

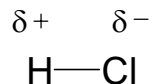


3. Induced dipole-induced dipole interaction



Attraction: Dipole-dipole interaction

Dipole: a separation of positive and negative charge



- dipole of certain molecules can change dramatically depending on their environment and solvent medium (for example: aminoacid)

Dipole moment (u): $u = ql$

- permanent dipole moments only occur in asymmetric molecules (not atoms)
- dipole moment of a molecule can be estimated from bond moments

<i>Molecules</i>			
Alkanes	0 ^b	H ₂ O	1.85
C ₆ H ₆ (benzene)	0	CH ₃ OH, C ₂ H ₅ OH	1.7
CCl ₄	0	Hexanol, octanol	1.7
CO ₂	0	C ₆ H ₁₁ OH (cyclohexanol)	1.7
CO	0.11	CH ₃ COOH (acetic acid)	1.7
CHCl ₃ (chloroform)	1.06	C ₂ H ₄ O (ethylene oxide)	1.9
HCl	1.08	CH ₃ COCH ₃ (acetone)	2.9
\NH ₃	1.47	HCONH ₂ (formamide)	3.7
SO ₂	1.62	C ₆ H ₅ OH (phenol)	1.5
CH ₃ Cl	1.87	C ₆ H ₅ NH ₂ (aniline)	1.5
\NaCl	8.5	C ₆ H ₅ Cl (chlorobenzene)	1.8
CsCl	10.4	C ₆ H ₅ NO ₂ (nitrobenzene)	4.2

<i>Bond moments</i>					
C—H ⁺	0.4	C—C	0	C ⁺ —Cl	1.5–1.7
\—H ⁺	1.31	C=C	0	N ⁺ —O	0.3
O—H ⁺	1.51	C ⁺ —N	0.22	C ⁺ =O	2.3–2.7
F—H ⁺	1.94	C ⁺ —O	0.74	N ⁺ =O	2.0

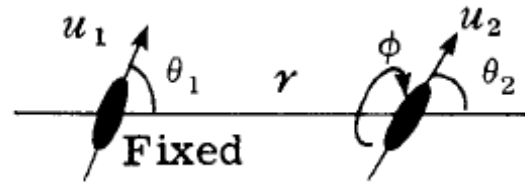
<i>Group moments</i>					
C— ⁺ OH	1.65	C— ⁺ CH ₃	0.4	C— ⁺ COOH	1.7
C— ⁺ NH ₂	1.2–1.5	C ⁺ —NO ₂	3.1–3.8	C— ⁺ OCH ₃	1.3

Attraction: Dipole-dipole interaction

Dipole energy (u^i):

$$u^i = \frac{q^2}{4\pi\epsilon_0\epsilon l} = \frac{u^2}{4\pi\epsilon_0\epsilon l^3}$$

Dipole-dipole interaction:



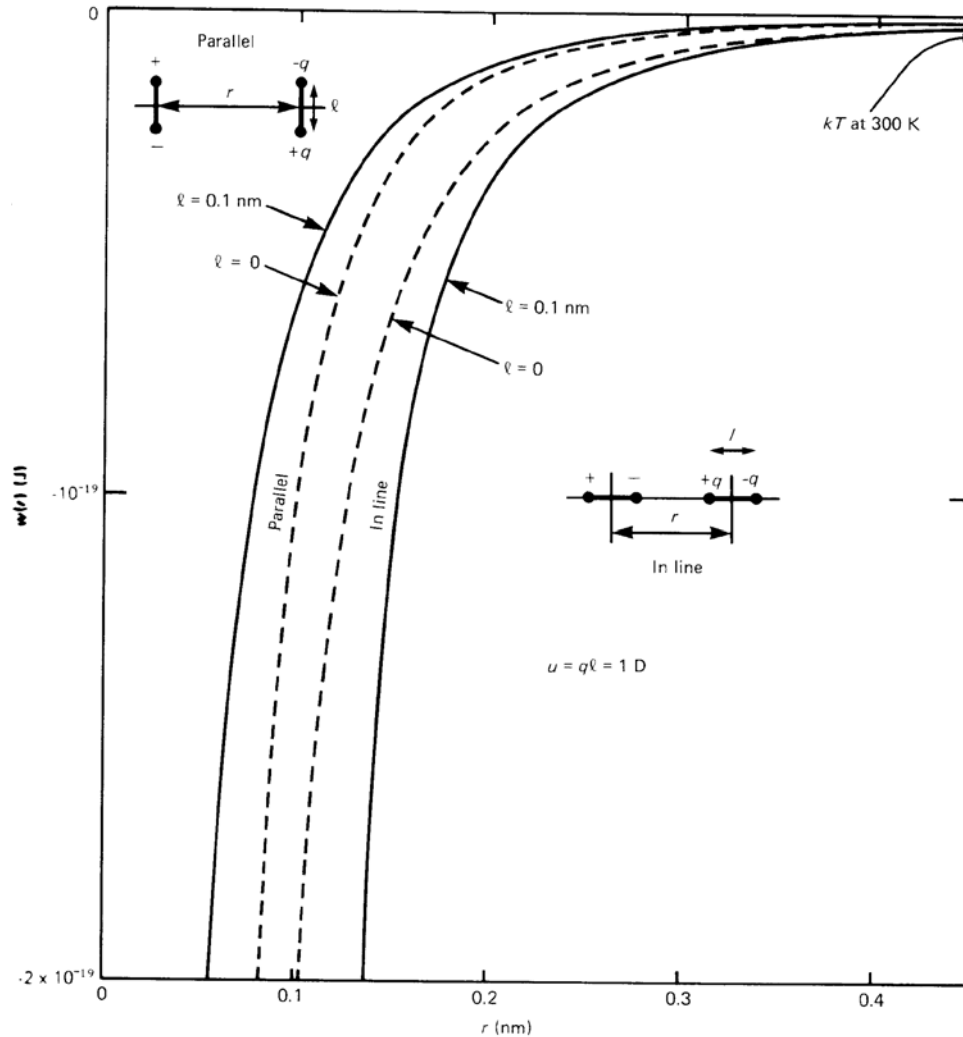
$$w = - \frac{u_1 u_2}{4\pi\epsilon_0\epsilon r^3} [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi] \quad \text{for } r > 3 l$$

