Aromatic compounds or aromatic hydrocarbons are a class of hydrocarbons that contain at least one aromatic ring. These compounds are known for their stable ring-like molecular structures featuring delocalized pi electrons across the conjugated system of atoms. Let's learn in detail about aromatic compounds.1.0What are Aromatic Compounds?The definition of aromatic compounds highlights their structure as ring-shaped molecules with delocalized electrons across alternating double and single bonds, which significantly enhances their chemical stability.Aromatic compounds involve ring-shaped compounds, also known as arenes or aromatics. They are a class of chemical compounds characterized by their stable ring-shaped molecular structures that include delocalized electrons. These electrons are typically shared over a conjugated system of alternating double and single bonds, allowing the molecule to have higher stability due to resonance. The concept of aromaticity is central to understanding the chemistry of these compounds.Aromatic compound examples mainly include Benzene, Toluene, Xylene.Here is a list of aromatic compounds and aromatic compound's structure shared below:2.0Structure and Nomenclature of Aromatic CompoundsIn organic chemistry, the International Union of Pure and Applied Chemistry (IUPAC) provides guidelines for the systematic naming of aromatic hydrocarbons, which are primarily derivatives of benzene, the simplest aromatic compound.BenzeneThe simplest aromatic hydrocarbon is benzene, depicted as a six-carbon ring with alternating single and double bonds, symbolized often by a circle within a hexagon to represent delocalized electrons.Benzene, represented as a hexagon with alternating double bonds (or a circle inside a hexagon indicating delocalized electrons), is highly symmetrical. This symmetry implies that the position of a single substituent on the ring does not affect the compound's identity because all positions on the hexagon are equivalent.In the IUPAC naming system, aromatic hydrocarbons are classified and named based on benzene derivatives.While some compounds are commonly identified by their IUPAC names, others are often referred to by their traditional or common names.3.0Important Characteristics of Aromatic CompoundsAromatic compounds possess several distinct characteristics that set them apart from other chemical compounds. These are given below-Stable Ring Structure: Aromatic compounds typically feature a planar ring structure with alternating double bonds, known as an aromatic ring. The most common example is benzene, which has a six-carbon ring with alternating single and double bonds.The resonance stabilization contributes to the overall stability of benzene.Resonance: This is a key characteristic of aromaticity. In aromatic compounds, the electrons in the pi bonds are delocalized around the ring. This delocalization allows the electron density to be spread over the entire structure, contributing to the compound's overall stability.Special Bonding: The chemical bonds in aromatic compounds are of a unique type that lies between a single and a double bond. This partial double bond character further stabilizes the molecule.Highly Unreactive: Compared to alkenes, aromatic rings are relatively unreactive due to their stability. They do not readily participate in addition reactions but can undergo substitution reactions where the ring structure remains intact.Distinctive Aromatic Smell: Historically, many aromatic compounds were named because of their distinctive smells. Although this is not a scientific measure of aromaticity, the odors of substances like benzene (albeit toxic) and naphthalene (mothballs) are notable.Absorption in the UV-Visible Spectrum: Aromatic compounds typically absorb ultraviolet or visible light due to the presence of conjugated pi systems. This feature is exploited in various analytical techniques to identify and quantify aromatic compounds.4.0Physical Properties of Aromatic Compounds5.0Conditions for Aromatic CompoundsCyclic Structure: Aromatic compounds must be cyclic, which means they are arranged in closed rings. This geometric configuration is essential as it allows for the delocalization of pi electrons across the ring, contributing to stability.Hückel's Rule - (4n + 2) π Electrons: For a molecule to exhibit aromaticity, it must obey Hückel's rule. This rule states that an aromatic compound must have a certain number of pi electrons (4n + 2 where n is an integer) in the cyclic π electron cloud. This specific configuration allows for enhanced stability due to electron delocalization.Preference for Substitution Reactions: Aromatic compounds generally resist addition reactions which would disrupt the pi electron cloud. Instead, they favor substitution reactions where the ring structure remains intact but one of the substituents is replaced, preserving the aromatic stability.6.0Heterocyclic Aromatic CompoundHeterocyclic aromatic compounds