

Subject Index

- a*
activity, 415
conformational descriptor, 116
hyperfine coupling constant, 260
- A*
equatorial preference, 130
in Edwards equation, 507
overall solute hydrogen bond acidity, 339
preexponential factor, 349
A value in conformational analysis, 131, 135, 151, 169
*A*₁ mechanism, 447
A^(1,2) strain, 122
*A*₂ mechanism, 447
A^(1,3) strain, 122
*A*_{Ac}1 mechanism, 450, 451
*A*_{Ac}2 mechanism, 450–452
*A*_{Al}1 mechanism, 450–452
*A*_{Al}2 mechanism, 450
Ab initio calculation, 223
acidity, 419
amide hydrolysis, 461
bromonium ion, 566
carbene rearrangement, 286
carbocation, 593
carboxylate stability, 418
chloronium ion, 580
computational resources, 223
computational time, 136
Cope rearrangement, 772
Diels–Alder reaction, 736
electrophilic addition, 557
epoxidation, 606
ethyl cation, 294
formic acid, 429
gas phase acidity, 428
hydration of alkene, 593
hydroboration, 604
in chirality determination, 91
in conformational studies, 150
methyl anion, 315
nucleophilic addition to
 carbonyl, 626
 nucleophilic vinylic substitution, 532
 ozonolysis, 747
 pericyclic reaction, 706, 771
 S_N2 reaction, 496, 502
Ab initio theory, 223
- Ablation, 790
Abnormal addition, 589
Absolute configuration, 68, 91
Absolute electronegativity, 23
Absolute hardness and aromaticity, 220
Absolute hardness, η , 220, 506
Absolute softness, σ , 506
Absorption of UV-vis radiation, 787, 794
 by CT complex, 557
 + *ac*, 115
 − *ac*, 115
Acceptable representations of stereochemistry, 56
Acenaphthylene, syn addition of chlorine, 579
Acene, 206
Acetal hydrolysis, 447
Acetic acid
 acidity, 418
 acidity and thermodynamic values, 429
 acidity in gas phase and in solution, 428
Acetolysis, 481, 485, 488–491
Acetone
 as solvent for nucleophilic substitution, 498
 basicity, 421
 gas phase acidity, 425
 gas phase basicity, 427
 hydration, 441
 photochemical reaction, 833
 photophysical data, 808, 809
 reaction with hydroxylamine, 441
 solvent parameters, 340
Acetylenic carbanion hybridization, 311
Achiral structure, 64
Achirotopic, 98
Acid
 Brønsted, 413, 414
 hydron, 414
 Lewis, 413
 proton, 414
 triton, 414
Acid catalysis
 Brønsted catalysis law, 437
 buffer ratio, 437
 general, 435
 in alcohol dehydration, 670
 in alkene hydration, 592, 594
 in alkyne hydration, 614
 significance of Brønsted α , 437, 438
 specific, 434
Acidity
 and bent bond description of double bonds, 45
 and Hammett equation, 415
 and hybridization, 41, 44
 and ion pairing, 415
 and *J*_{13-C-H}, 41
 and photochemical reaction, 834
 and Taft equation, 418
 and σ, π description of double bonds, 44
 ΔG_{acid} , 424
 ΔH_{acid} , 424
 ΔS_{acid} , 424
 ethane, 44
 ethene, 44
 ethyne, 44
 formic acid, 419
 gas phase data for selected compounds, 425
 importance of ΔS in solution, 429
 in aqueous solution, 416
 in cyclohexylamine solution, 421
 in DMSO solution, 422
 in gas phase, 422, 423
 in nonaqueous solvents, 420
 in THF solution, 421
 *K*_a, 414
 *K*_a^T, 415
 *K*_i, 415
 kinetic, 41
 leveling effect, 422
 leveling effect of solvent, 430
 of electronically excited states, 812, 813
 p*K*_a, 414
 p*K*_{CsCHA}, 421
 radical cation, 309
 solvation effects, 428
 trends of alcohols in gas phase and in solution, 426
Acidity constant, 414
Acidity function
 excess acidity, 433
 H^{'''}, 431
 *H*_A, 431
 *H*_C, 432
 *H*_R, 432
 other, 432

- Actinometry, 804
 Activated complex, 350
 Activation energy, 348
 negative value of E_a , 350
 Activation enthalpy, ΔH^\ddagger , 350
 Activation entropy, ΔS^\ddagger , 350
 and mechanism, 353
 Activation free energy, ΔG^\ddagger , 350
 Activation volume, ΔV^\ddagger , 448
 Activity (a), 415
 Activity coefficient (γ), 415
 Acylium ion
 in $A_{AC}1$ mechanism, 451
 in acyl substitution, 460
 in Friedel–Crafts acylation, 330
 Ad mechanism label, 552
 Adamantene, 669
 1-Adamantyl radical, 267
 1,4-Addition, 285, 553, 620
 1,6-Addition, 553
 Addition, 551
 anti, 552
 anti-Markovnikov orientation, 568
 chemoselectivity, 567
 IUPAC terminology, 552
 kinetics, 558
 Markovnikov orientation, 567
 of Br_2 to alkene, 553
 photochemical, 841
 regiochemistry, 568
 solvent effects, 561
 stereochemistry, 552, 554
 syn, 552
 Taft equation, 555
 to carbonyl group, 439
 Ad_E2 mechanism, 552, 586, 613
 denoted as ($A_E + A_N$), 552
 Ad_E2M mechanism, 586
 Ad_E3 mechanism, 586, 610, 611, 613
 Ad_E4 mechanism, 611
 Ad_EC1 mechanism, 557
 Ad_EC2 mechanism, 557
 Adiabatic process, 812, 827, 850
 Adjacent exchange integral, 239
 $A_E + A_N$ mechanism, 552
 AFM, 3
 $A_h + A_N + A_hD_h + D_N + D_h$
 mechanism, 450
 $A_h + D_N + A_N + D_h$ mechanism, 450
 AIBN, 271
 AIM, 232
 Alcohol acidity in gas phase and in
 solution, 426
 Aldol reaction, 318, 621
 acid and base catalysis, 446
 reverse aldol reaction, 638
 Alkane acidity, 44
 Alkaplane, 161
 Alkene
 acidity, 44
 addition of Br_2 , 331, 342, 553
 addition of Br_2 by radical pathway,
 576
 addition of Cl_2 , 575
 addition of F_2 , 580
 addition of HX, 585
 addition of mixed halogens, 584
 anti-Markovnikov addition of HBr, 589
 as dipolarophile in 1,3-dipolar
 cycloaddition, 743
 di- π -methane rearrangement, 828
 electronically excited states, 818
 epoxidation, 605
 hydration, 592
 hydroboration, 600
 oxymercuration, 595
 ozonolysis, 404, 745
 photochemical carbocation formation
 from cycloalkene, 824
 photocycloaddition, 828
 photohydration of cyclic alkene, 825
 photoisomerization, 820
 radical addition of HBr, 271
 reaction with carbene, 284
 reaction with XeF_2 , 581
 solvomercuration, 596
 UV-vis absorption, 818
 Alkoxymercuration, 596
 1,2-Alkyl shift, 272
 Alkyne
 acidity, 44
 addition of Br_2 , 609
 addition of HX, 612, 614
 and angle strain, 164
 electrophilic addition, 609
 hydration, 614, 615
 hydroboration, 616
 oxymercuration, 615
 radical addition of HBr, 611
 reaction with peroxyacids, 616
 Allen electronegativity, 23
 Allowed pericyclic reaction, 705
 Allowed process, 274, 705, 796
 Allowed spectroscopic transition, 816
 Allyl anion
 DE_{π} , 188
 in cycloaddition, 743
 q_i , 192
 resonance structures, 189
 ρ_i , 192
 Allyl cation, 482
 DE_{π} , 188
 HMO calculation, 188
 in cycloaddition, 743
 q_i , 192
 resonance structures, 189
 ρ_i , 192
 Allyl radical
 DE_{π} , 188
 HMO calculation, 188
 q_i , 192
 resonance structures, 189
 ρ_i , 192
 Allyl system
 HMO calculation, 182
 NBMO, 196
 α
 in Brønsted catalysis law, 437
 in Edwards equation, 507
 in HMO theory, 179
 in Leffler equation, 363
 in Taft–Topsom equation, 400
 solvent parameter, 339
 stereochemical descriptor, 79
 α effect in nucleophilicity, 512
 α secondary kinetic isotope effect, 380, 772
 $[\alpha]$ (specific rotation), 86
 α,β -unsaturated carbonyl compound
 and conjugate addition, 620
 photochemical deconjugation, 842
 photochemistry, 841
 α',β -elimination, 635
 α -cleavage, Norrish type I reaction, 832
 α -cyclodextrin, and phosphorescence, 801
 α -diazoketone, in Wolff
 rearrangement, 288
 α -elimination, 634
 and carbene generation, 283
 Alternant structure, 194, 195
 even alternant, 195
 odd alternant, 195, 243
 AM1 method, 223
 AMBER force field, 136
 Amide hydrolysis, 460
 Amine
 basicity, 421
 basicity in solution, 420
 deamination, 677
 gas phase basicity, 427
 Aminolysis, 459
 $A_N + D_N$ mechanism, 528
 A_ND_N mechanism, 471
 3/1/ A_ND_N mechanism, 472
 $A_N + D_N + A_{xh}D_h$ mechanism, 453
 A_N mechanism label, 471
 3/ A_N mechanism label, 471
 Anchimeric assistance, 485, 487–489, 553,
 562, 674, 683
 Angle strain, 137
 and carbocations, 291
 and carbonyl hydrate formation, 441
 and cycloalkanes, 124
 Baeyer strain, 123
 calculation, 123
 in hemiketal formation, 441
 in molecular mechanics, 138
 in planar annulenes, 216
 in ΔH_f calculation, 13
 Angstrochemistry, 3
 Anh–Eisenstein model, 626
 Anisochronous groups, 96
 Anisotropic hyperfine coupling, 261
 Annulene, 215–217, 769, 770
 [4*n*]Annulene, 218
 [4*n* + 2]Annulene, 218
 [8]Annulene, 216
 [10]Annulene, 216
 [12]Annulene, 769
 [16]Annulene, 769, 770