- dipole-dipole interaction is comparatively weak (for dipole moment of 1 Debye at 0.35 nm in vacuum, the interaction is already weaker than kT)
- in certain molecules (small size and large dipole moment O-H, N-H, and F-H), dipole-dipole interaction can lead to short range association in liquid (part of H-bond)

Attraction: Dipole-dipole interaction

Dipole-dipole interaction (cont.):

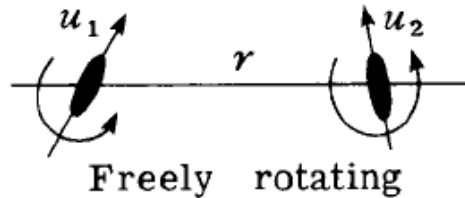
- dipole-dipole interaction is strongest when the two dipoles mutually orient themselves in line.



Attraction: Dipole-dipole interaction

Dipole-dipole interaction (cont.):

at large separation or in a medium of high ϵ , when interaction falls below kT , dipoles can now rotate more freely. The angle averaged potentials are not zero because of Boltzmann weighting factor, the energy (**Keesom interaction** or orientation interaction) becomes:



$$w = - \frac{u_1^2 u_2^2}{3(4\pi\epsilon_0\epsilon)^2 kT r^6} \quad \text{for } kT > \frac{u_1 u_2}{4\pi\epsilon_0\epsilon r^3}$$

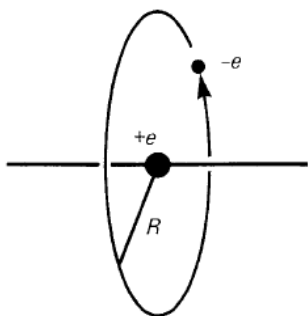
Attraction: Dipole-induced dipole interaction

Polarizability (α_0)

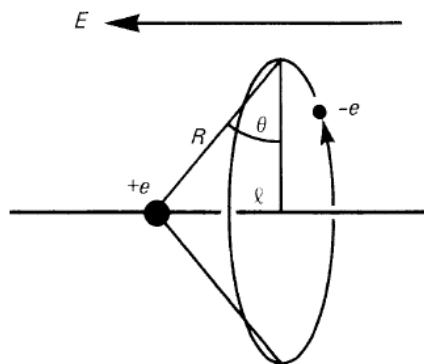
The ease of distortion of the electron cloud of a molecular entity by an electric field (such as that due to the proximity of a charged reagent). It is experimentally measured as the ratio of induced dipole moment (u_{ind}) to the field E which induces it:

$$\alpha_0 = \frac{u_{\text{ind}}}{E}$$

IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). <http://goldbook.iupac.org> (2006-).



(a)



(b)

$$u_{\text{ind}} = \alpha_0 E = le$$

$$F_{\text{ext}} = eE$$

$$F_{\text{int}} = \frac{e^2}{4\pi\epsilon_0 R^2} \sin \theta = \frac{e^2 l}{4\pi\epsilon_0 R^3} = \frac{eu_{\text{ind}}}{4\pi\epsilon_0 R^3}$$

$$F_{\text{int}} = F_{\text{ext}}; \quad u_{\text{ind}} = 4\pi\epsilon_0 R^3 E$$

$$\alpha_0 = 4\pi\epsilon_0 R^3$$

Attraction: Dipole-induced dipole interaction

Polarizability (α_0) (cont.)

- polarizability is approximately proportional to the volume of a molecule
- polarizability of a molecule can be approximated to the sum of its bond/group polarizabilities with exception of molecule with non-bonded lone pair electrons (which also contributed to the polarizability)

TABLE 5.1 Electronic polarizabilities α_0 of atoms, molecules, bonds, and molecular groups^a

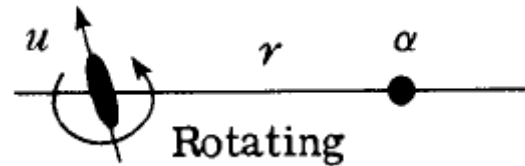
<i>Atoms and molecules</i>					
He	0.20	NH ₃	2.3	CH ₂ =CH ₂	4.3
H ₂	0.81	CH ₄	2.6	C ₂ H ₆	4.5
H ₂ O	1.48	HCl	2.6	Cl ₂	4.6
O ₂	1.60	CO ₂	2.6	CHCl ₃	8.2
Ar	1.63	CH ₃ OH	3.2	C ₆ H ₆	10.3
CO	1.95	Xe	4.0	CCl ₄	10.5
<i>Bond polarizabilities</i>					
Aliphatic		C—C	0.48	C—O	0.60
Aromatic		C \equiv C	1.07	C=O	1.36
		C=C	1.65	N—H	0.74
Aliphatic		C—H	0.65	C—Cl	2.60
		O—H	0.73	C—Br	3.75
<i>Molecular groups</i>					
C—O—H	1.28	CH ₂		1.84	
C—O—C	1.13	Si—O—Si		1.39	
C—NH ₂	2.03	Si—OH		1.60	

^a Polarizabilities α_0 are given in units of $(4\pi\epsilon_0)\text{\AA}^3 = (4\pi\epsilon_0)10^{-30}\text{ m}^3 = 1.11 \times 10^{-40}\text{ C}^2\text{ m}^2\text{ J}^{-1}$. Note that when molecules are dissolved in a solvent medium their polarizability can change by up to 10%. Data compiled from Denbigh (1940), Hirschfelder *et al.* (1954) and Smyth (1955).