are a class of organic chemical compounds characterized primarily by their ring-shaped structure, which includes at least one atom other than carbon (commonly referred to as a heteroatom). These heteroatoms can be nitrogen, oxygen, sulfur, or others. These compounds are termed "aromatic" due to their stability and electron configuration, which follows the rules of aromaticity—typically adhering to Hückel's rule, which states the ring must contain a particular arrangement of electron pairs.Heterocyclic aromatic compounds examples:Pyridine: Contains one nitrogen atom in a six-membered ring, similar to benzene.Pyrrol: A five-membered ring structure containing one nitrogen atomFuran: A five-membered ring with one oxygen atom.Thiophene: Contains a sulfur atom in a five-membered ring.Imidazole: Features two nitrogen atoms in a five-membered ring.Note-Aromatic compounds that consist of two or more fused benzene rings are referred to as polycyclic aromatic hydrocarbons (PAHs). These compounds have a general aromatic compounds formula- C4r+2 H2r+4when they lack any substituents, where r represents the number of rings. This formula highlights how the number of carbon and hydrogen atoms relates to the number of fused rings in the structure.Examples:For r=2 (Naphthalene)C4×2+2 H2×2+4 = C10H8Naphthalene has two fused benzene rings.For r=3 (Anthracene or Phenanthrene)C4×3+2 H2×3+4 = C14H10Anthracene has three fused benzene rings.7.0Important reactions of aromatic compoundsIt also known as Hydroforming or dehydrogenation or cyclization or catalytic reforming,When unbranched higher alkanes containing 6 to 10 carbon atoms are heated at 500°C in the presence of oxides of chromium, molybdenum, or vanadium on an alumina (Al2O3) support, aromatic hydrocarbons are produced.Electrophilic Aromatic Substitution (EAS) Reaction The reaction involves the aromatic ring, rich in electron density, undergoing substitution where an electrophile (electron-seeking species) replaces a hydrogen atom on the benzene ring or other aromatic systems. Ar–H + E–A → Ar–E + H–AThe most important five electrophilic aromatic substitution reactions are outlined in figure:Here's a brief overview of these aromatic substitution reactions:Aromatic halogenation involves the substitution of a hydrogen atom on an aromatic ring with a halogen (chlorine or bromine typically) using a Lewis acid catalyst such as FeCl3 or FeBr3. The reaction is a type of electrophilic aromatic substitution.Application: Halogenated aromatic compounds are used in the production of dyes, disinfectants, and pharmaceuticals.Nitration involves substituting a hydrogen atom on an aromatic ring with a nitro group (NO2). This is typically achieved by treating the aromatic compound with a mixture of nitric acid (HNO3) and sulfuric acid (H2SO4).Sulfonation involves adding a sulfonyl group (SO3H) to an aromatic ring. This is typically done using sulfuric acid or oleum (fuming sulfuric acid). The reaction adds a sulfonic acid group to the ring, making it more soluble in water.Friedel-Crafts AlkylationFriedel-Crafts alkylation involves the addition of an alkyl group to an aromatic ring using an alkyl halide (R-X) and a Lewis acid catalyst like AlCl3. The reaction can sometimes lead to polyalkylation, where more than one alkyl group is added.Friedel-Crafts acylation involves the addition of an acyl group to an aromatic ring. This is typically done using an acyl chloride (R-CO-Cl) and a Lewis acid catalyst such as AlCl3. The product is a ketone, where the acyl group is directly connected to the aromatic ring.8.0Sample Questions on Aromatic CompoundsWhat is the difference between aromatic, antiaromatic, and nonaromatic compounds?Answer: Here is brief description of difference between aromatic, antiaromatic, and nonaromatic compounds- In the traditional sense, 'having a chemistry typified by benzene'.A cyclically @C01267@ with a stability (due to @D01583@) significantly greater than that of a hypothetical localized structure (e.g. @K03373@) is said to possess aromatic character. If the structure is of higher energy (less @S05900@) than such a hypothetical classical structure, the molecular entity is 'antiaromatic'. The most widely used method for determining @A00442@ is the observation of diatropicity in the 1HNMR spectrum.See also: Hückel (4n + 2) rule, Möbius aromaticityThe terms aromatic and antiaromatic have been extended to describe the stabilization or destabilization of @T06468@ of @P04491@. The hypothetical reference structure is here less clearly defined, and use of the term is based on application of the @H02867@ and on consideration of the topology of orbital overlap in the @T06468@. Reactions of molecules in the @G02704@ involving antiaromatic transition states proceed, if at all, much less easily than those involving aromatic transition states.Page 2 "Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994)", Muller, P., Pure and Applied Chemistry 1994, 66(5), 1077 Simple