- [18]Annulene, 217
 [20]Annulene, 769
 Anomalous fluorescence, 795
 Anomeric effect, 151
 Anomers, 79, 81
Antara, 716
 Antarafacial pathway, 716, 717, 719, 721, 731, 739, 741, 743, 754, 767, 773, 774
 Antarafacial-antarafacial pathway, 722
 Antarafacial-suprafacial pathway, 722
 Anthracene
 calculation of resonance energy, 239
 DRE, 219
 Kekulé structures, 238
 Kekulé structure count (KSC), 242
 number of Kekulé structures, 242
 photodimerization, 844
 photophysical data, 809
 resonance energy, 206, 238
 SRT resonance energy, 244
 UV-vis absorption and fluorescence, 798
 VB calculation, 239
 Anti, 77
 Anti addition, 552, 583, 617, 619
 in oxymercuration of alkenes, 598
 in oxymercuration of alkynes, 614
 of Br₂ to alkene, 566
 of Br₂ to alkyne, 610
 of Cl₂ to alkene, 577
 of HBr to alkyne, 611
 of HCl to cyclohexene, 586
 Anti conformation, 114, 115
 Anti elimination, 633, 648–651, 667, 668
 Antiaromatic destabilization, 212
 Antiaromatic structure, 201
 DRE value, 219
 NCIS value, 217
 η value, 220
 Antiaromatic transition state, 764
 Antiaromatic transition structure, 763
 Antibonding orbital, 42, 150, 180, 182, 231, 712, 791
 H₂, 28
 Anti-Bredt compound, 162
 Anti-clinal conformation, 115, 647, 649
 + Anti-clinal conformation, 115
 – Anti-clinal conformation, 115
 Anti-coplanar conformation, 647
 Anti-coplanar orientation, in
 dehalogenation of vicinal
 dihalide, 667
 Anti-Hammond effect, 365
 Anti-Markovnikov addition, 271, 567, 568, 588–590, 600
 Anti-Markovnikov orientation, 590
 Anti-Michael orientation, 622
 Anti-periplanar, 115, 358, 623, 647, 651
 + Anti-periplanar, 115
 Antisymmetric molecular orbital, 33, 707, 708, 712, 732, 739, 750
 Aprotic solvent, 131, 498, 512, 562, 574, 666
 aR, 70, 72
 Aracemic, 85
 Aromatic structure, 201
 Aromatic transition state, 764
 Aromatic transition structure, 763, 764
 Aromaticity, 201
 4*n* + 2 rule, 201
 and delocalization energy, 218
 Clar notation, 210
 Möbius, 767
 of transition structures in pericyclic
 reactions, 763
 Arrhenius equation, 348
 Arrhenius plot, 350
 Artificial photosynthesis, 862
 Aryne, 168, 541, 542
 in cycloaddition reactions, 741
 aS, 70, 72
 A_{SE}2 mechanism, 593
 A-S_E2 mechanism, 593
 Association process, 450
Asym-methylethylethylene, 592
 Asymmetric induction, 623
 Asymmetric structure, 62
 Atactic polymer, 93
 Atom transfer reaction, 378, 749
 selection rules, 750
 Atom type in molecular mechanics, 140
 Atomic carbon, 255
 Atomic force microscopy (AFM), 3
 Atomic radius in QTAIM, 235
 Atomic surface area, 6
 Atomic volume, 6
 calculated, 7
 in QTAIM, 235
 Atoms in molecules, 232
 Atropisomers, 66
 Attached atoms list, 139
 Attachment step, 533, 590
Aufbau principle, 187
 Autocatalytic reaction, 442
 Average bond dissociation energy, 16
 Avoided crossing, 514, 713, 734, 739, 848
 Avoided crossing rule, 713
 A_w (activity of water), 432
 A_{xh} mechanism descriptor, 639
 A_{xh}D_H + D_N mechanism, 639
 A_{xh}D_H + D_N[‡] mechanism, 644
 A_{xh}D_H^{*}D_N[‡] mechanism, 644
 A_{xh}D_H[‡] + D_N mechanism, 644
 A_{xh}D_H^{‡*}D_N mechanism, 644
 A_{xh}D_HD_N mechanism, 639
 Axial chirality, 70
 Axial substituent, 128, 626, 665
 Azobisisobutyronitrile, 271
 Azulene, 195, 244, 432, 795
 B
 in Edwards equation, 507
 overall solute hydrogen bond
 basicity, 339
 B3LYP functional, 237
 B-A_{Ac}3 mechanism, 450
 B_{Ac}1 mechanism, 453
 B_{Ac}2 mechanism, 453–456
 Back electron transfer, 306, 804
 Back-side attack in S_N2 reaction, 495
 Baeyer strain, 123, 148
 B_{Al}1 mechanism, 456
 B_{Al}2 mechanism, 453
 Baldwin's rules, 274
 Bamford–Stevens reaction, 286
 Banana bond, 42, 46
 Barrelene, 108, 167
 Base
 Brønsted, 413, 414
 Lewis, 413
 Base catalysis, 437
 alcohol dehydration, 676
 α-halogenation of carbonyl
 compounds, 444
 and carbonyl hydration, 439
 Brønsted catalysis law, 437
 enolate formation, 446
 ester hydrolysis, 457
 Base-promoted reaction, 449
 Basicity
 equilibrium concept, 504
 gas phase basicity, 426
 in aqueous solution, 420, 421
 proton affinity, 426
 selected gas phase data, 426
 Basicity function, 433
 Basis set, 224, 771
 in DFT, 236
 in HMO theory, 175
 Basis set function, 224
 Basketane, 163, 170
 Bathochromic shift, 817
 Beckmann rearrangement, 409
 Beer and photochemistry, 861
 Bell–Evans–Polanyi (BEP) principle, 363
 Beltene, 166
 Bema Hapothle, 363
 Benson electronegativity, 23
 Bent bond, 46, 47
 and acidity, 45
 and bond length, 44
 and conformation of propene, 46
 and LMO, 225
 and Pauling, Linus, 43
 and theoretical calculations, 46
 as starting point, 47
 banana bond, 42
 description of double bond, 42
 τ bond, 42
 Bent bond line representation of glycosidic
 linkage, 81
 Benzene
 DE_π, 190, 201
 DRE, 219
 electron diffraction, 202
 heat of hydrogenation, 190, 203
 HMO energy levels, 198
 Hückel MOs, 186
 isomer counting, 4
 Kekulé structures, 238
 Möbius molecular orbitals, 766

- Benzene (*Continued*)
 photochemistry, 843
 photophysical data, 809
 resonance energy, 190, 203, 238, 239
 SRT resonance energy, 245
 valence bond calculation, 238
- Benzene hexachloride, 648
- Benzil dipole moment in T1 state, 815
- Benzophenone
 DRE, 219
 photophysical data, 809
 photoreduction, 834
- Benzvalene, 167, 843
- Benzyl NBMO, 196
- Benzyl radical
 EPR spectrum, 197
 from toluene photodissociation, 847
- Benzynes, 168, 532, 536, 539, 541
 in cycloaddition reactions, 741
- m*-Benzynes, 168
- o*-Benzynes, 168
- p*-Benzynes, 168
- Benzynes mechanism, 537, 540, 549
- BEP principle, 363
- β
 in Edwards equation, 507
 in HMO theory, 179, 190
 isokinetic temperature, 402
 solvent parameter, 339
 stereochemical descriptor, 79
- β 2° kinetic isotope effect, 382
- β' in Möbius MO theory, 765
- β -bromovinyl cation, 610
- β -cleavage, 832, 836
- β_e (Bohr magneton), 259
- β -elimination, 633
- Bichromophoric structure, 829
- Bicyclo[1.1.0]butane, 108
 radical cation, 308
- Bicyclo[2.2.2]octane, 387
- Bicyclobutonium ion, 300
- In*-bicyclo[4.4.4]-1-tetradecene, 299
- Bifunctional catalysis, 448, 458
- Bifurcated potential energy surface, 370
- Biphenyl
 DRE, 219
 SRT resonance energy, 245
- Biradical, 308, 541, 697, 718, 726, 742, 776, 792, 798, 828, 833, 836–838
 as model for n, π^* state, 834
- Bishomocyclopropenyl structure, 494
- Bisulfite addition to carbonyl, 439
- Blue shift, 817
- Boat conformation, 124, 132, 782
- Boat transition structure
 for Claisen rearrangement, 724
 for Cope rearrangement, 722
- Boat-like transition structure, 782
- Bodenstein approximation, 345
- Bohr magneton (β_e), 259
- Bold wedge stereochemical descriptor, 55
- Boltzmann constant, 351
- Boltzmann distribution, 152, 157, 259
- Bond critical point, 235
- Bond curvature, 128
- Bond dipole moment calculation, 20
- Bond dissociation energy, 16
- Bond increment calculation, 10
- Bond order, 160, 192, 820
 in HMO theory, 193
 in QTAIM, 235
- Bond path, 234
- Bond stretch strain, 137
- Bonding orbital
 allyl, 182
 ethene π orbital, 180
 ethene π orbital from EHT
 calculation, 223
- H₂, 28
- Born–Oppenheimer approximation, 223, 796
- Bowsprit hydrogen, 125
- Boys method, 225
- Br₃[−] in electrophilic addition, 556, 558, 559, 562
- Brackets in pericyclic reaction
 designation, 744
- Bredt's rule, 162
- Bridgehead carbanion, 311
- Bridgehead carbocation, 475
- Bridgehead double bond, 162
- Bridgehead proton acidity, 51
- Bridgehead radical, 267
- Bridging in carbocations, 295
- Bridging power, 583
- Broken bold line in Maehr convention, 75
- Broken wedge in Maehr convention, 74
- Bromohydrin, 578
- Bromonium ion, 488, 553, 556, 598
 resonance structures, 564
- Brønsted acid, 413, 414
- Brønsted α , 438
- Brønsted base, 413, 414
- Brønsted β , 457
- Brønsted catalysis law, 437
- Brønsted correlation, 505
- Brønsted superacid, 296
- Brønsted–Lowry acid, 339, 413
- Buffer ratio, r , 437
- Bullvalene, 726, 854
- Bu₃SnH, 271
- 1,3-Butadiene
 C2–C3 rotational barrier, 190
 DE _{π} , 201
 Diels–Alder reaction, 731
 electrocyclic reaction, 702
 \mathcal{F}_i , 193
 HMO calculation, 184
 P_{ij} , 193
- Butane
 distribution of conformations, 121
 molecular mechanics calculation, 139
 radical cation, 307
- Butanoic acid acidity in gas phase and in solution, 428
- Butterfly mechanism, 606
- sec*-Butyl carbocation, 297, 298
 rearrangement, 304
- t*-Butyl alcohol gas phase acidity, 426, 428
- t*-Butyl carbocation
 ESCA, 321
 geometry, 291, 293
 reaction with nucleophile, 678
 rearrangement, 321
- t*-Butyl radical geometry, 267
- t*-Butylcyclohexane conformation, 132
- 1-Butyne gas phase acidity, 428
- c*
 conformational descriptor, 117
s-cis, 117
 stereochemical descriptor, 76
- 3c–2e bond, 290
- C₂H₅⁺, 294
- C₆₀, 209
- C₇₆, 63
- C₇₈, 63
- Cahn–Ingold–Prelog (CIP) system, 67
- Caldera, 777
- Calorimetry, 8
- Canonical MO, 225
- Carbanion
 racemization, 314
 rearrangement, 319
 stability, 317
- Carbene, 278
 cycloaddition with alkene, 284
 insertion, 285
 rearrangement, 286
- Carbenium ion, 289
- Carbenoid, 283
- Carbinolamine, 441
- Carbocation, 289
 and ion pairing, 298
 conformationally equilibrated, 594
 hydrogen-bridged, 299
 lifetime, 594
 rearrangement, 298, 302, 577, 674
 stability, 291, 302
- Carbonium ion, 289, 300
- Carbonyl hydrate dissociation
 constant, 439
- Carbonyl oxide in 1,3-dipolar
 cycloaddition, 744
- Carbyne, 255
- Carroll rearrangement, 728
- CASSCF, 225
- Catalytic antibody, 459
- Catenane, 67
- Cation radical, 305, 309. *See also* Radical cation
- CCSD(T), 225
- CD (circular dichroism), 89
- Centauric transition structure, 773
- Center of inversion (*i*), 60
- CH₂Cl₂
 and variable hybridization, 39
 geometry, 39
 isomer counting, 4

- CH₃Br geometry, 5
CH₃Cl
 and variable hybridization, 37
 and VSEPR theory, 36
 gas phase acidity, 429
 geometry, 5, 36, 38
 isomer counting, 4
CH₃F
 gas phase acidity, 429
 geometry, 5
CH₃I geometry, 5
Chain reaction, 542, 543, 592
Chair conformation, 80, 124, 128, 148, 383
Chair transition structure
 for Claisen rearrangement, 724
 for Cope rearrangement, 721
Chair-like transition structure, 782
Chameleonic transition structure, 773
Charge density (q_i), 192
Charge-transfer complex, 66, 229, 560. *See also* CT complex; CTC
 in electrophilic addition, 557
 in S_NAr reaction, 528
 spectroscopic detection, 520
CHARMM force field, 136
Cheletropic, 747
Cheletropic reaction, 747
 selection rules, 748
Chemical potential (μ), 23
Chemiluminescence, 859
Chemoselectivity, 567
 χ in Taft–Topsom equation, 400
 χ_s (Nagle electronegativity), 23
 χ_M (Mulliken electronegativity), 22
 χ_P (Pauling electronegativity), 21
 χ_{spec} (Allen electronegativity), 23
Chiral center, 68
Chiral plane, 72
Chirality, 58
 molecular designation, 86
Chirality about a plane, 66
Chirality about an axis, 64
Chirality center, 68
Chirotopic atoms and spaces, 98
Chirotopicity, 98
Chlorine substituent and acidity, 429
2-Chlorobutane representations, 55, 56
Chlorocarbene, 280
1-Chloroethyl carbocation, 580
Chlorohydrin, 578
Chloronium ion, 488, 556, 575, 577, 578, 580, 598
m-Chloroperbenzoic acid, 605
Chlorophenylcarbene, 287
Cholesterol, 54
 ent-cholesterol, 81
 specific rotation, 87
Chromophore, 87, 818, 843, 853
Chugaev reaction, 681, 683
CI (configuration interaction), 225
Cine substitution, 530
CIP (Cahn–Ingold–Prelog), 67
CIP system priority rules, 68
 in conformational designation, 116
 in *E* or *Z* designation, 76
Circle in Clar notation, 210
Circle mnemonic
 and Möbius molecular orbitals, 766
 in HMO theory, 198
Circle representation of aromaticity, 210
Circular birefringence, 88
Circular dichroism (CD), 89
Circular polarization of light, 88
Circumanthracene, 208
Cis addition, 552. *See also* Syn addition
Cis elimination, 663. *See also* Syn elimination
Cis,trans isomers, 58, 116
Claisen rearrangement, 333, 335, 715, 772
 kinetic isotope effect, 772
 Lewis acid catalysis, 728
Clar notation of aromaticity, 210
Classical carbocation, 290
Click chemistry, 746
Clinal conformation, 115
Closed shell configuration, 201
C_n
 chirality and point group, 62, 63
 proper rotation axis, 60
 symmetry operation, 59
Collisional energy transfer, 802
Combination of radicals, 276
Common ion effect, 338, 474
Competent intermediate, 332
Complex reaction, 342
Concerted process, 329
Concerted reaction, 700
 ab initio calculation, 771
 alternative models, 756
 orbital topology, 769
 synchronous and nonsynchronous pathways, 770, 773
Configuration, 67
 designation as *R* or *S*, 68
Configuration interaction (CI), 26, 225, 713
Conformation, 55, 113
 origin of the term, 113
Conformational analysis, 119
Conformationally equilibrated carbocation, 594
Conformer, 113
Conia-ene reaction, 753
Conical intersection, 821, 849
Conjugate addition, 620, 621
Connected atoms list, 139
Conrotatory pathway, 702, 703, 705, 708, 711–714, 754, 755, 767
Conservation of orbital symmetry, 707, 753
Constitution, 53
Constitutional isomers, 57
Constitutionally heterotopic substituents, 94
Contact ion pair, 313, 421, 485, 803
Conventional flash spectroscopy, 331, 807
Cope elimination, 685
Cope rearrangement, 353, 701, 715, 721, 726, 755, 772
 ab initio calculation, 772
 boat transition structure, 722
 chair transition structure, 721
Coplanar conformation, 647
Corannulene, 209
Cornforth model, 624
Coronene, 208
Correlation diagram
 MO, 707
 state, 712
Correlation line, 710
COT (cyclooctatetraene), 215
Cotton effect, 88
Coulomb integral, 177
Coulombic interaction, 120, 231
Covalent bond with ionic character, 21
Covalent radius, 5
Covalent radius (r_c), 6
*m*CPBA, 605
Cracking of dicyclopentadiene, 736
Cram's rule, 623
Criegee mechanism, 404, 745, 746
Crossover experiment, 333
12-Crown-4, 499
18-Crown-6, 499
Crown ether, 499
CS in molecular mechanics, 137
CT complex, 557, 560, 574
CTC, 560
Cubane, 108, 162, 170, 387, 853
Cubene, 166
Cubic stretching constant, 137
Cumulene
 addition of Br₂, 618
 chirality, 65
 electrophilic addition, 609, 617
 oxymercuration, 618
Cuneane, 163
Curtin–Hammett principle, 358, 360, 624, 651, 680
Curved bond, 128, 266
Cyanohydrin formation, 439
Cyclacene, 166
Cyclizable radical probe, 515
Cycloaddition, 731
 dimerization of ethene, 731, 755
 examples, 741
 FMO theory, 757
 higher order, 739
 participation of a σ bond, 753
 photochemical, 828, 831, 839, 841, 843, 853, 854
 selection rules, 739
 terminology, 731
 with singlet oxygen, 851
1,2-Cycloalkadiene, 164
Cycloalkyne, 164
Cyclobutadiene
 and resonance theory, 240
 DE π , 201
 DRE, 219