Attraction: Dipole-induced dipole interaction

Dipole-induced dipole interaction

Typically the strength of dipole-induced dipole interaction is not enough to mutually orient the molecules. The interaction needs to be angle-averaged. The interaction (**Debye interaction** or inductive interaction) becomes:



$$w = - \frac{u^2 \alpha_0}{(4\pi\epsilon_0\epsilon)^2 r^6}$$

Attraction: Induced dipole-induced dipole interaction

Induced dipole-induced dipole interaction (dispersion)

- dispersion is applicable to all atoms or molecules (unlike Keesom or Debye interaction)
- it is responsible for certain phenomena in macroscopic scale (adhesion, surface tension, physical adsorption, wetting, properties of gases and liquid, structures of condensed macromolecules,...)

for more information, see "Van der Waals Force: A Handbook for Biologists, Chemists, Engineers, and Physicists" Parsegian, V. D. New York: Cambridge University Press, 2006.

- it is a long range force that can be effective at large distance (>10 nm) to interatomic spacings
- dispersion is non-additive. The dispersion of two molecules is affected by the presence of the third molecules

London Dispersion

Fritz London (1937) proposed a theory based on quantum mechanics to explain dispersion.

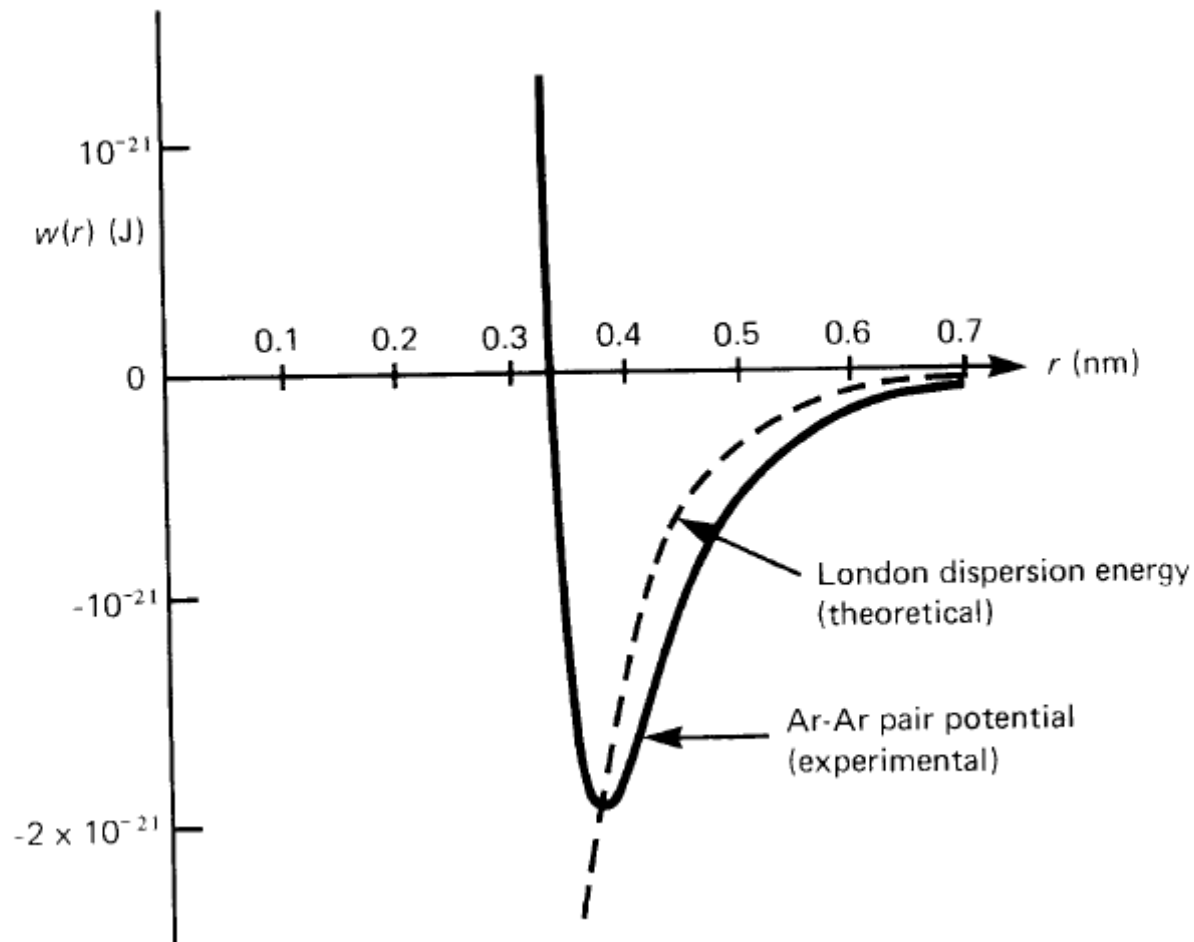
$$w = - \frac{3\alpha_{01}^2 \alpha_{02}^2 I_1 I_2}{2(4\pi\epsilon_0)^2 r^6 (I_1 + I_2)}$$

where I is the first ionization potential $I = h\nu$.

Attraction: Induced dipole-induced dipole interaction

London Dispersion (cont.)

This simple theory assumes molecules only have one ionization potential and does not take into account solvent effect. Therefore, London equation usually gives weaker dispersion compared to the experimental result.



Combined Attractions

Mclachlan (1963) presented a theory that included induction, orientation, and dispersion force and which could also be applied to interactions in a solvent medium

$$w = - \frac{6kT}{(4\pi\epsilon_0)^2 r^6} \sum \frac{\alpha_1(iv_n)\alpha_2(iv_n)}{\epsilon_3^2(iv_n)}$$

Some properties of van der Waals interaction:

1. Dominance of dispersion forces: dispersion forces generally exceed the dipole-dependent induction.

		vdW energy	
		Theoretical	From Gas law
HCl	HCl	123	157
HBr	HBr	189	207
HI	HI	372	350

2. Interactions of dissimilar molecules: Interactions between two dissimilar molecules can be approximated to the geometric means of that of two similar molecules

$$vdW(A B) = [vdW(A A) vdW(B B)]^{0.5}$$

HCl HI geometric mean = 214, computed value = 205

Repulsion

Van der Waals Radii

The Van der Waals radius of a given atom is the halve of the shortest distance observed in crystals between the nuclei of atoms of the same nature belonging to different molecules.