aromatic hydrocarbons come from two main sources: coal and petroleum. Coal is an enormously complex mixture consisting primarily of large arrays of benzene-like rings joined together. Thermal breakdown of coal occurs when heated to 1000 °C in the absence of air, and a mixture of volatile products called coal tar boils off. Fractional distillation of coal tar yields benzene, toluene, xylene (dimethylbenzene), naphthalene, and a host of other aromatic compounds (Figure 15.2). Figure 15.2 Some aromatic hydrocarbons found in coal tar. Unlike coal, petroleum contains few aromatic compounds and consists largely of alkanes (see Chapter 3 Chemistry Matters). During petroleum refining, however, aromatic molecules are formed when alkanes are passed over a catalyst at about 500 °C under high pressure. Aromatic substances, more than any other class of organic compounds, have acquired a large number of nonsystematic names. IUPAC rules discourage the use of most such names but do allow some of the more widely used ones to be retained (Table 15.1). Thus, methylbenzene is known commonly as toluene; hydroxybenzene as phenol; aminobenzene as aniline; and so on. Table 15.1 Common Names of Some Aromatic Compounds Monosubstituted benzenes are named systematically in the same manner as other hydrocarbons, with –benzene as the parent name. Thus, C6H5Br is bromobenzene, C6H5NO2 is nitrobenzene, and C6H5CH2CH2CH3 is propylbenzene. Alkyl-substituted benzenes are sometimes referred to as arenes and are named in different ways depending on the size of the alkyl group. If the alkyl substituent is smaller than the ring (six or fewer carbons), the arene is referred to as an alkyl-substituted benzene. If the alkyl substituent is larger than the ring (seven or more carbons), the compound is referred to as a phenyl-substituted alkane. The name phenyl, pronounced fen-nil and sometimes abbreviated as Ph or Φ (Greek phi), is used for the –C6H5 unit when the benzene ring is considered a substituent. The word is derived from the Greek pheno ("I bear light"), commemorating the discovery of benzene by Michael Faraday in 1825 from the oily residue left by the illuminating gas used in London street lamps. In addition, the name benzyl is used for the C6H5CH2– group. Disubstituted benzenes are named using the prefixes ortho (o), meta (m), or para (p). An ortho-disubstituted benzene has its two substituents in a 1,2 relationship on the ring, a meta-disubstituted benzene has its two substituents in a 1,3 relationship, and a para- disubstituted benzene has its substituents in a 1,4 relationship. The ortho, meta, para system of nomenclature is also useful when discussing reactions. For example, we might describe the reaction of bromine with toluene by saying, "Reaction occurs at the para position," meaning at the position para to the methyl group already present on the ring. As with cycloalkanes (Section 4.1), benzenes with more than two substituents are named by choosing a point of attachment as carbon 1 and numbering the substituents on the ring so that the second substituent has as low a number as possible. If ambiguity still exists, number so that the third or fourth substituent has as low a number as possible, until a point of difference is found. The substituents are listed alphabetically when writing the name. Note in the second and third examples shown that –phenol and –toluene are used as the parent names rather than –benzene. Any of the monosubstituted aromatic compounds shown in Table 15.1 can serve as a parent name, with the principal substituent (–OH in phenol or –CH3 in toluene) attached to C1 on the ring. Problem 15-1 Tell whether the following compounds are ortho-, meta-, or para-disubstituted: (a) (b) (c) Problem 15-2 Give IUPAC names for the following compounds: (a) (b) (c) (d) (e) (f) Problem 15-3 Draw structures corresponding to the following IUPAC names: (a) p-Bromochlorobenzene (b) p-Bromotoluene (c) m-Chloroaniline (d) 1-Chloro-3,5-dimethylbenzene 15.1 • Naming Aromatic Compounds Simple aromatic hydrocarbons come from two main sources: coal and petroleum. Coal is an enormously complex mixture consisting primarily of large arrays of benzene-like rings joined together. Thermal breakdown of coal occurs when heated to 1000 °C in the absence of air, and a mixture of volatile products called coal tar boils off. Fractional distillation of coal tar yields benzene, toluene, xylene (dimethylbenzene), naphthalene, and a host of other aromatic compounds (Figure 15.2). Figure 15.2 Some aromatic hydrocarbons found in coal tar. Unlike coal, petroleum contains few aromatic compounds and consists largely of alkanes (see Chapter 3 Chemistry Matters). During petroleum refining, however, aromatic molecules are formed when alkanes are passed over a catalyst at about 500 °C under high pressure. Aromatic substances, more than any other class of organic compounds, have acquired a large number of nonsystematic names. IUPAC rules