- Cyclobutadiene (*Continued*)
 geometry, 213, 214
 HMO energy levels, 198, 212
 matrix isolation study, 213
 Möbius molecular orbitals, 765
 tunneling, 214
- Cyclobutane
 conformation, 126
 electron density, 127
 strain energy, 158
 X-ray crystal structure, 127
- Cyclobutanol formation, 836
- Cyclobutene electrocyclic reaction, 702
- Cyclocumulene, 164
- Cyclodecapentaene, 216
 DRE, 219
- Cyclo- $D_E D_N A_n$ mechanism, 681
- Cycloheptatrienyl anion HMO calculation, 214
- Cycloheptatrienyl cation HMO calculation, 214
- trans*-Cycloheptene, 163
- Cycloheptyne, 164
- 1,3-Cyclohexadiene heat of hydrogenation, 203
- Cyclohexane
 conformation, 128
 steric isotope effect, 383
- Cyclohexene
 conformation, 134
 heat of hydrogenation, 203
- trans*-Cyclohexene, 163
- Cyclohexyne, 164
- Cyclooctatetraene (COT)
 DRE, 219
 HMO calculation, 215
- trans*-Cyclooctene, 163
 chirality, 66, 71
 configuration of (–) enantiomer, 66
 geometry, 66
- Cyclooctyne, 164
- Cyclopentadiene dimerization, 353
- Cyclopentadienyl anion
 acidity of cyclopentadiene, 214
 HMO calculation, 214
- Cyclopentadienyl cation, 214
- Cyclopentane conformation, 128
- Cyclopentyl carbocation, 297
 rearrangement, 302
- Cyclophane, 72, 168
- Cyclopropane
 angle strain, 123
 geometry, 40
- Cyclopropanone hydrate, 440, 464
- Cyclopropene dimerization, 752
- Cyclopropenyl anion, 212
- Cyclopropenyl cation
 HMO calculation, 211
 synthesis, 211
- Cyclopropenyl HMO energy levels, 198
- Cyclopropenyl radical, 211
- Cyclopropenyliene, 280
- Cyclopropyl carbanion and retention of configuration, 314
- Cyclopropyl radical and racemization, 314
- Cyclopropylmethyl cation, 299
- Cycloreversion, 733
- D mechanism label, 472
- ν stereochemical descriptor, 78
- Deamination of amines, 677
- cis*-Decalin, 171
- trans*-Decalin, 171
- Deconvolution, 808
- Degenerate energy levels, 200
- Degenerate molecular orbitals, 186
- Degenerate rearrangement, 715, 726
- Dehalogenation of vicinal dihalide, 665
 kinetics, 666
- Dehydration
 in gas phase, 676
 kinetic isotope effect, 380
 mechanism, 670
 of alcohols, 669
- 1,2-Dehydrocubane, 166
- Dehydronation, 414
- Delocalization energy (DE_π), 188
 and molecular orbital theory, 189
 and radical combination, 268
- Delocalized molecular orbital, 33
- $\delta\Delta G^\ddagger$, 354
- $\Delta\Delta G^\ddagger$, 354
- $\delta\Delta H^\ddagger$, 402
- $\Delta\Delta H^\ddagger$, 402
- $\delta\Delta S^\ddagger$, 402
- $\Delta\Delta S^\ddagger$, 402
- δ -elimination, 635
- ΔG_{acid} , 424
- ΔG^\ddagger (activation free energy), 350
- ΔG_{int}^\ddagger in Marcus theory, 364
- $^1\Delta_g O_2$, singlet oxygen, 851
- ΔH^\ddagger
 activation enthalpy, 350
 role of solvent, 354
- ΔH_{acid} , 424
- ΔH_{acid}° in gas phase, 423
- ΔS^\ddagger
 activation entropy, 350
 and reaction mechanism, 353, 448, 646
 and transition state, 488
 for pericyclic reaction, 720
 relationship to Arrhenius A , 353
 role of solvent, 354
- ΔS_{acid} , 424
- ΔV^\ddagger , 448
- Demercuration, 595
 stereochemistry, 599
- Density functional theory (DFT), 236
- DE_π , 188
- Deprotection, 856
- Deprotonation, 414
- Detachment step, 533
- Determination of product
 in mechanism study, 327
- Deuteron ($^2H^+$), 414
- Dewar benzene, 167, 705, 843, 854
- Dewar resonance energy (DRE), 219
- Dextrorotatory, 86
- DFT (density functional theory), 236
- DFT calculation
 acidity, 419
 Cope rearrangement, 773
 electrophilic addition, 557
 epoxidation, 608
 Markovnikov's rule, 585
 transfer hydrogenation, 341
- DH° , 16
- Diadamantylcarbene, 288
- Diamagnetic anisotropy, 217
- Diastereomers, 58
- Diastereotopic substituents, 94, 96
- 1,3-Diaxial interaction, 130, 665
- Diazoalkane and carbene generation, 282
- Diazonium ion, 527, 678
- Diborane, 600
- Dichlorocarbene, 280, 283, 285, 634
- Dicyclohexano-18-crown-6, 499
- Dicyclopentadiene cracking, 736
- Dielectric constant (ϵ), 20, 415, 477
 as measure of solvent polarity, 338
- Diels–Alder reaction, 701, 731, 734, 736, 755, 853, 855, 856
 aromaticity of transition state, 765
 endo product, 759
 exo product, 759
 FMO theory, 758, 761
 inverse electron demand, 762
 kinetic control of product
 distribution, 759
 Lewis acid catalysis, 762
 normal electron demand, 762
 regiochemistry, 760
 secondary orbital interactions, 759
 stereochemistry, 759
 thermodynamic control of product
 distribution, 759
 with benzyne, 741
- Dienophile, 734
- Differential rate equation, 343
- Diffusion-controlled reaction, 337
- Diffusion-limited process, 565, 800, 801
- 1,2-Difluoroethane conformation, 150
- Dig (in Baldwin's rules), 274
- Dihedral angle, 113
- 1,4-Dioxane radical cation, 308
- 1,2-Dioxetane chemiluminescence, 860
- Diphenylcarbene, 281, 287
- 1,3-Dipolar cycloaddition, 743
- Dipolarophile, 743
- Dipole moment (μ), 20, 477
- Disproportionation
 of biradical, 834
 of radicals, 276
- Disrotatory pathway, 702–704, 711
- Dissociation constant (K_d)
 of carbonyl hydrate, 439
 of hemiketals, 441

- Dissociation process, 450
 Dissociative state, 848
 Dissymmetric structure and point group, 63
 Dissymmetry, 63
 Distonic radical ion, 308
 Di-*t*-butylcarbene, 280, 288
 Di- π -methane rearrangement, 828, 855
 dm, 87
 1/D_N mechanism label, 471
 1/D_N + 3/A_N mechanism, 471
 D_N + A_N + A_{xh}D_H mechanism, 453
 D_N + A_N mechanism, 471
 D_N⁺A_N mechanism, 471
 D_N + A_{xh}D_H mechanism, 639
 D_N + D + A_N mechanism, 472
 D_N + D_E mechanism, 639
 D_N mechanism label, 471
 DNA, 4
 Dodecahedrane, 162
 Doering-Zeiss intermediate, 482
 Doering-Zeiss mechanism, 482
 Dot stereochemical descriptor, 58
 Dotted line in Maehr convention, 75
 Doublet state, 792
 DPPH, 258
 DRE, 219
 Dual attraction, 503
 Dynamic effects, 776
 Dyotropic reaction, 749

E, 77
 identity symmetry operator, 61
 in Mayr equation, 509
 solute excess molar refraction, 339
E_{av}, 348
E_{act}, 348
E(d) in molecular mechanics, 137, 139
 E1_(anion) mechanism, 642
 Early transition state, 362, 375, 457, 590, 595, 602, 605, 624, 625, 651, 662, 680
 and kinetic isotope effect, 375
 in diazonium ion decomposition, 680
 E2C mechanism, 639
 E1cb mechanism, 639, 650
 E1cb_(anion) mechanism, 642
 E1cb_I mechanism, 644
 E1cb_{IP} mechanism, 643
 E1cb_R mechanism, 643
 Eclipsed conformation, 114, 115
 E2 competition with S_N2, 646
 Edwards equation, 507
E_f in Mayr equation, 513
 E2H mechanism, 639
 EHT (extended Hückel theory), 221, 223
 EHT calculation
 electrocyclic reaction, 707
 ethene, 221
 ethyl anion, 317
 ethyl cation, 293
 ethyl radical, 263
 formaldehyde, 832

E_{HOMO}, 220
 E2_{IP} mechanism, 643
 E_i mechanism, 683
 E1 mechanism, 633, 639, 670
 E mechanism label, 471
 E2 mechanism, 633, 639
 and dehydration of 1° alcohol, 673
 Einstein, 789
 Electrocyclic reaction, 702
 and FMO theory, 757
 as cycloaddition reaction, 754
 cyclobutene-butadiene
 interconversion, 697, 702, 708, 710, 713, 714, 755, 757, 767, 768, 770
 cyclohexadiene-hexatriene
 interconversion, 699
 cyclopropyl-allyl interconversion, 743
 Möbius aromaticity, 767
 photochemical, 826, 829
 selection rules, 705
 Electrofuge, 450, 469, 513, 543
 Electron affinity, 18
 and absolute hardness, 506
 and charge transfer complex, 229
 and Mulliken electronegativity, 22
 in gas phase acidity determination, 424
 relationship to *E_{LUMO}*, 220
 Electron configuration, 26, 225, 711, 713, 733
 of formaldehyde electronic states, 791
 Electron correlation, 223
 Electron density
 and basis sets, 224
 and QTAIM, 233
 in DFT, 236
 in HMO theory, 191
 Kohn-Sham theory, 236
 Electron density contour, 127
 Electron donor-acceptor complex, 229
 Electron paramagnetic resonance (EPR), 259
 Electron pushing and MO following, 768
 Electron spin resonance (ESR), 259
 Electron transfer, photoinduced, 803
 Electronegativity, 21, 626
 absolute, 23
 Allen, 23
 and acidity, 386, 429
 and benzyne formation, 538
 and benzyne reaction, 541
 and bond curvature, 150
 and substituent effect, 400
 and variable hybridization, 37
 and VSEPR, 36
 Benson, 23
 comparison, 23
 group, 23
 Mulliken, 22
 Nagle, 23
 Pauling, 21
 Electronic chemical potential (μ), 23