Table 1. Van der Waals radii $r_{\text{vdw}}/\text{\AA}$ of atoms



























				H	1.20	He	1.30
N	1.50	O	1.40	F	1.35	Ne	1.40
P	1.90	S	1.85	Cl	1.80	Ar	1.70
As	2.00	Se	2.00	Br	1.95	Kr	1.80
Sb	2.20	Te	2.20	I	2.15	Xe	2.05

CH_3 and CH_2 groups: 2.00\AA from the center of the carbon atom via the H-atoms.

Thickness of aromatic ring: $2 \times 1.85\text{\AA}$.

Repulsion

Others Radii

Monovalent cations	Li ⁺	Na ⁺	K ⁺	NH ₄ ⁺	Cs ⁺	N(CH ₃) ₄ ⁺
						
	0.068	0.095	0.133	0.148	0.169	0.347
Divalent cations	Be ²⁺	Mg ²⁺	Fe ²⁺	Ca ²⁺	Ba ²⁺	
						
	0.031	0.065	0.076	0.099	0.135	
Trivalent cations	Al ³⁺	Fe ³⁺	La ³⁺			
						
	0.050	0.064	0.104			
Monovalent anions	F ⁻	OH ⁻	Cl ⁻	Br ⁻	I ⁻	NO ₃ ⁻
						
	0.136	0.176	0.181	0.195	0.216	0.264
Spherical molecules	Ne	Ar	Kr	Xe	CH ₄	CCl ₄
						
	0.154	0.188	0.201	0.216	0.20	0.275
Effective radii of nonspherical molecules and groups (approximate)	H ₂ O	O ₂	NH ₃	HCl	HBr	
	0.14	0.18	0.18	0.18	0.19	
	CH ₃ OH	CH ₃ Cl	CHCl ₃	C ₆ H ₆	C ₆ H ₁₂	
	0.21	0.215	0.255	0.265	0.285	
	-CH ₃ group	-CH ₂ - group	-NH ₂ group	-OH group	Aromatic ring thickness	
	0.20	0.20	0.17	0.145	0.37	

Repulsion

Others Radii



Exposed radii of atoms covalently bonded in molecules 	H	F	O	N	C	
	0.11	0.14	0.15	0.15	0.17	
Covalent bond radii of atoms 	Cl	S	Br	P	I	
	0.18	0.18	0.19	0.19	0.20	
	--H	--C	--N	--O	--F	--S
	0.03	0.077	0.070	0.066	0.064	0.104
		=C	=N	=O	--Cl	--P
		0.067	0.062	0.062	0.099	0.110
		=C	=N		--Br	--Si
		0.060	0.055		0.114	0.117

TABLE 7.1 Radii of molecules deduced from different methods

Molecule	Minimum radius, from van der Waals coefficient b^a Eq. (7.1) (nm)	Mean radius (van der Waals packing radius, from Fig. 7.1) (nm)	Maximum radius, from volume occupied in liquid at 20°C, Eq. (7.2) (nm)
CH ₃ OH	0.19	0.21	0.23
CHCl ₃	0.22	0.26	0.29
C ₆ H ₆	0.23	0.27	0.30
CCl ₄	0.24	0.28	0.305

^a Constants b taken from the *Handbook of Chemistry and Physics*, CRC Press, 56th ed.

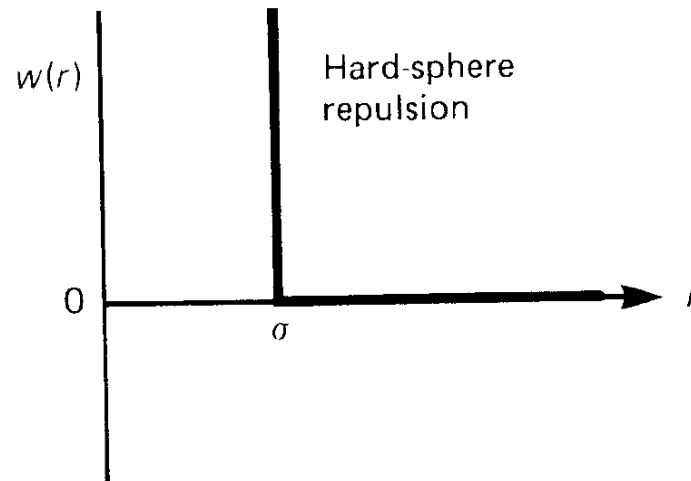
Repulsion

Repulsive Potentials

Hard Sphere Potential

$$w = + (\sigma / r)^n \quad \text{where } n = \text{infinity}$$

$$\begin{array}{ll} w = \text{infinity} & \text{when } r < \sigma \\ w = 0 & \text{when } r > \sigma \end{array}$$



Repulsion

Repulsive Potentials

Soft Sphere Potential

Power-law potential

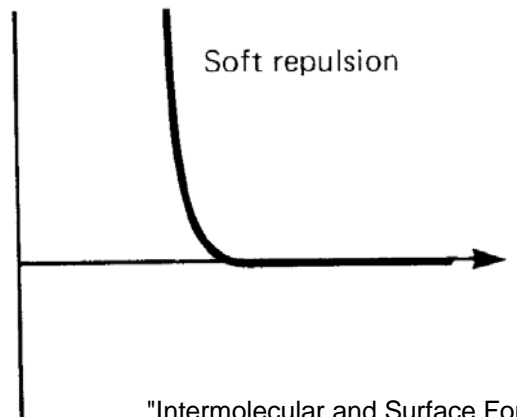
$$w = + (\sigma / r)^n$$

- typically $9 < n < 12$
- power-law potential has little theoretical basis, but is commonly used because of its mathematic convenience

