Molecular Interactions

CYL 725

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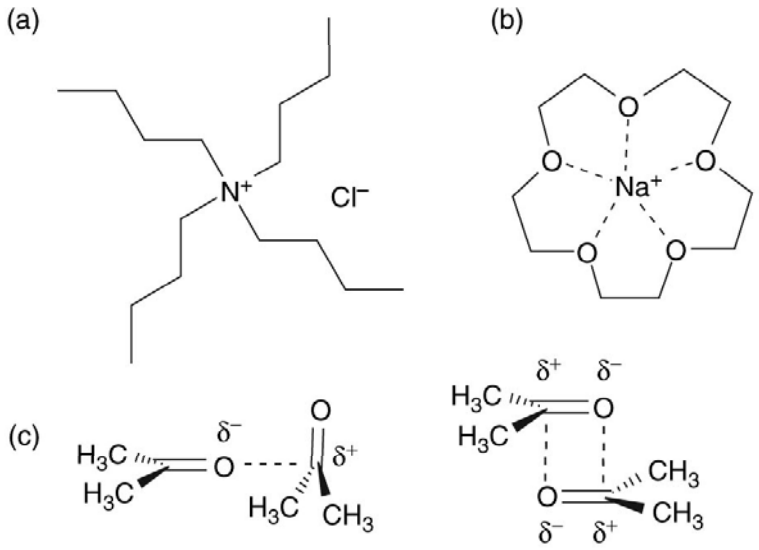
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Supramolecular interactions

Interaction	**Strength (kJ mol^{-1})**	**Example**
Ion-ion	200-300	Tetrabutylammonium chloride
Ion-dipole	50-300	Sodium [15] crown-5
Dipole-dipole	5-50	Acetone
Hydrogen bonding	4-120	D-H---A
Cation-π	5-80	K+ in benzene
π-π	0-50	Benzene, graphite
van der Waals	< 5 (variable, depends on surface)	Argon, molecular crystals
Solvophobic	Depends on solvents	Cyclodextrin inclusion compounds

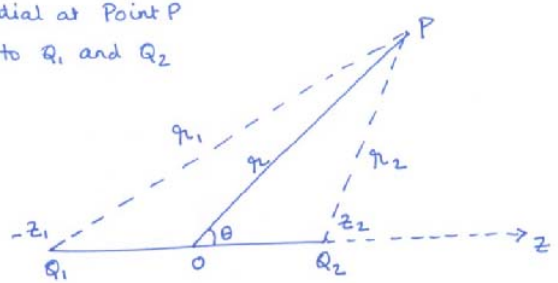
Ionic and dipolar interactions

- ion-ion
- ion-dipole (50-200 kJ mol^{-1})
- dipole-dipole (5-50 kJ mol^{-1})
  - despite being weakest dipole-dipole interactions result in alignment



orientation dependent

Potential at Point P
due to Q_1 and Q_2



$$\Phi = \frac{1}{4\pi\epsilon_0}\left[\frac{Q_1}{r_1} + \frac{Q_2}{r_2}\right]$$

Some trigonometry

$$(4\pi\epsilon_0)\,\Phi = \frac{Q_1}{\left[r^2 + z_1^2 + 2 z_1 r\cos\theta\right]^{1/2}} + \frac{Q_2}{\left[r^2 + z_2^2 \mp 2 z_2 r\cos\theta\right]^{1/2}}$$

when $r \gg z_1, z_2$ expand using binomial theorem

$$\left[(x+y)^n = \sum_{k=0}^{\infty} \frac{n(n-1)(n-2)\ldots(n-(k-1))}{k!}\, x^{n-k}\, y^k\right]$$

$$(4\pi\epsilon_0)\,\Phi = \frac{Q_1 + Q_2}{r} + \frac{(Q_2 z_2 - Q_1 z_1)\cos\theta}{r^2} + \frac{(Q_1 z_1^2 + Q_2 z_2^2)(3\cos^2\theta - 1)}{2r^3} + \ldots$$

$$\Rightarrow (4\pi\epsilon_0)\,\Phi = \frac{Q}{r} + \frac{\mu\cos\theta}{r^2} + \frac{\xi}{2}\frac{(3\cos^2\theta - 1)}{r^3} + \ldots$$

②

Interaction between two polar molecules.



electrostatic interaction energy

$$U_{el} = Q_1' \phi(r_1) + Q_2' \phi(r_2)$$

$\phi(r_1)$, $\phi(r_2)$: electrostatic potentials due to $Q_1 Q_2$ at the charges Q_1' and Q_2'.

Simple trigonometry

express in terms of $r, z_1, z_2, \theta_A, \theta_B, \phi$.