discourage the use of most such names but do allow some of the more widely used ones to be retained (Table 15.1). Thus, methylbenzene is known commonly as toluene; hydroxybenzene as phenol; aminobenzene as aniline; and so on. Table 15.1 Common Names of Some Aromatic Compounds Structure Name Toluene(bp 111 °C) Phenol(mp 43 °C) Aniline(bp 184 °C) Acetophenone(mp 21 °C) Benzaldehyde(bp 178 °C) Benzoic acid(mp 122 °C) ortho-Xylene(bp 144 °C) Styrene(bp 145 °C) Monosubstituted benzenes are named systematically in the same manner as other hydrocarbons, with -benzene as the parent name. Thus, C6H5Br is bromobenzene, C6H5NO2 is nitrobenzene, and C6H5CH2CH2CH3 is propylbenzene. Alkyl-substituted benzenes are sometimes referred to as arenes and are named in different ways depending on the size of the alkyl group. If the alkyl substituent is smaller than the ring (six or fewer carbons), the arene is referred to as an alkyl-substituted benzene. If the alkyl substituent is larger than the ring (seven or more carbons), the compound is referred to as a phenyl-substituted alkane. The name phenyl, pronounced fen-nil and sometimes abbreviated as Ph or Φ (Greek phi), is used for the –C6H5 unit when the benzene ring is considered a substituent. The word is derived from the Greek pheno ("I bear light"), commemorating the discovery of benzene by Michael Faraday in 1825 from the oily residue left by the illuminating gas used in London street lamps. In addition, the name benzyl is used for the C6H5CH2– group. Disubstituted benzenes are named using the prefixes ortho (o), meta (m), or para (p). An ortho-disubstituted benzene has its two substituents in a 1,2 relationship on the ring, a meta-disubstituted benzene has its two substituents in a 1,3 relationship, and a para-disubstituted benzene has its substituents in a 1,4 relationship. The ortho, meta, para system of nomenclature is also useful when discussing reactions. For example, we might describe the reaction of bromine with toluene by saying, "Reaction occurs at the para position," meaning at the position para to the methyl group already present on the ring. As with cycloalkanes (Section 4.1), benzenes with more than two substituents are named by choosing a point of attachment as carbon 1 and numbering the substituents on the ring so that the second substituent has as low a number as possible. If ambiguity still exists, number so that the third or fourth substituent has as low a number as possible, until a point of difference is found. The substituents are listed alphabetically when writing the name. Note in the second and third examples shown that -phenol and -toluene are used as the parent names rather than -benzene. Any of the monosubstituted aromatic compounds shown in Table 15.1 can serve as a parent name, with the principal substituent (–OH in phenol or –CH3 in toluene) attached to C1 on the ring. Problem 15-3 Draw structures corresponding to the following IUPAC names: (d) 1-Chloro-3,5-dimethylbenzene The phenyl group Remember that you get a methyl group, CH3, by removing a hydrogen from methane, CH4. You get a phenyl group, C6H5, by removing a hydrogen from a benzene ring, C6H6. Like a methyl or an ethyl group, a phenyl group is always attached to something else. Aromatic compounds with only one group attached to the benzene ring Cases where the name is based on benzene chlorobenzene This is a simple example of a halogen attached to the benzene ring. The name is self-obvious. The simplified formula for this is C6H5Cl. You could therefore (although you never do!) call it phenyl chloride. Whenever you draw a benzene ring with one other thing attached to it, you are in fact drawing a phenyl group. In order to attach something else, you have to remove one of the existing hydrogen atoms, and so automatically make a phenyl group. nitrobenzene The nitro group, NO2, is attached to a benzene ring. The simplified formula for this is C6H5NO2. methylbenzene Another obvious name - the benzene ring has a methyl group attached. Other alkyl side-chains would be named similarly - for example, ethylbenzene. The old name for methylbenzene is toluene, and you may still meet that. The simplified formula for this is C6H5CH3. (chloromethyl)benzene A variant on this which you may need to know about is where one of the hydrogens on the CH3 group is replaced by a chlorine atom. Notice the brackets around the (chloromethyl) in the name. This is so that you are sure that the chlorine is part of the methyl group and not somewhere else on the ring. If more than one of the hydrogens had been replaced by chlorine, the names would be (dichloromethyl)benzene or (trichloromethyl)benzene. Again, notice the importance of the brackets in showing that the chlorines are part of the side group and not directly attached to the ring. benzoic acid (benzenecarboxylic acid) Benzoic acid is the older name, but is still in common use - it's a lot easier to say and write than the modern alternative! Whatever