Exponential potential

$$w = + c \exp(- r / \sigma_0)$$

- σ_0 is of the order of 0.02 nm

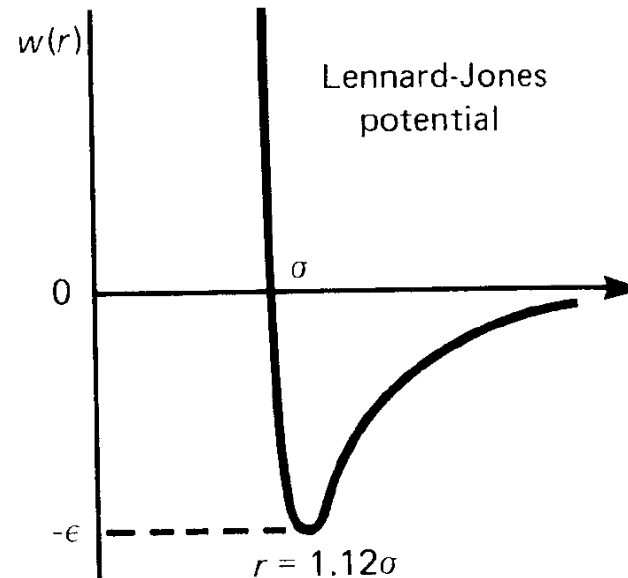


Lennard - Jones Potential

Lennard - Jones proposed a model that combines the attractive and repulsive potential.

$$w = A / r^{12} - B / r^6 = 4 \varepsilon [(\sigma / r)^{12} - (\sigma / r)^6]$$

- the attractive term has an inverse sixth-power term.
- the repulsive is chosen for mathematical convenience.



Attraction vs Repulsion

Repulsive forces are mainly responsible for the melting point of molecules.

Repulsive forces (which is orientation dependent) reflect the shape of molecules, which determines the melting point. If their shape allows the molecules to pack more efficiently, the melting point will be higher.

Attractive forces are mainly responsible for the boiling point of molecules.

Heat of vaporizations are closely associated with the cohesive energies in solids and liquids.

TABLE 7.2 Effect of double bonds and chain branching on melting and boiling points of hydrocarbons

Hydrocarbon		T_M (°C)	T_B^a (°C)
C_6H_{14}	<i>n</i> -Hexane	-95	69
C_6H_{12}	1-Hexene	-140	63
C_6H_{12}	2-Hexene (<i>cis</i>)	-141	69
C_6H_{14}	2-Methyl pentane	-154	60
C_8H_{18}	<i>n</i> -Octane	-57	126
C_8H_{16}	1-Octene	-102	121
C_8H_{16}	2-Octane (<i>cis</i>)	-100	126
C_8H_{18}	2-Methyl heptane	-120	119
$C_{12}H_{26}$	<i>n</i> -Dodecane	-10	216
$C_{12}H_{24}$	1-Dodecene	-35	213
$C_{16}H_{34}$	<i>n</i> -Hexadecane	18	287
$C_{16}H_{32}$	1-Hexadecene	4	284
$C_{18}H_{32}$	<i>n</i> -Octadecane	28.2	316
$C_{18}H_{30}$	1-Octadecene	17.5	
$C_{18}H_{30}$	9-Octadecene	-30.5	

^a At 760 mmHg.

Van der Waals Molecules

Van der Waals Molecules are weakly bounded complexes held together by intermolecular forces.

- "The level of detail that can be acquired in studies of carefully chosen van der Waals molecules far exceeds that usually achievable in investigations of bulk systems. Hence, the findings serve to bridge, at the molecular level, the knowledge of the varying interactions that occur as a gas-phase molecule transcends into the condensed phase."
- can be studied through spectroscopy (vibrations, rotations, and tunnelings)
- 3 issues of Chemical Reviews that focuses on Van der Waals molecules (both experimental and theoretical, including studies of homogeneous and heterogeneous complexes, hydrogen bonding, solvation effect).

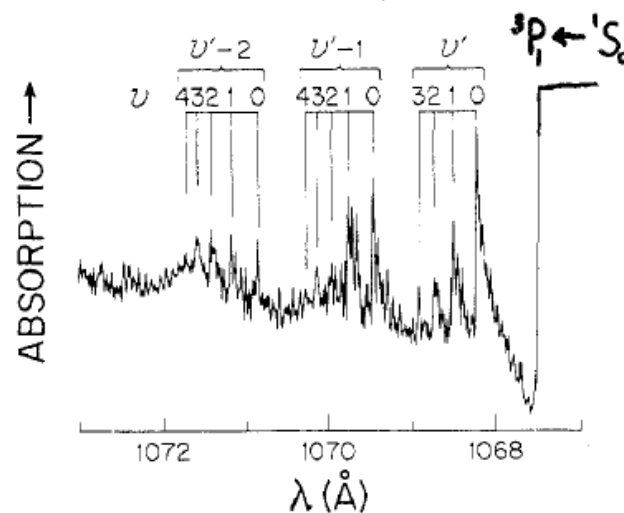
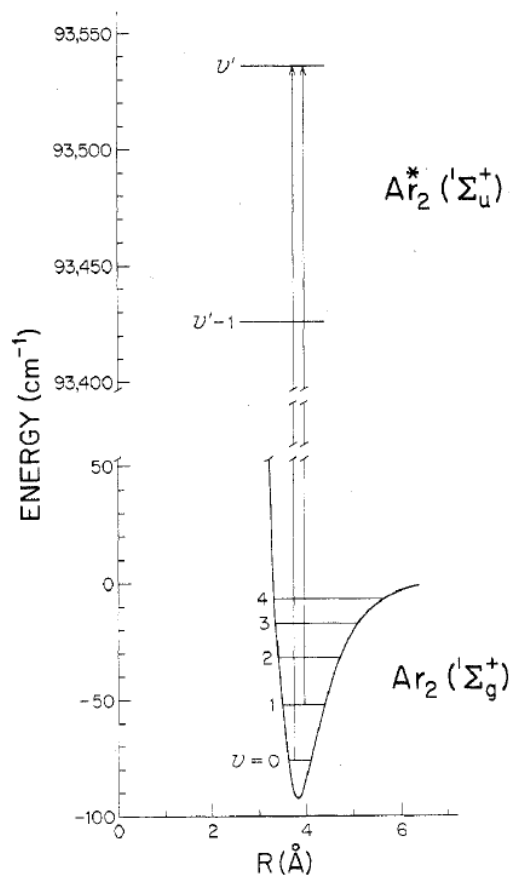
Chemical Reviews volume 100 issue 11 (2000),
volume 94 issue 7 (1994),
volume 88 issue 7 (1988).