If $r \gg z_1, z_2, z_1', z_2'$ expand in terms of z_1/r and z_2/r

$$(4\pi\epsilon_0) U_{el} = \frac{QQ'}{r} + \frac{1}{r^2}\left(Q'\mu\cos\theta_A - Q\mu'\cos\theta_B\right)$$

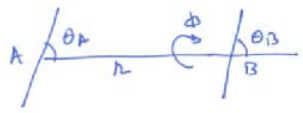
$$- \frac{\mu\mu'}{r^3}\left(2\cos\theta_A\cos\theta_B - \sin\theta_A\sin\theta_B\cos\phi\right)$$

$$+ \frac{1}{2r^3} Q\xi'\left(3\cos^2\theta_B - 1\right) + Q'\xi\left(3\cos^2\theta_A - 1\right)$$

$$+ \cdots$$

If total charge $Q = Q' = 0 \rightarrow$ dipole-dipole energy

$$U_{\mu\mu} = \frac{1}{4\pi\epsilon_0}\left[-\frac{\mu\mu'}{r^3}\left(2\cos\theta_A\cos\theta_B - \sin\theta_A\sin\theta_B\cos\phi\right)\right]$$



$$U_{AB} = \frac{\mu_A \mu_B}{(4\pi\epsilon_0) r^3} f_1(\theta_A, \theta_B, \Phi) + \frac{\mu_A \xi_B}{(4\pi\epsilon_0) r^4} f_2(\theta_A, \theta_B, \Phi)$$

$$- \frac{\mu_B \xi_A}{(4\pi\epsilon_0) r^4} f_2(\theta_B, \theta_A, \Phi) + \frac{\xi_A \xi_B}{(4\pi\epsilon_0) r^5} f_3(\theta_A, \theta_B, \Phi)$$

$$f_1(\theta_A, \theta_B, \Phi) = \sin\theta_A \sin\theta_B \cos\Phi - 2\cos\theta_A \cos\theta_B$$

$$f_2(\theta_A, \theta_B, \Phi) = \frac{3}{2}\left[\cos\theta_A(3\cos^2\theta_B - 1) - 2\sin\theta_A \sin\theta_B \cos\theta_B \cos\Phi\right]$$

$$f_3(\theta_A, \theta_B, \Phi) = \frac{3}{4}\left[1 - 5\cos^2\theta_A - 5\cos^2\theta_B - 15\cos^2\theta_A \cos^2\theta_B + 2(4\cos\theta_A \cos\theta_B - \sin\theta_A \sin\theta_B \cos\Phi)^2\right]$$

dipole - dipole

$\theta_A = \theta_B = 0$ — Orientation

$$\Rightarrow U_{\mu\mu} = -\frac{2\mu_A \mu_B}{(4\pi\epsilon_0) r^3}$$



$$= +\frac{2\mu_A \mu_B}{(4\pi\epsilon_0) r^3}$$



$$= 0$$



net average = 0 !!

But each configuration occurs with a probability $\propto$ Boltzmann factor $\exp\left(-U(\omega)/kT\right)$

favors configuration with -ve energy

average weighted energy

$$\langle U \rangle = \frac{\int U(\omega) \exp\left[-U(\omega)/kT\right] d\omega}{\int \exp\left[-U(\omega)/kT\right] d\omega}$$

For high temperatures,

$$\langle U \rangle = \frac{\int U(\omega)\left[1 - U(\omega)/kT + \cdots\right] d\omega}{\int \left[1 - U(\omega)/kT + \cdots\right] d\omega}$$

First term $\int U(\omega)\, d\omega = 0$ (av. over all orientations)

First non-zero term

$$\langle U \rangle_{\mu\mu} = -\frac{2\mu_A^2 \mu_B^2}{3r^6 kT (4\pi\epsilon_0)^2}$$

Boltzmann weighted average is indeed -ve.

dipole-quadrupole $\langle U \rangle_{\mu\zeta} \sim \frac{1}{r^8}$

quadrupole-quadrupole $\langle U \rangle_{\zeta\zeta} \sim \frac{1}{r^{10}}$

Induction Energy

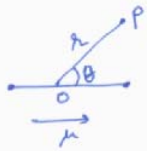
$$\vec{\mu}_{ind} = \alpha \vec{E}$$



α is a tensor quantity

Energy of induced dipole

$$U = -\int_0^{\mathcal{E}} \vec{\mu}_{ind} \cdot d\vec{\mathcal{E}} = -\int_0^{\mathcal{E}} \alpha \vec{\mathcal{E}} \cdot d\vec{\mathcal{E}} = -\frac{1}{2}\alpha \mathcal{E}^2$$



$$\mathcal{E}(r,\theta) = \frac{\mu\left[1+3\cos^2\theta\right]^{1/2}}{4\pi\epsilon_0 r^3}$$