you call it, it has a carboxylic acid group, -COOH, attached to the benzene ring. Cases where the name is based on phenyl Remember that the phenyl group is a benzene ring minus a hydrogen atom - C6H5. If you draw a benzene ring with one group attached, you have drawn a phenyl group. phenylamine Phenylamine is a primary amine and contains the -NH2 group attached to a benzene ring. The old name for phenylamine is aniline, and you could also reasonably call it aminobenzene. Phenylamine is what it is most commonly for UK-based exam purposes. Benzene is the "first and simplest" aromatic compound and many monosubstituted derivatives of benzene are named systematically by adding the name of the substituent to "benzene" which is the parent: For examples: If the substituent is an alkyl chain with more carbon atoms than benzene, then benzene can be treated as a substituent. The ring, in this case, is called a phenyl group just like the methyl, ethyl, etc. The phenyl group is often abbreviated as "Ph". There are also monosubstituted benzene rings that have common names. And when naming an aromatic compound with one of these rings, you need to use the common name as the parent and not the "benzene". Below is the list of these common names: Unfortunately, there are no other options and you need to memorize these names. At least the first row since they are more common, and you will encounter them all when dealing with aromatic compounds. Some disubstituted benzene rings also have common names, and the first thing here is to know the relative positions of ortho, meta, and para: For the other rings with common names, start numbering the ring from the substituent that is part of the common ring such that the other groups get the smallest possible locants: Using "benzene" as the parent can also be encountered, even though it is not what you'd commonly see: In general, to name an aromatic compound, you can follow these steps: Identify and name the parent. If it is not one of the common names, then use benzene. Identify and name the substituents. Number the ring to give the substituents the smallest possible number. Put the substituents alphabetically followed by the parent name. For example, in ortho-dibromobenzene, numbering from the top Br goes clockwise to have a 1,2, instead of 1,6 locant order: We do the same way if there are more substituents: If the numbering does not make a difference, then give a smaller locant to the alphabetical priority: If there are more than two groups, and numbering doesn't make a difference, start from the alphabetical priority and number the ring toward the next alphabetical priority: In reference to the question asked in the comments, I also wanted to address the situation when two common names are possible. For example phenol and aniline, we need to go based on the priority of the groups. In this case, we are comparing the amine and alcohol, and since OH stands above NH2 in the priority chart, the parent chain should be an alcohol (phenol) rather than aniline. Check this 60-question, Multiple-Choice Quiz with a 1.5-hour Video Solution covering the naming and electrophilic aromatic substitution reactions. 1. Give an acceptable IUPAC name for each molecule according to the nomenclature of aromatic compounds. For some compounds, there may be more than one acceptable name. a) b) c) d) e) f) g) h) i) j) By the end of this section, you will be able to: Describe the bonding in benzene and the way typical reactions of benzene differ from those of the alkenes. Recognize aromatic compounds from structural formulas. Name aromatic compounds given formulas. Write formulas for aromatic compounds given their names. Next, we consider a class of hydrocarbons with molecular formulas like those of unsaturated hydrocarbons, but which, unlike the alkenes, do not readily undergo addition reactions. These compounds comprise a distinct class, called aromatic hydrocarbons, with unique structures and properties. Historically, benzene-like substances were called aromatic hydrocarbons because they had distinctive aromas. Today, an aromatic compound is any compound that contains a benzene ring or has certain benzene-like properties (but not necessarily a strong aroma). You can recognize the aromatic compounds in this text by the presence of one or more benzene rings in their structure. Some representative aromatic compounds and their uses are listed in Table 22.4a., where the benzene ring is represented as C6H5. The simplest of these compounds. Benzene (C6H6) is of great commercial importance, but it also has noteworthy health effects. The formula C6H6 seems to indicate that benzene has a high degree of unsaturation. (Hexane, the saturated hydrocarbon with six carbon atoms has the formula C6H14—eight more hydrogen atoms than benzene.) However, despite the seeming low level of saturation, benzene is rather unreactive. It does not, for example, react readily with bromine, which, is a test for