 Electronic energy transfer, 802
 collisional, 802
 Förster, 802
 radiative, 802
 trivial, 802
 Electron-rich alkene, 555
 Electrophile, 469
 Electrophilic addition, 206, 575
 chemoselectivity, 567
 epoxidation, 605
 hydroboration, 600
 Markovnikov's rule, 585
 oxymercuration, 596
 regiochemistry, 568
 reversibility, 563
 solvent effects, 561
 solvent participation, 561
 solvomercuration, 596
 surface-mediated, 587
 Electrophilicity parameter, 509
 Electrostatic effect, 386
 Element effect, 529, 533, 642
 Elementary reaction, 328, 350, 363
 molecularity, 342
 Elimination, 633
 heterogeneous, 652
 1,1-Elimination, 634, 653
 1,2-Elimination, 633, 638
 1/2/Elimination, 633
 1,3-Elimination, 635
 1,4-Elimination, 635
 stereochemistry, 654
 1,6-Elimination, 636
 1,8-Elimination, 636
 1,10-Elimination, 636
E_{LUMO}, 220
E_n
 electronic energy level, 787
 in Edwards equation, 507
 Enantiomer, 57
 and optical activity, 86
 physical properties, 92
 Enantiomeric excess, 88
 Enantiomerically enriched, 85
 Enantiomerically pure, 85
 Enantiopure, 85
 Enantiotopic substituents, 94
 magnetic equivalence, 95
 Encounter complex, 520
 Encounter-controlled reaction, 337
 End absorption, 818
 Endo, 78
 Endo closure in Baldwin's rules, 274
 Endocyclic restriction test, 337, 607
 Endoscopic irradiation, 852
 Endothermic step and Hammond postulate, 362
 Ene reaction, 750
 FMO theory, 758
 Energy minimization, 141
 Energy of UV-vis radiation, 789
 Energy surface, 820

- Enol, 443
 in Conia-ene reaction, 753
 in oxy-Cope reaction, 727
 intermediate in Norrish type II reaction, 836
 photochemical generation, 446
 regiochemistry, 444
- Enolate, 443
 as model for dienophile, 763
 conjugate addition, 621
 in α -halogenation, 443
 nucleophilic addition, 318
 oxidative coupling, 320
 regiochemistry, 444
- Enolization, 442
- Ent*- (stereochemical descriptor), 81
- Entgegen*, 77
- Enthalpy-controlled reaction, 570
- Enthalpy-entropy compensation, 402
- Entropy units, 351
- Entropy-controlled reaction, 570
- Envelope conformation, 128
- EPA glass, 800
- $E(\Phi)$ in molecular mechanics, 137, 139
- Epi*-, 82
- E_π
 allyl anion, 188
 allyl cation, 188
 allyl radical, 188
 energy of the π system, 188
 in HMO theory, 188
- Epimer, 81
- Epimeric center, 81
- Epoxidation of alkenes, 605
- EPR, 259
- ϵ
 dielectric constant, 20, 338
 extinction coefficient, 466
- ϵ_{\max} , 797
- Equatorial preference (*A* value), 130
- Equatorial substituent, 128
- Equilibrium control of product distribution, 357, 759
- Equilibrium isotope effect, 382
 and acidity, 382
 and conformation, 383
- Equilibrium substituent effect, 390
- E2 reaction and Curtin-Hammett principle, 358
- $E(r)$ in molecular mechanics, 137
- Erythro, 83, 571
- Erythrose, 83
- E_s in Taft equation, 401
- E_{SB} in molecular mechanics, 138
- ESCA, 32
 2-norbornyl carbocation, 300
 cyclopentyl cation, 303
- Eschenmoser rearrangement, 729
- ESR (electron spin resonance), 259
- Ester
 acid-catalyzed hydrolysis, 449
 alkaline hydrolysis, 452
 aminolysis, 459
- $E_T(30)$ scale of solvent polarity, 339
- η (absolute hardness), 506
- Ethane
 acidity, 44
 conformational energy, 119
 gas phase acidity, 317
 gas phase basicity, 427
 origin of rotational barrier, 120, 231
 VSEPR description, 36
- Ethanol
 acidity, 386, 419
 gas phase acidity, 426, 428
 80% Ethanol, 646
- Ethanolysis, 476
- Ethene
 acidity, 44
 bent-bond description, 42
 dimerization, 731, 755, 757
 EHT calculation, 221
 electron density, 233
 gas phase acidity, 425
 gas phase basicity, 427
 geometry, 42
 HMO calculation, 176
 LMOs, 225
 natural bond orbitals, 226
 photochemical reaction with benzene, 843
 radical cation, 307
 π, π^* state, 819, 820
 σ, π description, 42
- $E(\theta)$ in molecular mechanics, 137
- Ethyl anion
 EHT calculation, 317
 HOMO, 317
 inversion barrier, 315
- Ethyl cation
 ab initio calculation, 294
 bridged structure, 294
 EHT calculation, 293
 formation in gas phase, 678
 geometry, 294
 hyperconjugation, 292
 LUMO, 293
 PMO analysis, 292
 rearrangement, 298
- Ethyl radical
 dimerization, 268
 EHT calculation, 263
 EPR spectrum, 261
 hyperconjugation, 262, 268
 PMO description, 264
 pyramidalization, 266
 SOMO, 263
- Ethyne
 acidity, 44
 bent-bond description, 44
 gas phase acidity, 425, 428
 gas phase basicity, 427
 σ, π description, 44
- eu, 351
- Even alternant structure, 195
- Excess acidity, 433
- Exchange-correlation functional, 237
- Excimer, 803
- Exciplex, 803
- Excitation spectrum, 801
- Excited state kinetics, 805
- Exciton migration, 802
- Exo, 78
- Exo closure in Baldwin's rules, 274
- Exothermic reaction
 and kinetic isotope effect, 376
 and Marcus theory, 365
- Exothermic step and Hammond postulate, 362
- Extended Hückel theory (EHT), 221
- Extent of reaction, 254
- Extrusion reaction, 747
- Eyring plot, 351
- F*
 in Swain-Lupton equation, 399
 in Taft-Topsom equation, 400
- f* in Swain-Lupton equation, 399
- f^Z , 522
- F1 fragmentation, 637
- F1cb fragmentation, 637
- F2 addition to alkene, 580
- F2 fragmentation, 637
- FA (flowing afterglow), 317, 423
- FA-SIFT, 423
- Fast reaction techniques, 331
- Favorskii rearrangement, 692, 853
- Felkin model, 624
- Femtosecond, 331
- Fenestrane, 161, 170
 [4.4.4]Fenestrane, 161
- \mathcal{F}_i (free valence index), 193
- Field effect, 386
 and substituent effect, 400
- Field effect constant, 399
- First-order decay process, 805
- Fischer projection, 72
 allowed operations, 73
 forbidden operations, 73
- Fischer-Tollens projection, 72
- Flagpole hydrogen, 124
- Flash photolysis, 807
- Flash spectroscopy, 807
 conventional, 807
 laser, 807
 pump-probe technique, 807
- Flowing afterglow (FA or FA-SIFT), 317, 423
- Fluorescence, 795, 798
 and excited state geometry, 799
- Fluorescence lifetime, 806
- Fluorescent chemosensor, 859
- Fluorine substituent
 and acidity, 386, 429
 as a bridging atom, 580
 as a leaving group, 663
 effect on radical geometry, 265, 311
- 2-Fluoroethanol acidity, 386
- Fluorohydrin, 578

- Fluoronium ion, 556
 Fluxional structure, 726
 FMO (frontier molecular orbital), 229
 FMO theory, 229
 and pericyclic reactions, 756
 and torquoselectivity, 757
 charge-transfer complex formation, 229
 Diels–Alder reaction, 758, 760, 761
 dimerization of ethene, 757
 electrocyclic reaction, 757
 ene reaction, 759
 stereochemistry of addition reactions, 553
 Forbidden pericyclic reaction, 705
 Forbidden process, 274, 796
 Forbidden transition, 796
 Force field, 135
 Force field method, 135
 Formaldehyde
 molecular orbitals, 790
 physical properties of excited states, 815
 Formic acid
 acidity, 419
 acidity and thermodynamic values, 429
 Formolysis, 480
 Förster cycle, 813
 Förster energy transfer, 802
 Fractional ionic character, 312
 Fragmentation reaction, 636
 Franck–Condon overlap, 820
 Franck–Condon state, 819
 Franck–Condon term, 796
 Free radical, 256
 Free rotation, 120
 Free valence index (\mathcal{F}_i), 193
 Frontier molecular orbital, 229
 fs (femtosecond), 331
 Fullerene, 209
 Fulvene, 167, 843
 Function, 236
 Functional, 236
 Functional group isomers, 57
 Furan resonance energy, 206
 Furanose, 80

 G (Gauss), 261
 g (spectroscopic splitting factor), 259
 g^+ conformational descriptor, 116
 g^- conformational descriptor, 116
 γ (activity coefficient), 415
 Γ_1 in structure-resonance theory, 243
 Γ_2 in structure-resonance theory, 243
 γ -elimination, 635
 γ -hydrogen abstraction
 photochemical, 835, 855
 Gas constant (R), 349
 Gas phase basicity (GB), 426
 Gauche conformation, 114, 115
 Gauche effect, 581
 and curved bonds, 150
 Gauche interaction, 12
 as 1,3-diaxial interaction, 130
 Gaussian type orbital (GTO), 224

 GB (gas phase basicity), 426
 General acid catalysis, 435, 437, 439, 447, 593
 Brønsted catalysis law, 437
 General base catalysis, 435, 437, 439, 447, 462
 Brønsted catalysis law, 437
 in ester hydrolysis, 456
 Geometric isomers, 58
 Gibbs diagram, 255
 Glass, 800
 Global minimum, 147, 294, 580
 Glucopyranose, 80
 Graph theory, 242
 Graphene, 207
 Graphene nanoribbon, 207
 Grob fragmentation, 636
 Group electronegativity, 23
 Group increment calculation, 10, 12
 Grunwald–Winstein equation, 477
 G^θ and Gibbs diagram, 255
 GTO (Gaussian type orbital), 224
 GVB calculation, 46, 240

 h (Planck's constant), 351
 H (nucleophile basicity), 507
 $^2\text{H}^+$ (deuteron), 414
 $^3\text{H}^+$ (triton), 414
 H_- basicity function, 433
 H' acidity function, 431
 H''' acidity function, 431
 H_0
 acidity function, 430, 431
 external magnetic field, 259
 H_0' acidity function, 431
 H_A acidity function, 431
 Half-life and first-order decay, 805
 Haloform reaction, 444
 Halohydrin
 dehydrohalogenation, 605
 synthesis and reaction, 578
 Hammett correlation, 392, 448, 529, 572, 594, 603, 605, 609, 650, 659, 672
 and ΔS^\ddagger , 402
 bent downward, 395
 bent upward, 395
 curved, 573
 nonlinear, 395, 399
 pK_a values, 415
 with maximum, 395
 Hammett equation, 390, 477
 Hammett ρ interpretation, 448
 Hammond postulate, 362, 524, 655
 and kinetic isotope effect, 375
 and S_N1 reaction, 474
 anti-Hammond effect, 365
 Hammond–Leffler postulate, 363
 Hard base, 505
 Hard-soft acid-base theory, 505
 Hartree–Fock limit, 225
 Hartree–Fock theory, 223, 226
 Hashed line stereochemical descriptor, 55

 Hashed wedge stereochemical descriptor, 55
 Haworth representation, 80
 H_{Az} acidity function, 432
 H_B acidity function, 432
 H_C acidity function, 432
 Head-to-head dimer, 841
 Head-to-tail dimer, 841
 Heat of combustion, 8, 148
 Heat of formation, 8
 Heat of fusion, 9
 Heat of hydrogenation, 190
 Heat of sublimation, 9
 Heat of vaporization, 9
 Heavy atom effect, 796, 801
 Helical chirality, 66
 Hemiacetal, 441
 carbohydrate anomers, 79
 formation, 439
 hydrolysis, 448
 Hemiketal, 439, 441
 Heptacene, 207
 Hermitian, 177
 Hess' law, 18
 Heterogeneous catalysis
 alcohol dehydration, 677
 electrophilic addition, 614
 Heterogeneous reaction, 687
 syn elimination, 652
 Heterotopic substituents, 94
 Hexaasterane, 163
 Hexacene, 207
 Hexahelicene, 66
 chirality, 71
 Hexaphenylethane, 257
 Hexaplane, 161
 1,3,5-Hexatriene
 DE_π , 201
 Hückel MOs, 185
 HF (Hartree-Fock), 223
 H_I acidity function, 432
 $\text{HIA}(\text{R}^+)$, 291
 High pressure mass spectrometry (HPMS), 317, 423
 Higher order cycloaddition, 739
 Highest occupied molecular orbital, 229
 H_m acidity function, 432
 HMO theory, 175
 Hofmann elimination, 656, 662
 Hofmann product, 657
 Hofmann rule, 656
 HOMO, 220, 229
 and Diels–Alder regiochemistry, 761
 1,3-butadiene, 702
 in electrocyclic reaction, 702
 in FMO theory, 756
 in hydroboration, 604
 of alkene, 818
 of ethene, 222
 of formaldehyde, 790
 of 1,3,5-hexatriene, 705
 of methanol, 306
 of nitrobenzene, 845