- For scientific history of the study of van der Waals molecules, see "Cohesion: a scientific history of intermolecular forces" Rowlinson, J. S. Cambridge: University Press, 2002.

Van der Waals Molecules

Argon dimer

Rare gases absorb light to give characteristic atomic line spectra. However, under appropriate condition (pressure and temperature), additional features can be observed. These additional absorptions correspond to vibrational and rotational level of dimer.



Steric Attraction

Steric Effect

The effect on a chemical or physical property (structure, rate or equilibrium constant) upon **introduction of substituents having different steric requirements**. The steric effect in a reaction is ascribed to the difference in steric energy between, on the one hand, reactants and, on the other hand, a transition state (or products). A steric effect on a rate process may result in a rate increase ('steric acceleration') or a decrease ('steric retardation'). (The adjective 'steric' is not to be confused with stereochemical.) **Steric effects arise from contributions ascribed to strain as the sum of (1) non-bonded repulsions, (2) bond angle strain and (3) bond stretches or compressions.**

Steric Approach Control

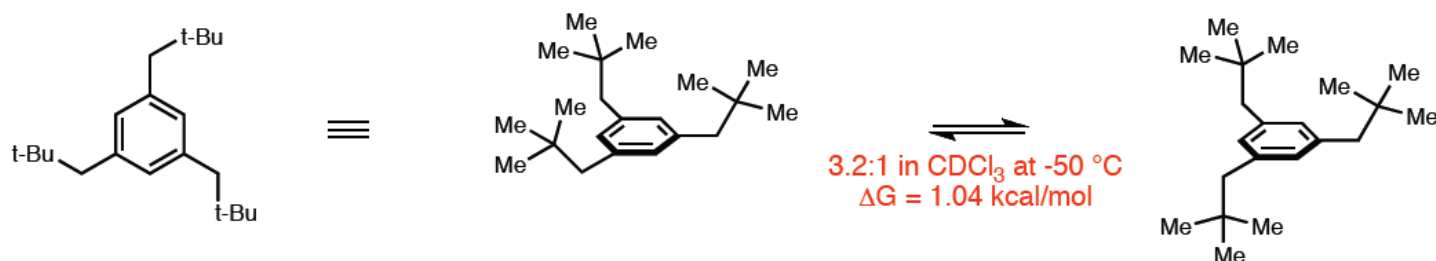
Control of stereoselectivity of a reaction by steric hindrance towards attack of the reagent, which is directed to the less hindered face of the molecule.

see also: Facial Selectivity within the t-Butylcyclohexyl Scaffold: Qualitative Insight into Reagent Size?
Joseph Wzorek (3/20/09)

Steric Attraction (Selected Cases)

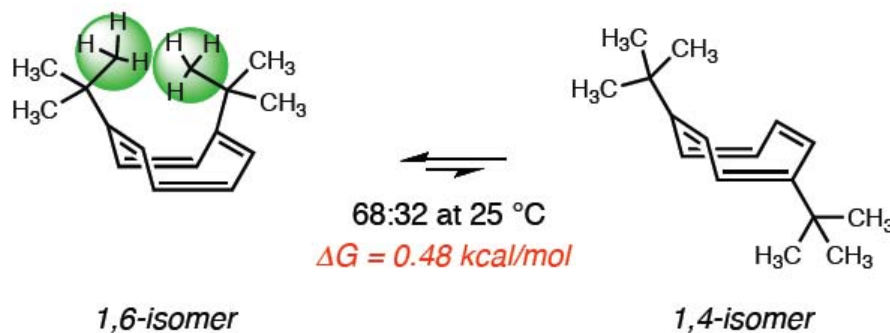
Previously discussed in Relative Hyperconjugative Electron Release from σ_{C-H} and σ_{C-C} Bonds:
Experimental and Theoretical Approaches Andrew Weiss (3/20/09)

1,3,5-trineopentylbenzene



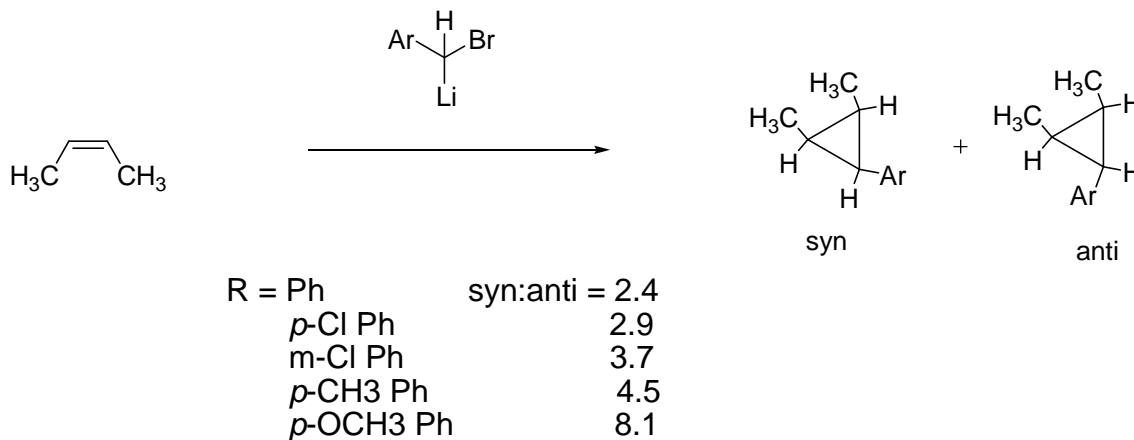
Carter, R. E.; Stilbs, P. *J. Am. Chem. Soc.* **1976**, 98, 7515.