unsaturation. To explain the surprising properties of benzene, chemists suppose the molecule has a cyclic, hexagonal, planar structure of six carbon atoms with one hydrogen atom bonded to each. We can write a structure with alternate single and double bonds, either as a full structural formula or as a line formula as shown in Figure 22.4a. However, these structures do not explain the unique properties of benzene. Furthermore, experimental evidence indicates that all the carbon-to-carbon bonds in benzene are equivalent, and the molecule is unusually stable. Chemists often represent benzene as a hexagon with an inscribed circle as in Figure 22.4b. The inner circle indicates that the valence electrons are shared equally by all six carbon atoms (that is, the electrons are delocalized, or spread out, over all the carbon atoms). It is understood that each corner of the hexagon is occupied by one carbon atom, and each carbon atom has one hydrogen atom attached to it. Any other atom or groups of atoms substituted for a hydrogen atom must be shown bonded to a particular corner of the hexagon. We use this modern symbolism, but many scientists still use the earlier structure with alternate double and single bonds. Table 22.4a. Some Representative Aromatic Compounds Name Structure Typical Uses aniline C6H5–NH2 starting material for the synthesis of dyes, drugs, resins, varnishes, perfumes; solvent; vulcanizing rubber benzoic acid C6H5–COOH food preservative; starting material for the synthesis of dyes and other organic compounds; curing of tobacco bromobenzene C6H5–Br starting material for the synthesis of many other aromatic compounds; solvent; motor oil additive nitrobenzene C6H5–NO2 starting material for the synthesis of aniline; solvent for cellulose nitrate; in soaps and shoe polish phenol C6H5–OH disinfectant; starting material for the synthesis of resins, drugs, and other organic compounds toluene C6H5–CH3 solvent; gasoline octane booster; starting material for the synthesis of benzoic acid, Table source: "13.8: Structure and Nomenclature of Aromatic Compounds" In Basics of GOB Chemistry (Ball et al.), CC BY-NC-SA 4.0. Many aromatic based compounds have pleasant odours but they are generally toxic with some being carcinogenic. Users should avoid inhaling any vapours. Lighter weight aromatic hydrocarbons are highly flammable and have a sooty flame. Like all hydrocarbons, aromatics are less dense than water and not soluble in water. Their boiling points tend to increase in molar mass, but their melting points are independent on molar mass. Symmetry in the molecule leads to much higher melting points. (Roberts & Caserio, 1977). August Kekule was the first one to depict the benzene structure as a ring-like structure with alternating single and double bonds. For more information refer to infographic 22.4a. below. Infographic 22.4a. Read more about "Today in Chemistry History: August Kekulé and the structure of benzene" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 22.4a [New tab]. Which compounds are aromatic? (credit: Intro Chem: GOB (V. 1.0)., CC BY-NC-SA 3.0). Solution The compound has a benzene ring (with a chlorine atom substituted for one of the hydrogen atoms); it is aromatic. The compound is cyclic, but it does not have a benzene ring; it is not aromatic. The compound has a benzene ring (with a propyl group substituted for one of the hydrogen atoms); it is aromatic. The compound is cyclic, but it does not have a benzene ring; it is not aromatic. Benzene is a liquid that smells like gasoline, boils at 80°C, and freezes at 5.5°C. Most of the benzene used commercially comes from petroleum. It is employed as a starting material for the production of detergents, drugs, dyes, insecticides, and plastics. It was formerly used to decaffeinate coffee and was a significant component of many consumer products, such as paint strippers, rubber cements, and home dry-cleaning spot removers. It was removed from many product formulations in the 1950s, but others continued to use benzene in products until the 1970s when it was associated with leukemia deaths. Benzene is still important in industry as a precursor in the production of plastics (such as Styrofoam and nylon), drugs, detergents, synthetic rubber, pesticides, and dyes. It is used as a solvent for such things as cleaning and maintaining printing equipment and for adhesives such as those used to attach soles to shoes. Benzene is now known to have both short- and long-term toxic effects. The inhalation of large concentrations can cause nausea and even death due to respiratory or heart failure, while repeated exposure leads to a progressive disease in which the ability of the bone marrow to make new blood cells is eventually destroyed. This results in a condition called aplastic anemia, in which there is a decrease in the numbers of both the red and white blood cells. Though benzene alone has been shown to potentially affect your health, substances