- Homoallylic structure, 494
Homoaromaticity, 493
Homochiral, 84
Homoconjugation, 493
Homodesmotic reaction, 12
HOMO-LUMO crossing, 769
HOMO-LUMO gap, 220, 506, 762
and excitation wavelength, 829
HOMOMERS, 769
Homo-[1,5] sigmatropic rearrangement, 752
Homotopic substituents, 94, 96
Homotropolidene, 726
Horizontal plane of symmetry (σ_h), 60
HPMS, 317, 423
 H_R , 96
 H_R acidity function, 432
 H_S , 97
Hückel $4n + 2$ rule, 201
Hückel cyclobutadiene, 765
Hückel molecular orbital theory, 175, 702
Hund's rule, 278
Hybrid orbitals
energies, 29
shapes, 30
Hybridization, 3, 29, 31
and electronegativity, 37
and geometry, 38
Hybridization index, 37
Hybridization parameter, 37
Hydration
of alkene, 592
of alkyne, 614
of carbonyl compound, 439
Hydride ion affinity, 291
Hydride shift, 301
1,2-Hydride shift, 303, 304
1,3-Hydride shift, 304
1,4-Hydride shift, 304
Hydroboration, 600
regioselectivity, 600
stereochemistry, 601
Hydrogen abstraction, 834
Hydrogen shift, 719, 720
[1,3], 717, 718, 754, 764, 767
[1,5], 715, 719, 763, 767
[1,7], 719, 720
[1,9], 719
Hydrolysis
nucleophilic catalysis, 457
of acetals, 447, 448
of amides, 460
of esters, 449, 452
of hemiacetals, 448
of mesitoate esters, 451
Hydron, 414
Hydronation, 414
Hydroperoxide (HOO^-)
nucleophilicity, 511
Hydroxymethyl radical, 264
Hyperchromic effect, 817
Hyperconjugation, 151, 230
and EPR spectra, 262
and ethane torsional barrier, 231
and kinetic isotope effect, 383
ethyl radical, 264
in carbene, 280, 282
in carbocation, 292
in radical cation, 307
Hypercoordinate structure, 290, 320
Hyperfine coupling
anisotropic, 261
in EPR, 260
isotropic, 261
Hyperfine coupling constant (a), 260
in methyl radical, 265
Hypersurface, 253
Hypochromic effect, 817
Hypsochromic shift, 817
- i*
center of inversion, 60
symmetry operation, 59
+I inductive effect, 385
-I inductive effect, 385
Ibuprofen, 689
Iceane, 159
ICR (ion cyclotron resonance), 423
Identity reaction, 366
Identity symmetry operator (E), 61
 I_f (fluorescence intensity), 805
IIP (intimate ion pair), 560
Improper rotation axis (S_n), 60, 99
InChI, 54
Induction, 280
and acidity, 419
and Hofmann orientation, 659
structural representation, 386
substituent effect, 385
Inert radical, 258
Inherent fluorescence lifetime, 806
Inherent singlet lifetime, 806
Inherent strain, 156
Initial ozonide, 745
Initiation step in chain reaction, 270, 271, 589
In silico experiment, 339
Integrated rate equation, 343
1,3-Interaction, 269
Internal conversion, 794
Internal return, 482
Internally compensated structure, 82
International Chemical Identifier (InChI), 54
Internuclear bond angle, 39
Interorbital angle and hybridization, 38, 39
Intersystem crossing, 794
and heavy atom effect, 796
of carbonyl n, π^* singlets, 841
Intimate ion pair (IIP), 482, 483, 560, 804
Intramolecular charge transfer in
electronic excitation, 799, 814, 817, 845
- Intrinsic barrier ($\Delta G_{\text{int}}^\ddagger$) in Marcus theory, 364
Inverse electron-demand in Diels-Alder reaction, 762
Inverse secondary kinetic isotope effect, 381
Inversion of configuration, 92
in hydrolysis of β -butyrolactone, 453
in pericyclic reaction, 773
in S_N2 reaction, 337
Inverted region in Marcus theory, 364
Iodine addition to alkene, 583
Iodinium ion, 556
Iodoform reaction, 444
Iodohydrin, 578
Ion pairing, 298
and acidity, 415
in solvolysis, 482
Ionic radius (r_i), 5
Ionization potential, 479
and absolute hardness, 506
and charge transfer complex formation, 229, 557
and gas phase acidity determination, 424
in EHT theory, 223
in Mulliken electronegativity, 22
in reaction of alkenes with XeF_2 , 581
of alkyl anions, 423
relationship to E_{HOMO} , 220
Ionization potential, 18
Ionizing power of a solvent, 477
Ipso substitution, 519
Ireland-Claisen rearrangement, 730
Irreversible reaction, 344, 354
Isoaromatic structure, 167
Isobenzene, 167
Isobutane gas phase acidity, 317
Isochronous groups, 96
Isodensity surface, 233
Isodesmic reaction, 12, 264
Isoequilibrium relationship, 403
Isoergonic reaction, 364
Isokinetic relationship, 403
Isokinetic temperature, 403
Isologous structures, 12
Isomers, 56
constitutional, 57
functional group, 57
positional, 57
stereoisomers, 57
Isopropyl cation, 297
rearrangement, 303
Isotactic polymer, 93
Isotopic dilution, 330
Isotopic exchange
in ester hydrolysis, 455
in ketones, 443
Isotopic fractionation factor, 384
Isotopic labeling, 304, 335, 453, 454, 495, 586, 774
in alcohol dehydration, 674
in alkaline hydrolysis of esters, 455

- in amide hydrolysis, 460
 in amine deamination, 679
 in benzyne reaction, 537
 in carbocation rearrangement, 302
 in elimination, 634
 in ester hydrolysis, 457
 in ester pyrolysis, 684
 in hydrolysis of ethyl propionate, 453
 in hydrolysis of methyl mesitoate, 451
 in pericyclic reaction, 699, 719, 749, 772, 774, 777
 in von Richter reaction, 530
 Isotopologue, 94
 Isotopomer, 94
 Isotropic hyperfine coupling, 261

 $J_{13\text{-H}}$
 and hybridization parameter, 41
 and kinetic acidity, 41
 Jablonski diagram, 792
 Jackson–Meisenheimer complex, 316, 529
 Jahn–Teller effect and geometry of methyl radical cation, 308
 J_n (rotational energy level), 789
 Johnson rearrangement, 729

 K_a , 414
 k_{app} , 344
 Karplus equation, 152
 Kasha's rule, 795
 K_a^T , 415
 K_b , 420
 K_{BH^+} , 420
 κ in transition state theory, 351
 k_d , 809
 Kekulé molecular models, 125
 Kekulé structure, 48, 53, 202, 210, 238
 counting, 241
 k_f (fluorescence rate constant), 805
 K_i , 415
 Kinetic acidity, 41, 421
 Kinetic control of product
 distribution, 356, 357, 581, 670, 759
 Kinetic isotope effect, 370, 371
 and temperature, 379
 and tunneling, 378
 in aryldiazoniium reaction, 527
 in bromine addition to alkene, 559
 in Chugaev reaction, 683
 in Claisen rearrangement, 772
 in elimination, 642–644, 673
 in Hofmann elimination, 665
 in hydroboration, 605
 in hydrolysis of formamide, 462
 in hydrolysis of methyl formate, 452, 456
 in pyrolysis, 684
 in $S_{\text{E}}\text{Ar}$ reaction, 519
 intramolecular, 378
 usual range, 377
 1° Kinetic isotope effect, 371
 2° Kinetic isotope effect, 371, 380
 Kinetically stable radical, 258

 Kinetics and mechanism
 determination, 341
 K_{ion} , 420
 Koelsch radical, 258
 Kohn–Sham theory, 236
 Koopmans' theorem, 32
 Kosower Z scale of solvent polarity, 339
 k_{Ψ} , 344
 K_{SC} , 244

 l (like), 84
 l (sensitivity to solvent nucleophilicity), 478
 L (stereochemical descriptor), 78
 Ladenburg benzene, 21, 163
 λ
 hybridization parameter, 37
 weighting parameter for ionic character, 21
 λ_{max} , 797
 Lapworth mechanisms, 443
 Laser flash spectroscopy, 331, 807
 Late transition state, 362, 376, 452, 680
 and kinetic isotope effect, 375
 Law of definite proportions, 2
 LCAO (linear combination of atomic orbitals), 175
 L-CPL, 858
 Left-handed helix, 71
 Leveling effect of solvent, 422, 430
 Levorotatory, 86
 Lewis acid, 413
 Lewis acid catalysis
 Claisen rearrangement, 728
 Diels–Alder reaction, 762
 Friedel–Crafts reaction, 330
 Lewis base, 413, 504
 Lewis cubical bonding model, 19
 Lewis structure, 226, 524, 564, 814
 representation of electronically excited state, 814, 832, 840, 841, 845
 LFER, 389
 Lifetime
 of 1,4-biradical, 837
 of bromonium ion, 564
 of carbene, 288
 of carbocation, 298, 674
 of excited state, 805, 809, 810, 862
 of intermediate, 254, 320, 533, 555, 565, 571, 594
 of singlet oxygen, 851
 relationship to half-life, 806
 Lightstruck flavor of beer, 861
 Limonene
 deprotonation, 315
 photohydration, 825
 Line formula conventions, 54
 Linear cheletropic reaction, 747
 Linear free energy relationship (LFER), 389, 477, 507
 and gas phase acidity, 423
 Hammett equation, 390
 Linear Hammett correlation, 392

 lk (like), 84
 LMO, 33, 225
 Local minimum, 147
 and reactive intermediate, 254
 Localized molecular orbital, 33, 225
 London dispersion forces, 139
 Lowest unoccupied molecular orbital, 229
 Luminol, 859
 LUMO, 220, 229
 and conjugate addition, 621
 and Diels–Alder regiochemistry, 761
 in FMO theory, 756
 of alkene, 818
 of ethyl cation, 293
 of formaldehyde, 790
 of nitrobenzene, 845
 LUMOMERS, 769
 Lyate ion, 435
 Lyonium ion, 434

 M chirality descriptor, 71, 72
 m in Grunwald–Winstein equation, 477
 $-M$ mesomeric effect, 385
 $+M$ mesomeric effect, 385
 M05-2X functional, 237
 Maehr convention for stereochemical drawings, 74
 Magic acid, 296
 Magnetic susceptibility and triphenylmethyl radical, 258
 Manifold, 793
 singlet, 793
 triplet, 793
 Marcus equation, 364
 Markovnikov orientation, 567, 592, 595, 597, 603
 Markovnikov spelling, 585
 Markovnikov's rule, 405, 585, 631
 Mass law effect, 474
 Matrix isolation study, 213, 307, 308, 320, 331, 830
 benzyne, 541
 MC (Monte Carlo statistical mechanics), 154
 MD (molecular dynamics), 153
 Mechanism of a reaction, 327
 * Mechanism descriptor, 644
 ‡ Mechanism descriptor, 644
 Menschutkin reaction, 500
 Menshutkin reaction, 500
 Mercurinium ion, 598, 614, 615, 617
 Mercuronium ion, 598
 Meso
 alternative definition, 82
 stereochemical descriptor, 82
 Meso structure, 82
 and stereogenicity, 98
 physical properties, 93
 with internal plane of symmetry, 82
 without internal plane of symmetry, 82
 Mesomeric effect, 385
 Metal ion catalysis, 458