di(tert-butyl)cyclooctatetraene

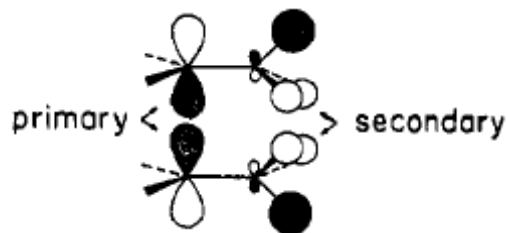


Paquette, L. A.; Hefferon, G. J.; Samodral, R.; Hanzawa, Y. *J. Org. Chem.* **1983**, 48, 1262.

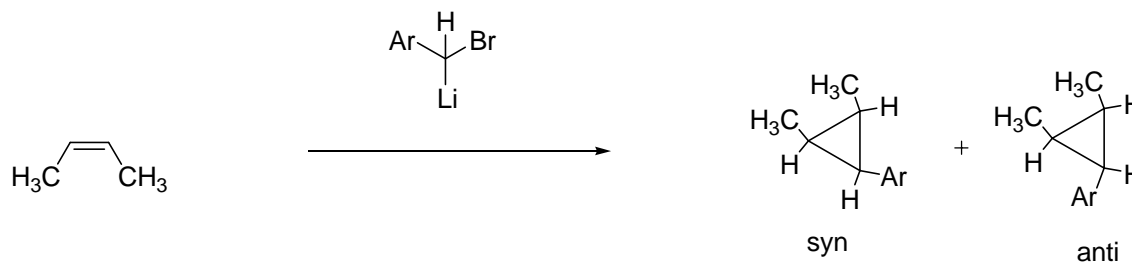
cyclopropanation of unsymmetrical carbenes to cis-substituted olefins



Hoffmann (1973) proposed that in highly exothermic association reactions, where the transition state occurs at large separation of reaction partners, the activation energy for the path leading to the sterically more hindered product may be lower.



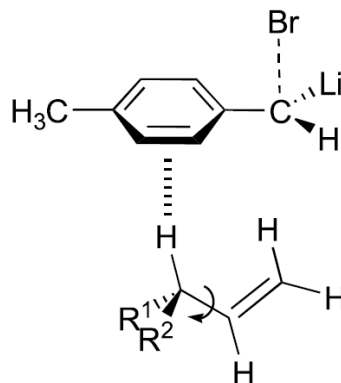
cyclopropanation of unsymmetrical carbenes to cis-substituted olefins (cont.)



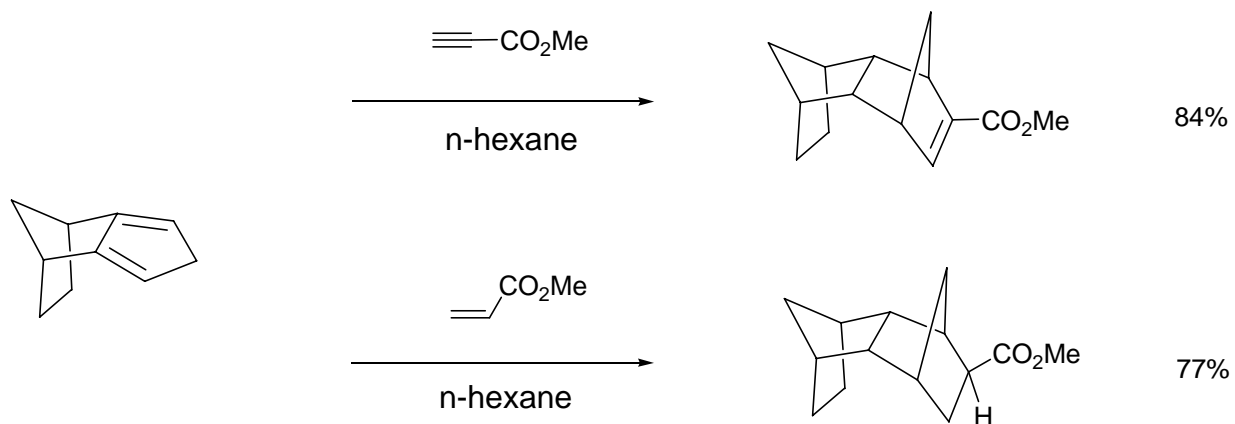
R = Ph	syn:anti = 2.4
<i>p</i> -Cl Ph	2.9
<i>m</i> -Cl Ph	3.7
<i>p</i> -CH ₃ Ph	4.5
<i>p</i> -OCH ₃ Ph	8.1

Reactions with 1-butene gives much lower ration (but still favoring syn product).

This result could be explained through C-H / π interaction:

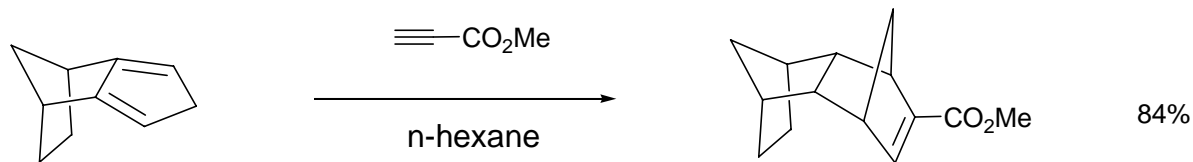


syn selectivity in Diels-Alder Reaction of Isodicyclopentadiene



High selectivity for syn addition is in contrast with preferential exo addition of norbornenes and its homologues.

