

Isomerism (Structural and Stereoisomerism)

$$v - 2 \cdot C + 2 \cdot N + 1 \cdot O, S \cdot 0 \cdot H, X - 1$$

$$\text{Na D-line } \lambda = 5893 \text{ \AA}$$

Notation C* chiral centre · a active forms · m meso forms · r = a/2 racemic forms · a/e axial/equatorial

1 Isomers: Chain, Position and Ring-Chain

- Chain: skeleton differs · position: group moves · ring-chain: open vs ring (call it functional if ring-chain isn't an option).

2 Functional Isomerism

- $C_nH_{2n+2}O$ alcohol/ether · $C_nH_{2n}O$ carbonyls, unsat. alcohols/ethers, rings · $C_nH_{2n}O_2$ acids, esters, hydroxy carbonyls · C_nH_{2n-2} alkynes, dienes, cycloalkenes.

3 Metamerism

- Metamers: same functional group (–O–, –S–, –NH–, –CO–, –COO–), different alkyl groups on its two sides. Offered? Prefer metamerism over position.

4 Tautomerism and Keto-Enol Equilibrium

Enol order: $CH_3COCH_3 < CH_3COCH_2COOC_2H_5 < C_6H_5COCH_2COOC_2H_5 < CH_3COCH_2CHO < CH_3COCH_2COCH_3 < C_6H_5COCH_2COCH_3 < \text{cyclohexane-1,3-dione} < C_6H_5COCH_2COC_6H_5$

- Needs an α -H + EWG; never at a bridgehead. Polar protic solvent lowers enol %.

5 Other Types of Tautomerism

- N triads: nitrite-nitro, nitro-aci, nitroso-oxime, imine-enamine, azo-hydrazone, amide-imidol.

6 Degree of Unsaturation and Counting Isomers

$$\text{D.B.E.} = \frac{\sum n(v-2)}{2} + 1$$

- $v - 2$: C +2, N +1, O/S 0, H/X -1. Each D.B.E. = ring or π bond. C_6H_8 (no rings) = 9; C_3H_6O = 7 (+2 enols).

7 Geometrical (cis-trans) Isomerism

$$N = 2^n \text{ (unsymmetrical)}$$

$$N = 2^{n-1} + 2^{n/2-1} \text{ (symmetrical, } n \text{ even)}$$

$$N = 2^{n-1} + 2^{(n-1)/2} \text{ (symmetrical, } n \text{ odd)}$$

- m.p. trans higher · b.p., μ cis higher · trans more stable. cis + syn $\rightarrow$ meso, trans + anti $\rightarrow$ meso.

8 Optical Activity, Symmetry and Chirality

$$[\alpha] = \frac{\alpha_{\text{obs}}}{l \times C}$$

- $[\alpha] = \alpha_{\text{obs}} / (l \times C)$, l in dm, C in g/mL; Na D-line 5893 Å. C* = four different groups.

9 Optical Isomerism Without a Chiral Carbon

- abC=C=Cab chiral; abC=C=C=Cab flat (cis-trans). Biphenyls: two different ortho groups on each ring.

10 Lactic Acid, Tartaric Acid and Counting Stereoisomers

$$a = 2^n, m = 0$$

$$a = 2^{n-1}, m = 2^{n/2-1}$$

$$a = 2^{n-1} - 2^{(n-1)/2}, m = 2^{(n-1)/2}$$

$$\text{total} = a + m$$

$$r = \frac{a}{2}$$

- Meso: internal compensation, one compound · racemic: external, a mixture. Tartaric: 3 stereoisomers.

11 Racemic Mixtures, Optical Purity and Configuration

$$\% ee = \frac{n_1 - n_2}{n_1 + n_2} \times 100$$

$$\% ee = \frac{[\alpha]_{\text{obs}}}{[\alpha]_{\text{pure}}} \times 100$$

$$[\alpha]_{\text{obs}} = \frac{\% ee}{100} \times [\alpha]_{\text{pure}}$$

- ee 25 % with $[\alpha]_{\text{pure}} 13.5^\circ \rightarrow [\alpha]_{\text{obs}} 3.375^\circ$. Sign change $\neq$ configuration change.

12 Diastereomers, Fischer Projections and D/L Configuration

- Fischer: vertical back, horizontal forward; 180° same, 90° enantiomer. Erythro: similar groups same side.

13 Conformations of Ethane, Propane and Butane

Stability: anti > gauche > partially eclipsed > fully eclipsed

$$\mu = \mu_{\text{anti}} X_a + \mu_{\text{gauche}} X_g$$

$$X_a + X_g = 1$$

- Ethane barrier 12.5 kJ/mol; butane gauche 3.8, partly eclipsed 14.6, fully eclipsed 18.4 kJ/mol.

14 Conformations of Cyclohexane

$$d = \frac{1}{2} (109^\circ 28' - \text{ring angle})$$

cyclopropane $24^\circ 44'$, cyclobutane $9^\circ 44'$, cyclopentane $0^\circ 44'$, cyclohexane $-5^\circ 16'$

Stability: chair > twist boat > boat > half chair

$$1,2: \text{trans} = ee/aa, \text{cis} = ae$$

$$1,3: \text{cis} = ee/aa, \text{trans} = ae$$

$$1,4: \text{trans} = ee/aa, \text{cis} = ae$$

- Big groups equatorial (CH_3 95 %). Diequatorial isomers: 1,2 trans · 1,3 cis · 1,4 trans.