Electron Withdrawing Electron Donating Groups

Inverse electron-demand Diels–Alder reaction A prototypical DAINV reaction is shown on the right. It is related to the Diels–Alder reaction, but unlike the Diels–Alder (or DA) reaction, the DAINV is a cycloaddition between an electron-rich dienophile and an electron-poor diene. This The inverse electron demand Diels–Alder reaction, or DAINV or IEDDA is an organic chemical reaction, in which two new chemical bonds and a six-membered ring are formed. inverse electron demand Diels-Alder reactions are, unlike in the standard DA, very electron rich, containing one or more electron donating groups. During a DAINV reaction, three pi-bonds are broken, and two sigma bonds and one new pi-bond are formed 605c54098d

The sEDA parameter for a given substituent is calculated by means of quantum chemistry methods. The model molecule is the monosubstituted benzene. First the geometry should be optimized at a suitable model of theory, then the natural population analysis within the framework of Natural Bond Orbital theory is performed. The molecule have to be oriented in such a way that the aromatic benzene ring lays in the xy plane and is perpendicular to the z-axis. Then, the 2s, 2px and 2py orbital occupations of ring carbon atoms are summed up to give the total sigma system occupation. From this value the sum of sigma-occupation for unsubstituted benzene is subtracted resulting in original sEDA parameter. For sigma-electron donating substituents like -Li, -BH2, -SiH3, the sEDA parameter is positive, and for... 605c54098d The halogen atoms in an alkyl halide are electron withdrawing while the alkyl groups have electron donating tendencies. If the electronegative atom (missing an electron, thus having a positive charge) is then joined to a chain of atoms, typically carbon, the positive charge is relayed to the other atoms in the chain. This is the electron-withdrawing inductive effect, also known as the −I effect. In short, alkyl groups tend to donate electrons, leading to the +I effect. Its experimental basis is the ionization constant. It is distinct from and often opposite to the mesomeric effect. 605c54098d with regard to Lewis

acidity, electron... 605c54098d == Background == 605c54098d The Buchner ring expansion reaction was first used in 1885 by Eduard Buchner and Theodor Curtius who prepared a carbene from ethyl diazoacetate for addition to benzene using both thermal and photochemical pathways in the synthesis of cycloheptatriene derivatives. The resulting product was a mixture of four isomeric carboxylic acids. Variations in the reaction arise from methods of carbene preparation. Advances in organometallic chemistry have resulted in increased selectivity of cycloheptatriene derivatives. In the 1980s it was found that dirhodium catalysts provide single cyclopropane isomers in high yields. 605c54098d == History == 605c54098d

Dakin oxidation Boric acid and The Dakin oxidation (or Dakin reaction) is an organic redox reaction in which an ortho- or para-hydroxylated phenyl aldehyde (2-hydroxybenzaldehyde or 4-hydroxybenzaldehyde) or ketone reacts with hydrogen peroxide (H2O2) in base to form a benzenediol and a carboxylate. Overall, the carbonyl group is oxidised, whereas the H2O2 is reduced. reactants with electron-donating groups meta to the carbonyl group or electron-withdrawing groups ortho or para to the carbonyl group 605c54098d

Inductive effect in a molecule is a local change in the electron density due to electron-withdrawing or electron-donating groups elsewhere in the molecule, resulting in In organic chemistry, the inductive effect in a molecule is a local change in the electron density due to electron-withdrawing or electron-donating groups elsewhere in the molecule, resulting in a permanent dipole in a bond 605c54098d

EDGs and EWGs also determine the positions (relative to themselves) on the aromatic ring where substitution reactions are most likely... 605c54098d The term polar effect is sometimes used to refer to electronic effects, but also may have the more narrow definition of effects resulting from non-conjugated substituents. 605c54098d

Electron-withdrawing group This electron density transfer is often achieved by resonance or inductive effects. Both describe functional groups, however, electron-withdrawing groups pull An electron-withdrawing group (EWG) is a group or atom that has the ability to draw electron density toward itself and away from other adjacent atoms. Electron-withdrawing groups have significant impacts on

fundamental chemical processes such as acid-base reactions, redox potentials, and substitution reactions. Electron-withdrawing groups are the opposite effect of electron-donating groups (EDGs) 605c54098d

== Bond polarization == 605c54098d Buchner's first synthesis of cycloheptatriene derivatives in 1885 used photolysis and thermal conditions to generate the carbene. A procedure for preparation of the hazardous... 605c54098d

Buchner ring expansion The ring expansion occurs in the second step, with an electrocyclic reaction opening the cyclopropane ring to form the 7-membered ring. The first step involves formation of a carbene from ethyl diazoacetate, which cyclopropanates an aromatic ring. and material science (fullerene derivatives). possible for both electron withdrawing and electron donating groups at the C7 carbon. The molecular orbitals of electron withdrawing groups at C7 overlap The Buchner ring expansion is a two-step organic C-C bond forming reaction used to access 7-membered rings 605c54098d

The Dakin oxidation starts with (1) nucleophilic addition of a hydroperoxide ion to

the carbonyl carbon, forming a (2) tetrahedral intermediate. The intermediate collapses, causing [1,2]-aryl migration, hydroxide elimination, and formation of a (3) phenyl ester. The phenyl ester is subsequently hydrolyzed: nucleophilic addition of hydroxide ion from solution to the ester carbonyl carbon forms a (4) second tetrahedral intermediate, which collapses, eliminating a (5) phenoxide ion and forming a carboxylic acid. Finally, the phenoxide extracts the acidic hydrogen from the carboxylic acid, yielding the (6) collected products. 605c54098d It is present in a σ (sigma) bond, unlike the electromeric effect which is present in a π (pi) bond. 605c54098d