Field produced by dipolar molecular at P

$$\therefore\ U = -\frac{\alpha\mu^2\left(3\cos^2\theta+1\right)}{2r^6\left(4\pi\epsilon_0\right)^2} \longrightarrow \text{attractive for all orientations}$$

averaged with Boltzmann weighting

$$\langle U\rangle_{ind} = \frac{-\mu^2\alpha}{\left(4\pi\epsilon_0\right)^2 r^6}$$

no T dependence since the first term in the expansion is non-zero.

For two identical dipolar molecules

$$\langle U\rangle_{ind} = \frac{-2\mu^2\alpha}{\left(4\pi\epsilon_0\right)^2 r^6}$$

Complete treatment requires higher order moments

Non-spherical molecules → anisotropic polarisability

α is a tensor

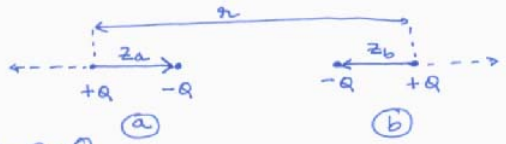
⑥ Dispersion energy

Drude model

Assume: +ve charge is stationary.

−ve charge performs simple harmonic oscillations about the +ve charge

frequency ν in the z-dir.



$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

Non-interacting ⓐ & ⓑ

For large r, Schrödinger eqn. for ⓐ

$$\frac{1}{m}\frac{\partial^2\psi}{\partial z_a^2} + \frac{8\pi^2}{h^2}\left[E_a - \underbrace{\frac{1}{2}kz_a^2}_{\text{P.E. of S.H.E.}}\right]\psi = 0$$

Eigenvalues

$$E_a = \left(n_a + \tfrac{1}{2}\right)h\nu \quad ; \quad E_b = \left(n_b + \tfrac{1}{2}\right)h\nu$$

Lowest energy (zero point energy) $= E(\infty) = E_a + E_b = h\nu$

Interacting ⓐ & ⓑ.

$$\frac{1}{m}\frac{\partial^2\psi}{\partial z_a^2} + \frac{1}{m}\frac{\partial^2\psi}{\partial z_b^2} + \frac{8\pi^2}{h^2}\left[E - \frac{1}{2}kz_a^2 - \frac{1}{2}kz_b^2 - \underbrace{\frac{2z_a z_b Q^2}{(4\pi\epsilon_0)r^3}}_{\text{dipole interaction}}\right]\psi = 0$$

Use $z_1 = \frac{z_a + z_b}{\sqrt{2}}$; $z_2 = \frac{z_a - z_b}{\sqrt{2}}$

$$\Rightarrow \frac{1}{m}\frac{\partial^2\psi}{\partial z_1^2} + \frac{1}{m}\frac{\partial^2\psi}{\partial z_2^2} + \frac{8\pi^2}{h^2}\left[E - \frac{1}{2}k_1 z_1^2 - \frac{1}{2}k_2 z_2^2\right]\psi$$

7)

$$\nu_1 = \nu \sqrt{\left(1 - \frac{2Q^2/4\pi\epsilon_0 r^3}{k}\right)}$$

$$\nu_2 = \nu \sqrt{\left(1 + \frac{2Q^2/4\pi\epsilon_0 r^3}{k}\right)}$$

Zero point energy :

$$E(r) = \frac{1}{2} h(\nu_1 + \nu_2)$$

$$= h\nu - \frac{Q^4 h\nu}{2(4\pi\epsilon_0)^2 r^6 k^2}$$

Interaction energy U

$$U = E(r) - E(\infty) = -\frac{Q^4 h\nu}{2(4\pi\epsilon_0)^2 r^6 k^2}$$

Force constant k represents displacement of charge $\therefore$ related to polarizability.

$$\alpha = Q^2/k$$

$$\Rightarrow U = \frac{-\alpha^2 h\nu}{2(4\pi\epsilon_0)^2 r^6}$$

Considering oscillations in 3-D

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

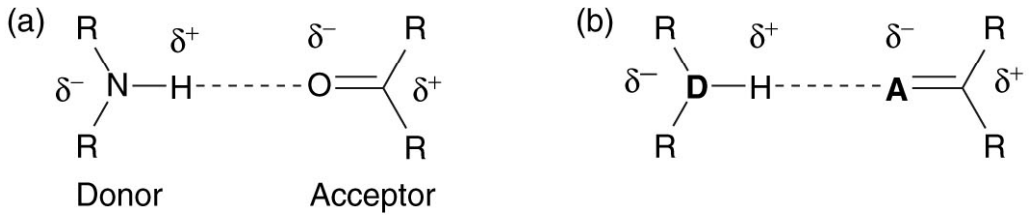
$h\nu = E_1$
First Ionization Energy (proposed by London)