containing the benzene ring are common in both animals and plants. Plants can synthesize the benzene ring from carbon dioxide, water, and inorganic materials. Animals cannot synthesize it, but they are dependent on certain aromatic compounds for survival and therefore must obtain them from food. Phenylalanine, tyrosine, and tryptophan (essential amino acids) and vitamins K, B2 (riboflavin), and B9 (folic acid) all contain the benzene ring. Many important drugs, a few of which are shown in Table 22.4b., also feature a benzene ring. In the International Union of Pure and Applied Chemistry (IUPAC) system, aromatic hydrocarbons are named as derivatives of benzene. Figure 22.4c. shows four examples. In these structures, it is immaterial whether the single substituent is written at the top, side, or bottom of the ring: a hexagon is symmetrical, and therefore all positions are equivalent. Figure 22.4c. Some Benzene Derivatives. These compounds are named in the usual way with the group that replaces a hydrogen atom named as a substituent group: Cl as chloro, Br as bromo, I as iodo, NO2 as nitro, and CH3CH2 as ethyl (credit: Intro Chem: GOB (V. 1.0)., CC BY-NC-SA 3.0). Although some compounds are referred to exclusively by IUPAC names, some are more frequently denoted by common names, as is indicated in Table 22.4a. and shown in Figure 22.4d. Naming Polysubstituted Benzenes When there is more than one substituent, the corners of the hexagon are no longer equivalent, so we must designate the relative positions. There are three possible disubstituted benzenes, and we can use numbers to distinguish them (Figure 22.4e.). We start numbering at the carbon atom to which one of the groups is attached and count toward the carbon atom that bears the other substituent group by the shortest path. Figure 22.4e. The three isomeric dichlorobenzenes (credit: Intro Chem: GOB (V. 1.0)., CC BY-NC-SA 3.0). The structural differences in the three dichlorobenzene compounds in Figure 22.4e. lead to differences in physical properties. Table 22.4c. highlights some of the key physical properties of dichlorobenzenes. Table 22.4c. Physical properties of dichlorobenzenes (Data sources credit: National Center for Biotechnology Information, 2024a, b, c) Compound Chemical Formula Molecular Weight Boiling Point Melting Point 1,2-dichlorobenzene (o-dichlorobenzene) C6H4Cl2 147.00 g/mol 180oC -17oC 1,3-dichlorobenzene (m-dichlorobenzene) C6H4Cl2 147.00 g/mol 173oC -25oC 1,4-dichlorobenzene (p-dichlorobenzene) C6H4Cl2 147.00 g/mol 174oC 53oC In Figure 22.4e., common names are also used: the prefix ortho (o-) for 1,2-disubstitution, meta (m-) for 1,3-disubstitution, and para (p-) for 1,4-disubstitution. The substituent names are listed in alphabetical order. The first substituent is given the lowest number. When a common name is used, the carbon atom that bears the group responsible for the name is given the number 1 as demonstrated in Figure 22.4f. Name each compound using both the common name and the IUPAC name. (credit: Intro Chem: GOB (V. 1.0)., CC BY-NC-SA 3.0). The benzene ring has two chlorine atoms (dichloro) in the first and second positions. The compound is o-dichlorobenzene or 1,2-dichlorobenzene. The benzene ring has a methyl (CH3) group. The compound is therefore named as a derivative of toluene. The bromine atom is on the fourth carbon atom, counting from the methyl group. The compound is p-bromotoluene or 4-bromotoluene. The benzene ring has two nitro (NO2) groups in the first and third positions. It is m-dinitrobenzene or 1,3-dinitrobenzene. Note: The nitro (NO2) group is a common substituent in aromatic compounds. Many nitro compounds are explosive, most notably 2,4,6-trinitrotoluene (TNT). Name each compound using both the common name and the IUPAC name. Exercise and image credit: Intro Chem: GOB (V. 1.0)., CC BY-NC-SA 3.0 Sometimes an aromatic group is found as a substituent bonded to a nonaromatic entity or to another aromatic ring. The group of atoms remaining when a hydrogen atom is removed from an aromatic compound is called an aryl group. The most common aryl group is derived from benzene (C6H6) by removing one hydrogen atom (C6H5) and is called a phenyl group (Figure 22.4g.), from pheno, an old name for benzene. Figure 22.4g. Different ways to represent the phenyl group using a condensed structure, line structure and phenyl as a substituent (credit: Intro Chem: GOB (V. 1.0)., CC BY-NC-SA 3.0). Name this compound. (credit: Samantha Sullivan Sauer / Biovia Draw, CC BY-NC 4.0.) Check Your Answer: Activity source: Exercise 22.4b is created by Samantha Sullivan Sauer, using images from Biovia Draw, licensed under CC BY-NC 4.0 A number of sunscreens that are UVA and UVB blockers are made with ingredients that contain benzene structures. For a detailed look at the various substituted benzene ingredients, see infographic 22.4c. below. Infographic 22.4c. Read more about "The Science of Sunscreen & How it Protects