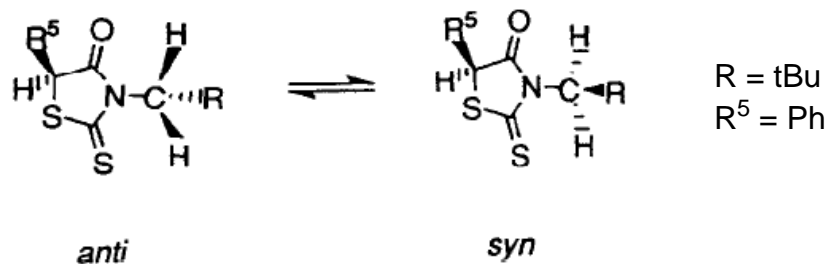
The authors proposed that greater steric attraction by the ethano bridge might stabilize the syn transition state.

syn selectivity in Diels-Alder Reaction of Isodicyclopentadiene (cont.)

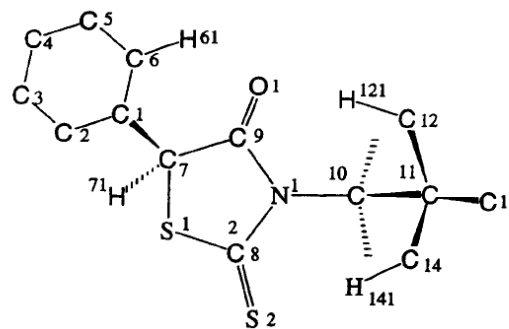
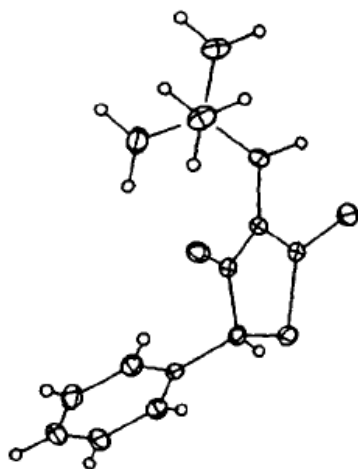
Houk (1985) computed transition state energy of a model system (MM2 calculation). The model supports the hypothesis that torsional factors influence the stereoselectivities of the reactions of the parent system.

The difference in energy between the isodicyclopentadiene moiety bent up for bottom attack or bent down for top attack is 0.4 kcal/mol, with the bent up geometry more stable. For bottom attack, the norbornene moiety is found to bend in an endo direction. This is the bending found in norbornene itself.

3-neopentylrhodanines



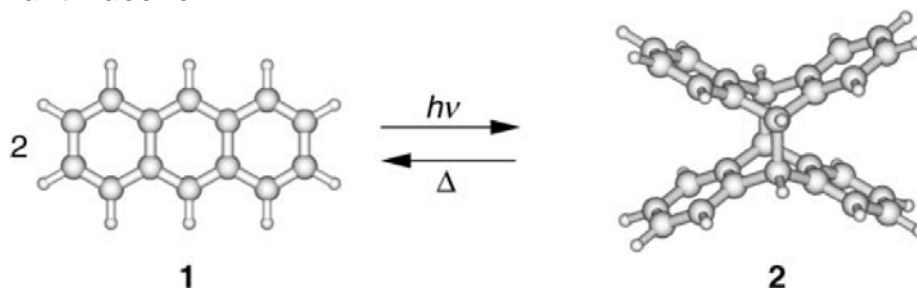
- NOE from tBu to Ph
- MM2 calculation gives energy difference 2.60 favoring syn isomer
- X-ray structure: syn isomer



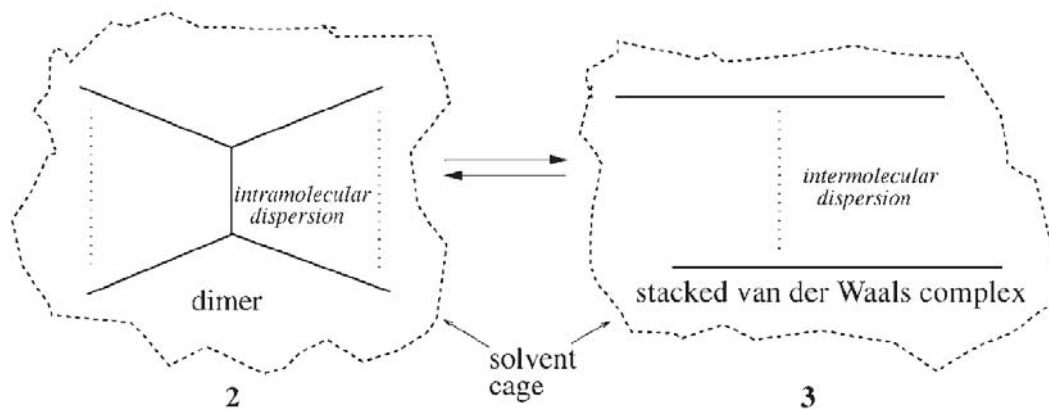
selected bond lengths:

C(6) - C(12)	483 pm
C(6) - C(14)	538 pm
H(61) - H(121)	307 pm
H(61) - H(141)	330 pm

dimerization of anthracene



Experimentally, the dissociation was found to be exothermic, but ab initio calculation gives different result. The authors proposed the role of intermolecular van der Waals attraction to correct the initial ab initio calculation.



" we believe that a delicate balance between inter- and intramolecular dispersion effects is a quite general phenomenon for larger molecules that must be considered more carefully in the future."