Considering higher order moments

$$U = \frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} + \cdots$$

Hydrogen bonding

- most important non-covalent interaction in the design of supramolecular architectures
- special kind of dipole-dipole interaction



- strength depends upon the type of electronegative atom that the H is attached to
  - typically 4-120 kJ mol^{-1}
  - majority 60 kJ mol^{-1}

H-bonding geometries (primary interactions)

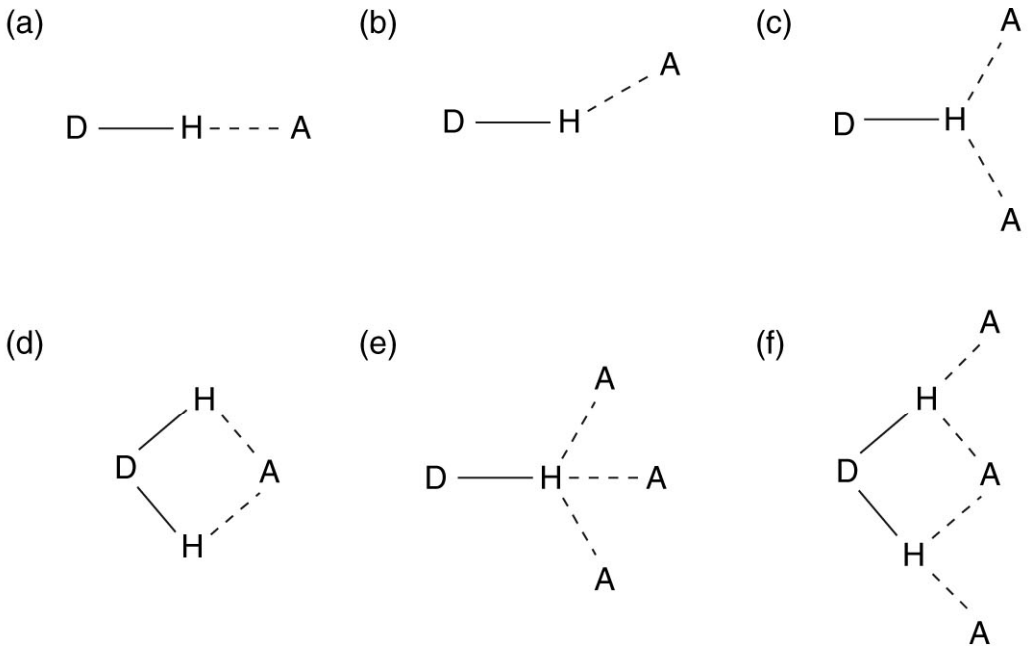
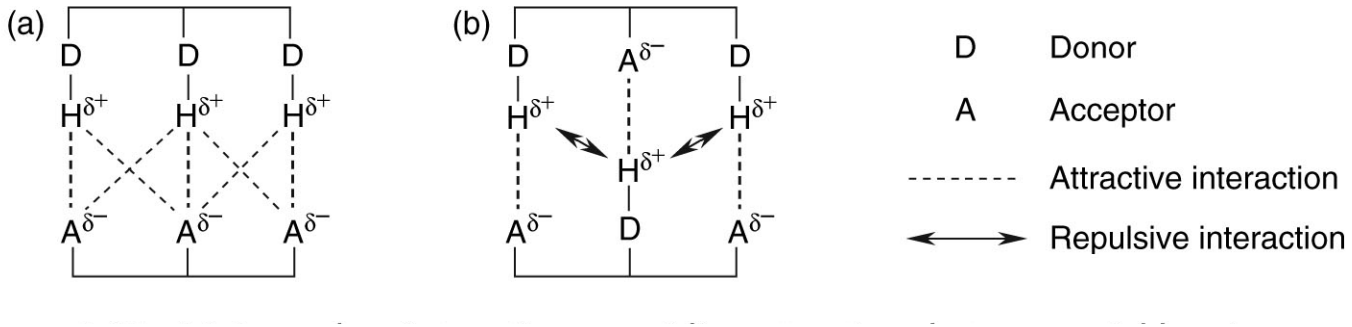
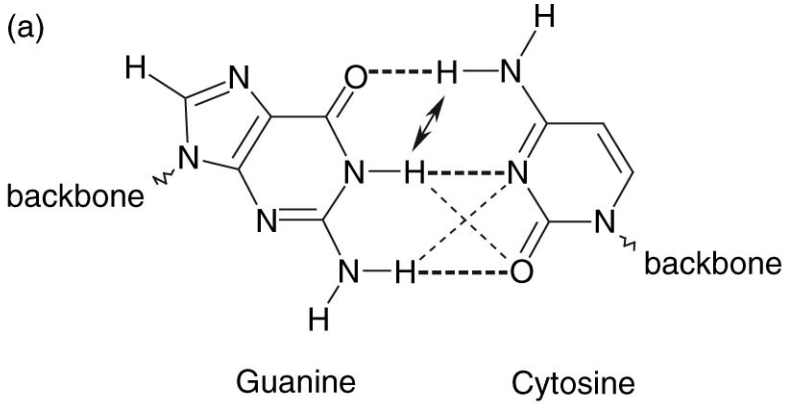