Your Skin" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 22.4c [New tab]. Not only are benzene compounds found in products we use such as sunscreen, but they can also be found in objects we handle. A new car for example will often have a "new car smell". This smell is associated with numerous volatile organic compounds (VOCs) that are made up of compounds that contain a benzene ring. For more information about the types of VOCs found within a new car see Infographic 22.4d. Infographic 22.4d. Read more about "The Chemicals Behind the 'New Car Smell'" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 22.4d [New tab]. Some common aromatic hydrocarbons consist of fused benzene rings—rings that share a common side. These compounds are called polycyclic aromatic hydrocarbons (PAHs). A few examples are shown in Figure 22.4h. Figure 22.4h. Examples of polycyclic aromatic compounds naphthalene, anthracene and phenanthrene. (credit: Intro Chem: GOB (V. 1.0)., CC BY-NC-SA 3.0). The three examples (naphthalene, anthracene and phenanthrene), shown here are colourless, crystalline solids generally obtained from coal tar. Naphthalene has a pungent odour and is used in mothballs. Anthracene is used in the manufacture of certain dyes. Steroids, a large group of naturally occurring substances, contain the phenanthrene structure. Glow sticks are effectively used at night so that you can be visible or to add some fun to an event. They come in all sorts of colours such as red, orange, yellow, green and blue. Benzene containing compounds are responsible for the various colours produced. Additionally, the reaction that allows the glow stick to glow, is from the reactions involving benzene containing compounds. Next time you use a glow stick, you can thank the benzene rings! For more information, see infographic 22.4e. below. Infographic 22.4e. Read more about "The Chemistry of Glow Sticks" by Andy Brunning / Compound Interest, CC BY-NC-ND, or access a text-based summary of infographic 22.4e [New tab]. 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(1977). Basic Principles of Organic Chemistry, (2nd ed.) W. A. Benjamin, Inc. definitioncompounds containing a benzene ring Aromatic compounds will likely contain one or more benzene rings. Benzene has the molecular formula C6H6 with each of the carbon atoms in the planar hexagonal ring covalently bonded to one hydrogen atom. A substituent you will likely meet in your study of organic chemistry is the phenyl group (-C6H5), a phenyl group is simply a benzene ring where one of the hydrogen atoms has been removed. This is shown below: Benzene (C6H6) can be drawn using the Kekulé structure showing the presence of carbon carbon double bonds (C=C) or by using the circle notation to represent the delocalised electrons. The phenyl group (-C6H5) is simply formed when one of the hydrogen atoms on a benzene ring is removed, it will be replaced by another atom or group. Monosubstituted aromatic rings You will no doubt meet aromatic rings which have been substituted with various atoms and groups including: chlorine (-Cl), bromine (-Br), nitro group (-NO2), methyl group (-CH3) as well as many other atoms and groups. Naming these monosubstituted aromatic rings follows the same rules you have used for other hydrocarbon molecules. These molecules are simply named as substituted benzene rings e.g. Aromatic rings with more than one attached substituent need to be named by numbering the carbon atoms that any substituents are attached to. The substituents are listed alphabetically and they must be given the lowest possible numbers e.g. consider the following substituted aromatic rings: Disubstituted benzene rings may also be named using one of the prefixes ortho, meta or para. These three positions are shown below: As an example consider the following three molecules: Arenes Alkyl substituted benzene ring are often referred to as arenes. Arenes are named in two different ways, depending on the size of the alkyl substituent: If the alkyl substituent is small, that is fewer than six carbon atoms, then the arene is simply named as a substituted benzene ring e.g. If the alkyl substituent is larger than six carbon atoms; that is larger than the benzene ring then the arene can be named as a phenyl substituted alkane. The phenyl group (-C6H5) as mentioned above is simply a benzene ring where one of the hydrogen atoms is removed. Trivial names The naming of aromatic compounds can at times become rather frustrating to new students simply because many traditional trivial names that is non-systematic names are frequently used. Some of these are shown below and I am afraid to say that it is just a case of remembering these names and molecular structures: Key Points Aromatic compounds likely contain benzene rings. Arenes are alkyl substituted benzene rings. A phenyl group has the molecular formula C6H5 Many aromatic compounds are commonly named using trivial names. Practice questions 