- Methane
 gas phase acidity, 317, 429
 heterolysis in gas phase, 423
 homolytic dissociation in gas phase, 423
 PES spectrum, 32
 radical cation, 307
 VSEPR description, 36
- Methanol
 acidity, 417
 gas phase acidity, 426
 radical cation, 306
 reaction with singlet carbene, 287
- Methanolysis, 480, 481
- '657 Method' and geometry, 51
- Methonium ion (CH_5^+), 290
- Methyl anion
 ab initio calculation, 315
 from gas phase heterolysis of methane, 423
 geometry, 310
 inversion barrier, 315
- Methyl radical, 256, 260
 EPR spectrum, 261
 geometry, 264, 265
 hyperfine coupling constant, 265
- Methylcyclohexane
 conformation, 129
 Newman projection, 129
- Methylene
 electronic energy levels, 279
 electronic states, 278
 geometry, 279
- Metropolis sampling, 154
- Michael addition, 620
- Microenvironment characterization, 859
- Microwave spectroscopy, 5, 118
- Mills–Nixon effect, 206
- Minimized geometry, 141
- Mixed halogen
 addition to alkenes, 584
 addition to alkynes, 611
- MM1, 136
- MM2, 136
- MM2(77), 136
- MM3, 136
- MM4, 136
- MMX, 139
- MO correlation diagram, 709
 atom transfer reaction, 749, 750
 Diels–Alder reaction, 736
 electrocyclic reaction, 710
 ethene dimerization, 732, 733
 ozonolysis, 745
 photo-Diels–Alder reaction, 736
- MO following, 768
- Möbius antiaromaticity, 767
- Möbius aromaticity, 763, 767, 769
- Möbius cyclobutadiene, 765
- Möbius molecular orbitals, 765
- Möbius π system, 765
- Möbius strip, 765
- Molecular dimensions, 3, 5, 154, 858
- Molecular dipole moment (μ), 20
 as measure of solvent polarity, 338
- Molecular dynamics, 153
- Molecular graph in QTAIM, 235
- Molecular ladder, 857
- Molecular mechanics, 135
 computational time, 136
- Molecular orbital symmetry, 707
 and basis set symmetry, 33
- Molecular orbital theory (MO theory), 24, 25, 175
 and delocalization energy, 189
- Molecular 'ship in a bottle', 858
- Molecular simulation, 153
- Molecular surface area, 6
- Molecular tweezers, 858
- Molecular volume, 6, 233
 calculated, 7
- Molarity, 342
 and Ingold designation, 470, 471
 in IUPAC mechanism label, 552
- Molozonide, 745
- Monochiral, 85
- Monochloroborane, 605
- Monte Carlo statistical mechanics, 154
- More O'Ferrall–Jencks diagram, 367, 472, 639
- MP2, 225
- MP3, 225
- m_s (spin quantum number), 259
- mT (millitesla), 261
- μ
 chemical potential, 23
 dipole moment, 338, 477
- μ -hydridobridged cation, 299, 304
- Mulliken electronegativity, 22
- Mulliken relationship
 charge-transfer complex absorption, 229
- Multiphoton excitation, 790
- Multiplicity of electronic state, 284, 792
- Mustard gas, 488
- n
 hybridization index, 37
 in Swain–Scott equation, 507
 nonbonding MO, 790
- N (solvent nucleophilicity), 478
- $4n + 2$ rule, 201
- n, π^* state, 792
- $^1n, \pi^*$ state, 793
- $^3n, \pi^*$ state, 793
- $n \rightarrow \pi^*$ transition, 790
 in benzophenone, 816
 solvent effect, 817
- N_+ in Ritchie equation, 479
- Nagle electronegativity, 23
- Nanosecond, 331
- Naphthalene
 Clar notation, 211
 DRE, 219
 electrophilic aromatic substitution, 206
 Kekulé structures, 238
 photophysical data, 809
 resonance energy, 206, 238
 SRT resonance energy, 245
- 2-Naphthol excited state acidity, 813
- 1-Naphthylmethyl radical, 849
- Natural bond orbital, 226
- NBMO (nonbonding molecular orbital), 183, 243
- NBO (natural bond orbital), 226, 232, 302
- Neat reagent, 576
- Negative activation energy, 557
- Negative electron affinity, 310
- Negative kinetic temperature effect, 350
- Neighboring group participation, 487, 568
- Newman projection, 55
 and dihedral angle, 113
- N_f in Mayr equation, 513
- NICS, 217
- m*-Nitroanisole, solubility of T_1 state, 817
- Nitrone in 1,3-dipolar cycloaddition, 744
- No-crossing rule, 713
- Node, 182
- 'No mechanism' rearrangement, 700
- Nonadiabatic process, 812
- Nonalternant structure, 194
- Nonaromatic structure, 215
- Nonbonding molecular orbital (NBMO), 183
 designated as n , 790
 in odd alternant system, 195
- Nonclassical carbocation, 290, 294, 300, 491
- Nonconcerted pathway for electrocyclic reaction, 714
- Nondissymmetric structure
 and point group, 64
- Non-Kekulé structure, 238
- Nonlinear cheletropic reaction, 747
- Nonlinear Hammett correlation, 395, 399
- Nonobservables, 40, 48, 120, 149, 203, 236, 388, 471
- Nonradiative process, 794
- Nonstereogenic atom, 98
- Nonsynchronous reaction, 770, 771, 772
- 2-Norbornyl cation, 300, 301
- 7-Norbornyl radical, 267
- Norbornyne, 284
- Norcarane, 285
- Normal addition, 589
- Normal E2 mechanism, 639
- Normal electron demand Diels–Alder reaction, 762
- Normal salt effect, 479
- Normal secondary kinetic isotope effect, 380
- Normalization integral, 177
- Normalized wave function, 181
- Norrish type I reaction, 832, 862
- Norrish type II reaction, 447, 836
- Norrish–Yang cyclization, 836, 857
- Not acceptable representations of stereochemistry, 56, 80

- N_{OTs} , 478
n-radical cation, 306
ns (nanosecond), 331
Nucleofugality, 512
Nucleofuge, 469
Nucleofugic detachment (D_N), 471
Nucleophile, 469
 as Lewis base, 504
Nucleophilic attachment (A_N), 471
Nucleophilic catalysis
 in ester hydrolysis, 457
 intermolecular, 457
 intramolecular, 457
Nucleophilic susceptibility, 567, 615
Nucleophilic vinylic substitution, 532
Nucleophilicity
 kinetic concept, 504
 of halide ions, 504
 trends, 504
Nucleus-independent chemical shift (NICS), 217
- Observables, 1, 19, 40, 48, 120, 236, 471
Octacyclopropylcubane, 853
Octahedrane, 162
Octant rule, 90
Odd alternant structure, 195, 243
Off-diagonal overlap integral, 221
Oligomeric species, 312
 ω
 component in pericyclic reaction, 743
 interaction energy in Mulliken relationship, 230
'onium compound, 657
Onset of UV-vis absorption and photochemistry, 797
 Cl₂, 846
Open shell configuration, 201
Optical activity, 86
 (*d*) Optical activity descriptor, 86
 (*l*) Optical activity descriptor, 86
 (–) Optical activity descriptor, 86
 (+) Optical activity descriptor, 86
Optical purity, 87
Optical rotary dispersion (ORD), 88
ORD, 88
Order of a reaction, 342
'Organic thinking', 48
ORTEP plot, 56
Orthogonal orbitals, 120, 189, 231, 541, 711, 816, 820
Orthogonene, 165
Ovalene, 208
 SRT resonance energy, 245
Overall order of a reaction, 342
Overlap integral, 177, 179
Oxetane formation, 839
Oxibase scale, 507
Oxirene, 617
Oxonium ion, 434
Oxy-Cope reaction, 727
Oxygen perturbation of singlet-triplet transitions, 801
- Oxymercuration, 595
 stereochemistry, 599
Ozone pericyclic reaction, 744
Ozonolysis, 404
 Criegee mechanism, 745
- P*
 chirality descriptor, 71, 72
 polarizability in Edwards equation, 507
PA (proton affinity), 426
Paclitaxel, 55
Pagodane, 163
 dication, 305
[2.2]Paracyclophane, 168
[6]Paracyclophane, 66, 168
Paradigm, xv, 212, 251, 279
Parallel orbitals, 42, 175, 215, 297, 648, 705, 711
Parameterization
 in semiempirical molecular MO calculations, 223
 of a force field, 135
Parentheses in 1,3-dipolar cycloaddition designation, 744
Parf, 84
Partial charge, 20
Partial rate factor, 522
Partially bridged intermediate, 565
Paterno-Büchi reaction, 839
 regiochemistry, 840
 stereochemistry, 840
Pauli exchange principle, 260
Pauli exclusion principle, 120, 231
PCMODEL, 139
Pentacene, 207
Pentadienyl MOs, 185
Pentaprismane, 163
1-Pentene radical cation, 307
2-Pentene radical cation, 307
Peracid, 605
Percent ionic character, 312
Percutaneous irradiation, 852
Pericyclic reaction, 701, 754
 aromaticity of transition structure, 763
 atom transfer, 749
 cheletropic, 747
 classification as cycloaddition, 753
 cycloaddition, 731
 electrocyclic, 702
 ene reaction, 750
 FMO theory, 756
 general selection rule, 755
 hydrogen shift, 715
 nonsynchronous, 772
 ozonolysis, 745
 participation of *p* orbital, 743
 photochemical, 703, 705, 719, 724, 733, 739, 750, 755
 semiempirical MO calculation, 771
 sigmatropic rearrangement, 715
 terminology, 731
Periplanar conformation, 115
Peristylane, 163
- Peroxidation reaction, 616
Peroxide effect, 589
Peroxy acid, 605
Perpendicular excited state, 820
Perpendicular orbitals, 189
Persistent radical, 258
Perturbational molecular orbital (PMO) theory, 226
PES of methane, 32
PET (photoinduced electron transfer), 306
Phenanthrene
 Clar notation, 211
 DRE, 219
 electrophilic addition, 206
 Kekulé structures, 238
 resonance energy, 206, 238, 239
 SRT resonance energy, 245
 VB calculation, 239
Phenonium ion, 490, 674
Phenyl radical, 256
1-Phenylethyl carbocation, 571
 Φ (quantum yield), 804
Phlogiston, xvi
Phosphorescence, 795, 800
Photochemical hydrogen abstraction, 834, 855
Photochemical oxetane formation, 839
Photochemical pericyclic reaction, 703, 705, 719, 724, 755
Photochemical pH change, 834
Photochemistry, 787
Photochromism, 858
Photo-Claisen reaction, 335, 847
Photoconductive materials, 859
Photocycloaddition, 828, 831, 839, 841, 843, 853, 854
Photodeconjugation, 842
Photodeprotection, 856
Photodimerization, 844
Photodissociation, 833, 847–850
Photodynamic therapy, 852
Photoelectron spectroscopy (PES), 32
Photo-Fries reaction, 847
Photography, 858
Photohydration, 447, 825
Photoinduced electron transfer (PET), 306, 543, 803, 804
Photoisomerization, 820, 821, 824, 830, 842, 844, 855, 862, 863
Photolysis, 807
Photophysical process, 793, 805, 837
Photophysics, 789
Photopolymerization, 859
Photoracemization, 836
Photoreduction, 834
Photosolvolysis, 845
Photostationary state, 823, 824
Photosubstitution, 845
pH-rate constant curve, 441
 π bond order (P_{ij}), 192
 π bonding orbital, 180
 π complex, 557, 603, 610