Figure 1.15 Various types of hydrogen bonding geometries: (a) linear; (b) bent; (c) donating bifurcated; (d) accepting bifurcated; (e) trifurcated; (f) three-centre bifurcated.

H-bonding geometries (secondary interactions)





Types of H-bonds

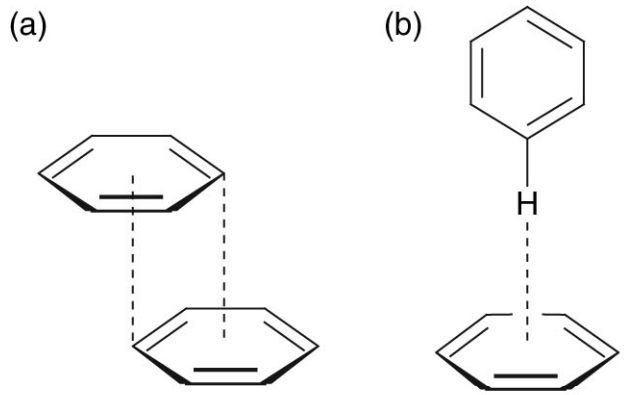
Interaction / property	**Strong**	**Moderate**	**Weak**
D-H…A	Mainly covalent	Mainly electrostatic	Electrostatic
Bond energy (kJ mol^{-1})	60-120	16-60	<12
Bond length (Å) H….A D….A	 1.2-1.5 2.2-2.5	 1.5-2.2 2.5-3.2	 2.2-3.2 3.2-4.0
Bond angle (degrees)	175-180	130-180	90-150
Example	HF complexes $H_5O_2^+$	Acids Alcohols DNA/RNA	C-H….A D-H….π

geometry, type of D and A → strength, length and nature of H-bond

π interactions

- cation - π
  - alkaline and alkaline-earth metals
  - typically between 5 – 80 kJ mol^{-1}

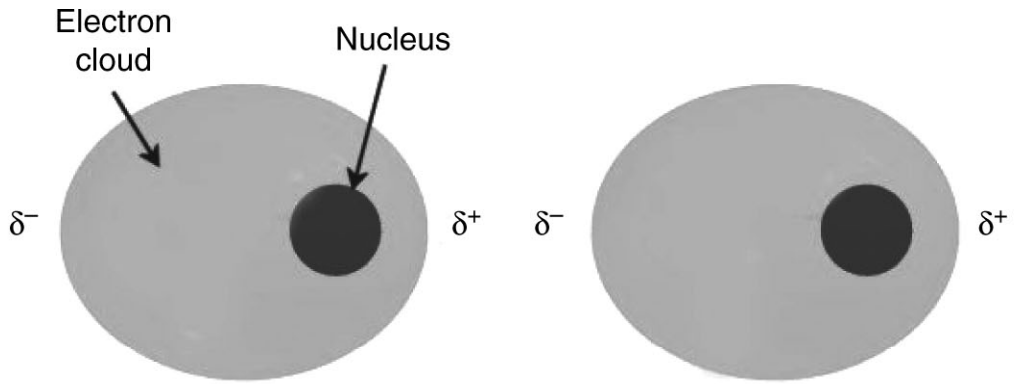
- π – π (attraction between π-electron cloud on one ring and σ-framework on other ring)
  - face to face
  - edge to face
  - graphite, DNA



van der Waals interactions

- London interaction
  - instantaneous dipoles attract
  - polarisability of the molecule
  - r^{-6} dependence

- exchange and repulsion interaction



Hydrophobic effects

- exclusion of non-polar groups from aqueous solution

- binding of organic molecules by cyclophanes
- cyclodextrins in water

- enthalpic and entropic factors