Electronic effect In organic chemistry, the term stereoelectronic effect is also used to emphasize the relation between the electronic structure and the geometry (stereochemistry) of a molecule. presence of the electron-withdrawing substituent has a stabilizing effect. Similarly, an electron-releasing group (ERG) or electron-donating group (EDG) releases An electronic effect influences the structure, reactivity, or properties of a molecule but is neither a traditional bond nor a steric effect 605c54098d

with regard to nucleophilic substitution reactions, electron-rich species are relatively strong nucleophiles, as judged by rates of attack by electrophiles. For example, compared to benzene, pyrrole is more rapidly attacked by electrophiles. Pyrrole is therefore considered to be an electron-rich aromatic ring. Similarly, benzene derivatives with electron-donating groups (EDGs) are attacked by electrophiles faster than in benzene. The electron-donating vs electron-withdrawing influence of various functional groups have been extensively parameterized in linear free energy relationships. 605c54098d with regard to electron-transfer, electron-rich species have low ionization energy and/or are reducing agents. Tetrakis(dimethylamino)ethylene is an electron-rich alkene because, unlike ethylene, it forms isolable radical cation. In contrast, electron-poor alkene tetracyanoethylene is an electron acceptor, forming isolable anions. 605c54098d == History == 605c54098d DAINV reactions often involve heteroatoms, and can be used to form heterocyclic compounds. This makes the DAINV reaction particularly useful in natural product syntheses, where the target compounds often contain heterocycles. Recently, the DAINV reaction has been used to synthesize a drug transport system which targets prostate cancer. 605c54098d == Reaction mechanism == 605c54098d == Types == 605c54098d

The Cieplak effect relies on the stabilizing interaction of mixing full and empty orbitals to delocalize electrons, known as hyperconjugation. When the highest occupied… 605c54098d The Dakin oxidation, which is closely related to the Baeyer–Villiger oxidation, is not to be confused with the Dakin–West reaction, though both are named after Henry Drysdale Dakin. 605c54098d An electron withdrawing group (EWG) will have the opposite effect on the nucleophilicity of the ring. The EWG removes electron density from a π system, making it less reactive in this type of reaction, and therefore called deactivating groups. 605c54098d The Diels–Alder reaction was first reported in 1928 by Otto Diels and Kurt Alder; they were awarded the Nobel Prize in chemistry for their work in 1950. Since that time, use of the Diels–Alder reaction has become widespread. Conversely, DAINV does not have a clear date of inception, and lacks the comparative prominence of the standard Diels… 605c54098d with regard to acid-base reactions, electron-rich species have high pKa's and react with weak Lewis acids. 605c54098d == Consequences of EWGs == 605c54098d

Electron-rich The electron-donating vs electron-withdrawing influence of various functional groups have been extensively parameterized Electron-rich is jargon that

is used in multiple related meanings with either or both kinetic and thermodynamic implications:. electrophiles faster than in benzene 605c54098d

Electrophilic aromatic directing groups Electron donating groups are generally ortho/para directors for electrophilic aromatic substitutions, while electron withdrawing groups (except In electrophilic aromatic substitution reactions, existing substituent groups on the aromatic ring influence the overall reaction rate or have a directing effect on positional isomer of the products that are formed. place 605c54098d

Sigma electron donor-acceptor The more positive is the value of sEDA the more sigma-electron donating is a substituent. There is also a complementary scale - pEDA. value of sEDA the more sigma-electron donating is a substituent. The more negative sEDA, the more sigma-electron withdrawing is the substituent (see the The sEDA parameter (sigma electron donor-acceptor) is a sigma-electron substituent effect scale, described also as inductive and electronegativity related effect. The more negative sEDA, the more sigma-electron withdrawing is the substituent (see the table below) 605c54098d

Cieplak effect This conclusion is supported In organic chemistry, the Cieplak effect is a predictive model to rationalize why nucleophiles preferentially add to one face of a carbonyl over another. The Cieplak effect is subtle, and often competes with sterics, solvent effects, counterion complexation of the carbonyl oxygen, and other effects to determine product distribution. The nucleophile may be any of a number of reagents, most commonly organometallic or reducing agents. In the Cieplak model, electrons from a neighboring bond delocalize into the forming carbon–nucleophile (C–Nuc) bond, lowering the energy of the transition state and accelerating the rate of reaction. Subsequent work has questioned its legitimacy (see Criticisms). This interaction may guide attack syn to the electron-withdrawing substituent, and anti to electron-donating substituents. Proposed by Andrzej Stanislaw Cieplak in 1980, it correctly predicts results that could not be justified by the other standard models at the time, such as the Cram and Felkin–Anh models. Whichever bond can best donate its electrons into the C–Nuc bond determines which face of the carbonyl the nucleophile will add to 605c54098d

An electron donating group (EDG) or electron releasing group (ERG, Z in structural formulas) is an atom or functional group that donates some of its electron density

into a conjugated π system via resonance (mesomerism) or inductive effects (or induction)—called +M or +I effects, respectively—thus making the π system more nucleophilic. As a result of these electronic effects, an aromatic ring to which such a group is attached is more likely to participate in electrophilic substitution reaction. EDGs are therefore often known as activating groups, though steric effects can interfere with the reaction. 605c54098d

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