- π -electron deficient carbene, 280
 π electron density (ρ_i), 191
 π molecular orbital, 175
 π -nucleophile, 509
 π, π^* state, 792
 $^1\pi, \pi^*$ state, 793, 819
 $^3\pi, \pi^*$ state, 793, 819
 π -radical cation, 306
 π system in pericyclic reaction, 702
 π^*
 antibonding orbital, 180
 solvent dipolarity/polarizability index, 338
 π^*_{azo} solvent parameter, 339
 $\pi \rightarrow \pi^*$ transition
 and solvent effect, 817
 in alkene, 818
 in benzene, 843
 in benzophenone, 816
 Picosecond (ps), 331
 Pilot atom, 72
 Pipek–Mezey method, 225
 Piperine, 867
 pK_a , 414
 of electronically excited state, 813
 $PK_{\text{CS-CHA}}$, 421
 PKIE, 371
 Plain curve, 88
 Planar carbon atom, 161
 Planar chirality, 70
 Planck's constant (h), 351
 Plane of chirality, 66
 Plane polarized light, 86
 Platonic solid, 161
 PM3, 223
 PM6, 223
 PMO calculation
 carbocation, 230, 292
 conformation of ethane, 231
 ethyl radical, 263, 264
 pericyclic reaction, 756
 torsional barrier in ethane, 231
 PMO theory, 226
 Point group, 61
 and chirality, 62, 63, 65
 and nondissymmetry, 64
 classification scheme, 61
 Polar Felkin–Anh model, 627
 Polarizability
 and acidity, 429
 and base softness, 505
 and nucleophilicity, 504, 507
 and pericyclic reaction, 771
 and substituent effect, 400
 Polarized light
 circularly polarized, 88
 plane polarized, 86
 Polyacene, 206
 Polymerization, 271
 Ponderal effect, 501
 Positional isomers, 57
 Positive Cotton effect, 88
 Post-Hartree–Fock method, 225
 Potential energy surface, 147, 216, 253,
 366, 370, 472, 566, 640, 645, 714, 777,
 812, 821, 848, 850
 acid-base reaction, 418
 and electrocyclic reaction, 714
 and kinetic isotope effect, 373
 and syn elimination, 651
 bifurcated, 370
 bromonium ion, 566
 for electronically excited state, 820
 pR , 70, 72
 Preassociation mechanism, 595
 Predissociation, 848
 Predissociative state, 848
 Preexponential factor (A), 349
 and kinetic isotope effect, 374
 Pref, 84
 Preferred representations of
 stereochemistry, 56, 81
 Previtamin D₃, 720
 pericyclic reaction, 720
 Primary kinetic isotope effect, 371, 374,
 607
 Primary ozonide, 745
 Primary solvent kinetic isotope effect, 384
 Principle of additivity, 6, 10
 Principle of microscopic reversibility, 344
 Prismane, 163, 170, 843
 (Pro)^{*p*}-chirality, 99
 Pro-(*R*) descriptor, 96, 97
 Pro-(*S*) descriptor, 97
 Prochiral structure, 96
 Prodrug, 636
 Product development control, 625
 Product distribution and $\delta\Delta G^\ddagger$, 354
 Pro-fragrance, 861
 Progress of reaction, 253, 361, 641
 Propagation step in chain reaction, 270,
 271, 543, 583, 589
 Propane gas phase acidity, 317
 2-Propanol
 acidity, 418
 gas phase acidity, 426, 428
 [1.1.1]Propellane, 160, 168
 Propene conformations
 and bonding models, 46
 Proper rotation axis (C_n), 60, 99
 Propionic acid acidity, 428
 1-Propyl cation, ab initio calculation, 298
 1-Propyl radical, 270
 hyperfine coupling, 262
 Propyne gas phase acidity, 428
 Protium (¹H), 516, 774
 Protobranching, 15
 Proton (¹H⁺), 414
 Proton affinity (PA), 426
 Proton inventory, 385
 Protonation, 414
 pS , 70, 72
 ps (picosecond), 331
 Pseudoasymmetric atom, 98
 Pseudoaxial substituent, 135
 Pseudoequatorial substituent, 135
 Pseudo-first-order kinetics, 344, 452, 474
 Pseudorotation, 128
 pss, 823
 PTOC ester, 272
 Puckered conformation, 126
 Pulsed ion cyclotron resonance (ICR)
 spectrometry, 423
 Push-pull carbene, 281
 Push-push carbene, 281
 Pyramidal carbon atom, 160
 Pyramidalization
 alkene distortion, 166
 in excited state, 820, 821
 Pyramidane, 163
 Pyrene SRT resonance energy, 245
 Pyridine reaction with singlet
 carbene, 287
 Pyridine-2-thione-*N*-oxycarbonyl
 ester, 272
 2-Pyridone-2-hydroxypyridine
 tautomerization, 449
 Pyridyne, 168
 Pyrolytic elimination, 681
 Q_i (charge density), 192
 QTAIM, 233
 methonium ion, 290
 Quantitative conformational analysis, 135
 Quantum Chemistry Program
 Exchange, 137
 Quantum efficiency, 804
 Quantum theory of atoms in
 molecules, 233
 Quantum yield, 804
 Quasi-steady-state approximation, 345
 Quencher, 800
 of electronically excited state, 809
 R
 gas constant, 349
 in Swain–Lupton equation, 399
 in Taft–Topsom equation, 400
 in Yukawa–Tsuno equation, 399
 stereochemical descriptor, 67, 68, 76
 +R resonance effect, 385
 -R resonance effect, 385
 R^* , 76
 R_a , 70
Rac- (stereochemical descriptor), 87
 Racemate, 87
 physical properties, 93
 Racemic mixture, 87
 Racemic modification, 87
 Racemization, 135
 and A1 mechanism, 447
 and carbanion, 314, 333
 and carbocation, 291
 and radicals, 314
 and SET mechanism, 517
 and S_N1 mechanism, 480
 of chiral ketones, 443
 [4]Radialene, 167
 Radiant intensity, 789

- Radiant power, 789
Radiationless decay, 794, 820
Radiationless process, 794
Radiationless transfer of electronic excitation, 802
Radiative process, 793
Radical
 bromine-bridged, 591
 inert, 258
 kinetically stable, 258
 origin of the term, 256
 persistent, 258
 stability, 268
 trapping, 270
Radical anion, 270, 310, 543
 and photoinduced electron transfer, 804
 EPR spectrum, 261
 generation, 310
 in SET reaction, 515
 reactions, 310
Radical cation, 270, 305
 acidity, 309, 422
 and photoinduced electron transfer, 804
 classification, 306
 distonic, 308
 generation, 305
 in nitration of benzene, 526
 reactions, 309
Radical clock, 275
Radical combination, 276
Radical cyclization, 273
Radical disproportionation, 276
Radical intermediate, 341
Radical ion pair, 803
Radical stabilization energy (RSE), 264
Radical trap, 515, 542
Rapidly equilibrating classical carbocations, 300, 494
Rate control of product distribution, 357
Rate equation, 342
 differential, 343
 integrated, 343
Rate expression, 342
Rate-limiting step (RLS), 336, 348, 443, 444
 and ‡ mechanism descriptor, 644
 and acid catalysis, 434
 and anchimeric assistance, 486
 and categories of elimination reactions, 644
 and ΔS^\ddagger , 353
 and Hammett correlation, 394
 and kinetic isotope effect, 370
 and molecularity of reaction, 342
 and pH, 441
 and preassociation mechanism, 595
 and reaction dynamics, 776
 and solvent isotope effect, 385
 and surface effects, 687
 in addition of Br₂ to alkene, 559, 561
 in alcohol dehydration, 670, 673
 in amide hydrolysis, 460, 463
 in benzyne formation, 538
 in dehalogenation reaction, 668
 in electrophilic aromatic substitution, 519, 520
 in ester hydrolysis, 449, 450, 452, 454, 456, 457
 in hydration of alkene, 594
 in nucleophilic acyl substitution, 459
 in nucleophilic aromatic substitution, 527
 in nucleophilic vinylic substitution, 533
 in oxymercuration, 597
 in photochemical process, 833
 in pyrolytic elimination, 683
 in reaction of XeF₂ with alkene, 581
 in S_N1 reaction, 473
r_c (covalent radius), 5
R-CPL, 858
Re face, 98
Reaction constant in Hammett equation, 390
Reaction coordinate, 253, 254, 367
 and excited states, 820
 and kinetic isotope effect, 376
 and VBCM, 514
 E1 reaction, 642
 Gibbs diagram, 255
 Marcus theory, 363
 pericyclic reaction, 711, 739
 photodissociation, 848
 S_N2 reaction, 361
Reaction coordinate diagram, 253
 acetal hydrolysis, 447
 and excited state acidity, 811
 and Hammond postulate, 362
 and product distribution, 357
 and reactive intermediate, 254
 and substituent effect, 390
 E1 reaction, 641
 E1c_B reaction, 643
 E2 reaction, 641
 elementary reaction, 348
 Gibbs diagram, 328
 Hofmann orientation, 658
 Saytzeff orientation, 655
 S_EAr reaction, 519
 S_N2 reaction, 361
 solvolysis, 485
Reaction mechanism, 327
Reaction velocity, 342
Reactive intermediate, 253, 254
 and Hammond postulate, 362
 detection, 531
 energy requirement, 329
 isolation, 329, 330
 lifetime, 254
 photochemical generation, 824, 842, 855
 spectroscopic detection, 330
 trapping, 331, 483
Rectus, 67
Red shift, 817
Regiochemistry, 621
 and Markovnikov's rule, 585
 in addition of HBr to alkene, 589
 in addition of HCl to alkyne, 612
 in benzyne reaction, 537
 in electrophilic addition, 568, 574, 582, 584
 in elimination, 654
 in hydration of alkene, 593
 in hydroboration of alkene, 596, 602
 in hydroboration of terminal alkyne, 616
 in nucleophilic addition, 620
 in oxymercuration of alkene, 597
 in oxymercuration of alkyne, 614
 in α -halogenation of ketones, 444
 of Cope elimination, 686
 of Diels–Alder reaction, 760
 of enol formation, 444
 of enolate formation, 444
Regioselective reaction, 86
Regioselectivity, 567, 584, 597, 603, 605, 661
Regiospecific reaction, 86
Rel, 76
Relative configuration, 74–76, 91, 92
Relative hardness and aromaticity, 220
Relative static permittivity, 338
Resolution of a racemate, 87
Resolve (a racemate), 87
Resonance, 189, 192, 197, 198, 239
 and acidity of carboxylic acids, 418
 and benzyne reaction, 541
 and substituent effect, 400
 bromonium ion, 564
 carbanion stabilization, 311
 carbene stabilization, 280
 carbocation stabilization, 292
 description of carbanion, 312
 nucleophilic aromatic substitution, 529
 substituent effect, 385
Resonance effect constant, 399
Resonance energy, 204
 and aromaticity, 206
 and heat of formation, 218
 and number of resonance structures, 238
 and SRT method, 241, 244
 and valence bond theory, 189
annulenes, 218
benzene, 190, 203–205, 238, 239
Dewar resonance energy, 218
furan, 206
naphthalene, 206
phenanthrene, 206
thiophene, 206
Resonance hybrid, 189
Resonance integral
 HMO theory, 177
 in Möbius π systems, 765
Resonance structure, 189, 197, 238
 and electrophilic aromatic substitution, 524
 and hyperconjugation, 230, 262
 and representation of electronically excited state, 814, 832, 841, 843, 845

- Retention of configuration, 92
 in ester hydrolysis, 453, 456
- Retro-1,3-cycloaddition, 746
- Retro-Diels–Alder reaction, 736, 854
- Retro-ene reaction, 683, 752
- Reverse aldol reaction, 638
- Reverse Michael addition, 638
- ρ
 in Hammett equation, 390, 400
 interpretation, 392
 negative value, 392
 positive value, 392
 reaction constant, 391
- ρ_i (electron density), 191
- $\rho(\mathbf{r})$ in QTAIM, 233
- ρ^* in Taft equation, 401
- 11-*cis*-Rhodopsin
 photoisomerization, 822
- r_i , 5
- Ring current, 203
- Ritchie equation, 479, 511
- RLS (rate limiting step), 336
- Robinson annulation, 621
- Rose bengal, 852
- Rose oxide, 852
- Rotamer, 113
- [3]Rotane, 163
- Rotational energy level notation, 789
- Rotational isomer, 113. *See also* Rotamer
- Rotundone, 867
- R_p , 70
- RS (stereochemical descriptor), 87
- RSE (radical stabilization energy), 264
- Rule of steric control of asymmetric induction, 623
- r_{vdW} (van der Waals radius), 5
- Rydberg state, 818, 819, 825, 826, 829, 843
- Rydberg transition, 818
- S**
 in Taft equation, 401
 solute dipolarity/polarizability parameter, 339
 stereochemical descriptor, 67, 68
- s in Swain–Scott equation, 507
- S^* , 76
- S_0 state, 792
- S_1 state, 792
- S_a , 70
- Saddle point, 641, 852
 and potential energy surface, 366
 and transition structure, 708
- Salt effect, 338
 normal, 479
 special, 483
- Sawhorse representation, 55
- Saytzeff orientation, 655, 662
- Saytzeff product, 657
- Saytzeff rule, 654, 656
- SC (structure count), 241
 +*sc*, 115
 –*sc*, 115
- Scalemic, 85
- Scanning tunneling microscopy (STM), 3
- SCF, 224, 225, 244
- Schrödinger equation, 25, 176
- s-cis* conformational descriptor, 117
- s-(E)*, 117
- s_E in Mayr equation, 510
- S_E mechanism label, 593
- S_EAr reaction
 and single-electron transfer, 525
 electrophilic aromatic substitution, 518
- Secondary kinetic isotope effect, 371, 380, 673
- Secondary orbital interactions, 759
- Secondary solvent kinetic isotope effect, 384
- Secular determinant, 178
- Selection rules
 and number of electrons, 743
 atom transfer reactions, 750
 cheletropic reactions, 748
 cycloaddition, 739
 electrocyclic reactions, 705
 pericyclic reactions in general, 755
 sigmatropic reaction, 717, 724
 transition state aromaticity, 767
- Self-consistent field (SCF), 224
- Semiempirical method, 223
- Semiempirical MO calculation, 223, 226
 computational resources, 223
 pericyclic reaction, 771
- Sensitization, 283, 809, 818, 820, 824, 830, 851
 electronic energy transfer, 803
 origin of the term, 803
- Sensitizer, 283
- SET, 513, 517
- S_i in Mayr equation, 513
- SF in molecular mechanics, 138
- Si face, 98
- σ
 absolute softness, 506
 in Hammett equation, 390, 400
 substituent constant, 391
 symmetry operation, 59
- σ bond
 heterolytic dissociation, 19
 photodissociation, 847
- σ complex, 520, 553
- σ^- substituent constant, 399
- σ^* in Taft equation, 400, 401
- σ, π description of double bond, 42
 and acidity, 44
- σ^+ substituent constant, 398
- σ^0 substituent constant, 400
- σ -complex, 526
- σ -electron rich carbene, 280
- $^1\Sigma_g^+$ O_2 (electronic state of O_2), 851
- $^3\Sigma_g^-$ state of O_2 , 851
- σ_h (horizontal plane of symmetry), 60
- σ_1 substituent constant, 400
- σ_m in Hammett equation, 395
- σ^n substituent constant, 400
- σ_p in Hammett equation, 395
- σ_R substituent constant, 400
- σ_R^- substituent constant, 400
- σ_R^+ substituent constant, 400
- σ -radical cation, 307
- σ_v (vertical plane of symmetry), 59
- Sigmatropic reaction, 715, 725
 as cycloaddition reaction, 754
 Möbius aromaticity, 767
 selection rules, 717, 724
- Simmons–Smith reaction, 283
- Single electron shift, 513, 515
- Single electron transfer (SET), 269, 513, 517, 525, 531, 581
- Single-molecule spectroelectrochemistry, 4
- Singlet lifetime, 806
- Singlet manifold, 793, 794
- Singlet oxygen, 851
 lifetime, 851
 photodynamic therapy, 852
- Singlet state, 792
 of carbene, 288
 of methylene, 278
- Singlet-singlet absorption, 795
- Singlet-triplet absorption, 795
- Single-walled nanotube, 208
- Singly-occupied molecular orbital, 262
- Sinister, 67
- Skew conformation, 114
- Slater type orbital (STO), 224
- SMILES notation, 54
- Smiles rearrangement, 529
- S_n
 chirality and point group, 63
 symmetry operation, 59
- s_N in Mayr equation, 509
- $S_N(EA)$ mechanism, 536
- S_N1 mechanism label
 meaning intended by Ingold, 471
- S_N1 reaction, 470
 anchimeric assistance, 485
 and salt effect, 479
 and solvent polarity, 477
 and steady-state approximation, 473
 and steric effects, 474
 designated as ($D_N + A_N$), 471
 kinetic isotope effect, 382
 nonclassical carbocations, 491
 potential energy surface, 472
 racemization, 337, 480
 rate equation, 470
 reactivity and carbocation stability, 362, 474, 475
- S_N1' mechanism designated as ($1/D_N + 3/A_N$), 471
- S_N2 mechanism label meaning intended by Ingold, 471
- S_N2 reaction, 337, 361, 381, 470, 494
 and 18-crown-6, 499
 and back-side attack, 496
 and $B_{A1}2$ mechanism, 453
 and Hammett ρ , 393, 394
 and radical intermediate, 515

