Configuration isomery Configuration isomers are stereo–isomers which molecules have different atom location in space without regarding conformation. According to the type of symmetry all stereo–isomers are divided into enantiomers and diastereomers. In 1915 French physicist J. B. Bio discovered the optical activity phenomenon, i.e. the capacity of fluids to rotate the light polarization plane. Optical activity is measured by devices called polarimeters. Monochromatic light having passed through the polarizer (Nicole's prism) becomes polarized. If a solution with optically active substance is placed into the device, the polarized light gets polarization plane deviated into –angle (it is measured in degrees). In 1948 L. Pasteur isolated crystals of two mirror forms of optically inactive sodium–ammonium salt of tartaric acid and obtained optically active substances from the inactive mixture. Both isomers deviated light polarization plane into one and the same angle, but in different directions: the first deviated the plane clockwise (rotating to the right, the sign "+"), the second – counterclockwise (rotating to the left, the sign "–"). In such a way right– and left–rotating tartaric acids were obtained from inactive tartaric acid for the first time. Those isomers were called optical antipodes or optical isomers. Equal mixture of right– and left–rotating isomers of the same compounds is called a racemate, it is optically inactive. Enantiomers (optical isomers, mirror isomers, antipodes) are stereo–isomers which molecules are related to each other as the subject and incompatible with its mirror reflection. This phenomenon is called enantiomery. Enantiomers may be only those compounds which contain one or several asymmetric (chiral) carbon atoms. The atom is asymmetric (chiral) in the following conditions: 1) sp3–hybride state; 2) all four substituters are different. In Fig. 3 the enantiomers of tartaric acid are represented. COOH HOOC HOHHOH HOHHOH 14 COOH D – (+) row HOOC L – (–) row Fig. 3 Enantiomers of tartaric acid All physical and chemical properties of enantiomers are similar, but for the light polarization plane rotation and biological activity they are different. Polarimeter permits to determine only the sign of rotation, but does not indicate what particular enantiomer has that rotation. For this purpose it is necessary 15 to establish absolute configuration, i.e. the real location of substituters in space with regard to chiral center. Absolute configuration is established by complex physico– chemical methods. After establishing absolute configuration of several compounds it becomes possible to characterize the rest compounds by comparing their configurations with configurations of model compounds, i.e. to determine relative configuration. In 1906 M. A. Rozanov proposed "+"–glycerin aldehyde as a standard which was conditionally attributed to D–configuration, while its antipode – left– rotating isomer was attributed to L–configuration (Fig.4). Thus, the substituters were located in the following way: HOC H OH HO H CH2OH HOH2C CHO L – form To illustrate configuration isomers Fischer's formulae are used. The chiral center is illustrated with 4 bonds located under the right angle. Vertical lines illustrate substituters behind the paper sheet plane; horisontal – above the plane; the central atom is at the plane of the paper sheet. Asymmetric (chiral) atom is often marked with the sign " ". The stereo–chemical row includes compounds of the D–glycerin aldehyde with similar configuration of the chiral centre; L–row includes similar configuration of L–glycerin aldehyde. It should be mentioned that the sign of rotation does not have direct connection with configuration. The number of isomers is determined with the help of the formula: N=2n, where N is the number of isomers, and n is the number of chiral atoms of carbon. Among enantiomers there may be symmetrical molecules without optical activity. They are called mesoisomers.

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–Diastereomery Optical isomers which are not mirror isomers with different configuration of several but all asymmetrical carbon atoms and different physical and chemical properties are called –diastereomers. For example, 2–hydroxy–3–chlor–butanoic acid (Fig.5) has four isomers: D – form Fig. 4 COOH HOOC COOH HOOC HOHHOHHOHHOH HClClHClHHCl CH3 H3C CH3 H3C II III IV D–L–D–L– Fig.5 , and , V are enantiomers; , ; , V; , V; , are diastereomers. If symmetry plane is drawn in the molecule of the isomer, this isomer will be optically inactive. It is called mesoisomer. For example, tartaric acid contains meso–form – mesotartaric acid. Thus, depending on the location of atoms in space there may be various space isomers possessing biological activity. –Diastereomers (geometric isomers) –Diastereomers are stereomers with –bond in the molecule. They are in alkenes, non–limited higher carbonic acids, non–limited dicarboxylic acids. Buten–2 may serve as an example of π–diastereomery (Fig.6). 16 I H3C CC CC H HH HCH3 Cis – butene – 2 Trans – butene – 2 COOH H Cis – butene–dioic acid, male– inic acid – is extremely Trans – butene–dioic acid, fu– maric acid is not poisonous, is poisonous present in organism Fig.7 CH3 H3C Fig.6 Biological activity of organic substances is connected with their structure. For example, buten–dioic acid has 2 isotops: cis– and trans– (Fig. 7). HOOC CC CC HOOC H H HCOOH All natural non–limited higher carboxylic acids are cis–isomers. LESSON 3: Theme 2.2: ISOMERY (II) I. Brief informational unit Isomery is the existence of substances having the same quantitative and qualitative composition but different structure. Isomery is subdivided into structural (different order of atoms' combination: chains, positions, functional groups) and stereo–isomery [different positions of atoms in space: conformation, configuration, enantiomery, diastereomery (– isomers, – isomers)]. Conformers are conformations with minimum of energy and, for that reason, more stable. Configuration isomers are stereo–isomers which molecules have different atom location in space regardless conformation. According to the type of symmetry all stereo–isomers are divided into enantiomers and diastereomers. Enantiomers (optical isomers, mirror isomers, antipodes) are stereo–isomers which molecules are related to each other as the subject and incompatible with its mirror reflection. –Diastereomers are optical isomers which are not mirror isomers with different configuration of several but all symmetric carbon atoms and different physical and chemical properties. –Diastereomers are stereomers with –bond in the molecule. Mesoisomers are enantiomers which symmetrical molecules .have no optical activity

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