- and single-electron shift, 515
back-side displacement, 495
competition with E2, 646
designated as ($A_N D_N$), 471
effect of leaving group, 512
effect of solvent, 496
inversion of configuration, 337
nucleophilicity of nucleophile, 506
of diazonium ion, 679
ponderal effect, 501
steric effect, 501
transition structure, 502
 S_N2' mechanism designated as (3/1/ $A_N D_N$), 472
 S_NAr reaction
and single-electron transfer, 531
first-order reaction, 527
nucleophilic aromatic substitution, 527
second-order reaction, 528
 S_Ni mechanism designated as ($D_N + D + A_N$), 472
Snoutane, 163
Soft base, 505
Solar energy storage, 862
Solid bold line in Maehr convention, 75
Solid dot stereochemical descriptor, 58
Solid wedge in Maehr convention, 74
Solvatochromism, 339
Solvent cage, 335, 515–517, 526, 599, 613
Solvent dipolarity/polarizability index (π^*), 338
Solvent effect on Hammett ρ , 393
Solvent isotope effect, 384, 594
1° Solvent kinetic isotope effect, 384
2° Solvent kinetic isotope effect, 384
Solvent kinetic isotope effect, 448, 559, 562, 615
in amide hydrolysis, 460
Solvent polarity and mechanism
determination, 338
Solvent reorientation time, 595
Solvent-separated ion pair, 313, 421, 483, 485, 560, 804
Solvent viscosity
and encounter-controlled reactions, 337
and reaction in solvent cage, 517
in mechanism determination, 338
Solvolysis, 477, 478
anchimeric assistance, 485
and carbocation stability, 475
and elimination, 645
and nonclassical carbocations, 300
and nonplanar carbocations, 475
and solvent polarity, 477
Grunwald–Winstein equation, 477
internal return, 482
ion pair intermediate, 485
kinetics, 344
LFER, 398
2-norbornyl system, 493
pseudo-first-order kinetics, 474
salt effect, 479
stereochemistry, 480
Solvomercuration, 596, 614
SOMO, 262
sp, 115
+ *sp*, 115
– *sp*, 115
Sp, 70
Special salt effect, 483
Specific acid catalysis, 434, 437, 670, 673
Specific acid, general base catalysis, 436
Specific base catalysis, 435, 437, 456
Specific base, general acid catalysis
in ester hydrolysis, 456
Specific hydroxide ion catalysis, 435
Specific lyate ion catalysis, 435
Specific lyonium ion catalysis, 434
Specific oxonium ion catalysis, 434, 435
Specific rotation, 86
conventions, 87
Spin adduct, 277
Spin-forbidden process, 796
Spin-forbidden transition, 801
Spin-orbit coupling, 796, 801
Spin polarization, 260
Spin quantum number, m_s , 259
Spin trap, 277
Spin trapping, 277
Spiro transition structure, 608
Spirocyclopentadiene, 163
sR, 70
SR (stereochemical descriptor), 87
 $S_{RN}1$ mechanism, 543
 $S_{RN}1$ reaction, 544
designated as ($T + D_N + A_N$), 543
SRT (structure resonance theory), 241
counting Kekulé structures, 241
resonance energy, 244
types of electron permutations, 243
SSIP, 560
Staggered conformation, 114
Standard heterolytic bond dissociation energy, 18
Standard homolytic bond dissociation enthalpy, 16
Stark effect, 20
State correlation diagram, 712, 734
Diels–Alder reaction, 736
Steady-state approximation, 345–348, 473, 642
Step-wise process, 329
Stereocenter, 75, 98
(\pm) Stereochemical descriptor, 87
Stereochemistry, 53
acceptable representations, 56
not acceptable representations, 56, 81
preferred representations, 56, 81
Stereochemical effect, 151
Stereogenic atom, 98
Stereogenicity, 98
and meso structure, 98
Stereoisotopic substituents, 94
Stereoisomers, 57
cis,trans, 58
configuration, 67
diastereomers, 58
geometric, 58
Stereoselective reaction, 85, 122
Stereospecific reaction, 85, 533, 569, 668, 669, 697, 735, 745
Stereotopicity, 94
Steric acceleration in solvolysis, 494
Steric energy, 136, 155
Steric interaction, 120, 231
Steric isotope effect, 383
Stern–Volmer equation, 809, 810
Stern–Volmer plot, 810
Stilbene
DRE, 219
SRT resonance energy, 245
STM, 3
STO (Slater type orbital), 224
STO-3G basis set, 224
Stokes shift, 798
Strain energy, 155
Strained molecule, 155
Strained π bond, 164
Strainless bond enthalpy, 157
s-trans conformational descriptor, 117
Stretch-bend term in molecular mechanics, 138
Structural isomers, 57
Structure-resonance theory (*SRT*), 241
Styrene
DRE, 219
SRT resonance energy, 245
Substituent constant
in Hammett equation, 390
selected values, 401
Substituent effects on reactions, 385
Substituent topicity
constitutionally heterotopic, 94
diastereotopic, 94
enantiotopic, 94
heterotopic, 94
homotopic, 94
stereoheterotopic, 94
Substitution, 469
Ingold notation, 470
IUPAC notation, 471
solvolysis, 474
Superacid media, 296, 298, 320
Suprafacial-antarafacial pathway, 722
Suprafacial pathway, 715, 717–721, 731, 739, 741, 743, 750, 777
Suprafacial-suprafacial pathway, 721
Surface effect, 681
Surface-mediated reaction, 587, 614, 687
Swain–Schaad equation, 374
Swain–Scott equation, 507, 508, 511
SWNT, 208
Symmetric molecular orbital, 33, 707, 708, 712, 732
Symmetry element, 59, 708, 736
Symmetry operation, 59, 708
and MO symmetry, 708
and substituent topicity, 99
Symmetry operation of the first kind, 99

- Symmetry point group, 61
 classification scheme, 61
- Symmetry-allowed transition, 796
- Symmetry-correct molecular orbital, 33, 707, 732
- Symmetry-forbidden process, 776
- Symmetry-forbidden reaction, 739
- Symmetry-forbidden transition, 796
- Syn, 77
- Syn addition, 552, 571, 581, 582, 586, 601, 602, 614
 in hydroboration, 600, 616
 of Cl₂ to acenaphthylene, 579
 of F₂ to alkene, 580
 of HCl to alkyne, 612
- Syn conformation, 114
- Syn elimination, 634, 649, 669, 682–685, 695
 and E1cb character, 650
 in β-elimination, 649
 in pyrolytic elimination, 681
 potential energy surface, 651
- Synchronous reaction, 459, 472, 513, 608, 664, 750, 770–773
- Syn-clinal conformation, 115, 647
 + Syn-clinal conformation, 115
 –Syn-clinal conformation, 115
- Syn-coplanar conformation, 647
- Syndiotactic polymer, 93
- Syn-pentane interaction, 122
- Syn-periplanar, 115, 647
 –Syn-periplanar conformation, 115
 + Syn-periplanar conformation, 115
- s*-(Z), 117
- t*
 conformational descriptor, 116, 117
 stereochemical descriptor, 76
s-trans, 117
- T mechanism label, 543
- T (³H), 782
- T + D_N + A_N mechanism, 543
- T₁ state, 792
- Taft equation, 401
- Taft *E_s*, 401
- Taft ρ*, 401
- Taft *S*, 401
- Taft σ*, 400
 and E2 reaction, 664
 and electrophilic addition, 555, 575
 and p*K_a*, 418
- τ
 excited state lifetime, 805
 lifetime of carbocation, 594
 NMR scale, 727
- τ bond, 42
- Tau bond, 42
- τ_p (phosphorescence lifetime), 809
- τ_s (singlet lifetime), 806
- τ_s⁰ (inherent singlet lifetime), 806
- Tele substitution, 530
- Termination step in chain reaction, 270, 276, 543, 589
- Tesla, 261
- Tet (in Baldwin's rules), 274
- Tetracene, 207, 427
- Tetrahydrene, 161, 170
- Tetramethyl-1,2-dioxetane
 chemiluminescence, 860
- Tetra-*t*-butylcyclobutadiene, 853
- Tetra-*t*-butylethylene, 165
- Tetra-*t*-butyltetrahedrane, 162, 168, 853
- Thermochemical cycle in gas phase acidity
 determination, 424
- Thermodynamic acidity constant, 415
- Thermodynamic control of product
 distribution, 356, 357, 581, 670
- Thermolysis, 349
- Thermoneutral reaction
 and Hammond postulate, 362
 and kinetic isotope effect, 377
 nature of transition state, 375
 reaction coordinate diagram, 363
- THF, 421
- Thiophene resonance energy, 206
- Threo, 83, 571
- Threose, 83
- Toluene
 bromination, 523
 fluorescence, 848
 gas phase basicity, 427
 intramolecular PKIE in radical
 halogenation, 378
 nitration, 520
 photodissociation, 847
 p*K_{HA}* value in DMSO, 309
- Toluene radical cation, p*K_{HA}*⁺
 value, 309
- Topic relationship classification
 scheme, 99
- Topicity, 94, 97, 99
- Topology and pericyclic reactions, 769
- Torquoselectivity, 757
- Torsion angle in radical cation, 307
- Torsional barrier, 120
 and hyperconjugation, 231
- Torsional energy, 119
 and nucleophilic addition, 625
- Torsional strain, 119, 137
 and syn elimination, 649
- Total bond order, 193
- Total emission spectrum, 801
- Trans addition, 552
- Trans elimination, 633. *See also* Anti
 elimination
- Transfer hydrogenation, 340
- 0,0 Transition, 797, 812
- 0,1 Transition, 797
- Transition state, 350
 and Brønsted α, 438
 and free energy surface, 708
 and Gibbs diagram, 255
 and Hammond postulate, 362
 and kinetic isotope effect, 375
 antiaromatic, 764
 aromatic, 764
- Transition state theory, 350, 776
- Transition structure, 254, 328
 and acid-catalyzed hydrolysis of
 acetals, 447
 and biases of computational
 methods, 771
 and Δ*S*[‡], 353
 and Hammett ρ, 392
 and kinetic isotope effect, 375
 and orbital symmetry, 708
 and potential energy surface, 708
- antiaromatic, 763
 aromatic, 763
 centauric, 772
 chameleonic, 772
 saddle point on potential energy
 surface, 366
 symmetry, 770
- Transition structure, 348
- Transmission coefficient in transition state
 theory, 351
- Trapping reactive intermediate, 163, 270, 277, 331, 341, 483, 515, 542, 555, 700, 824, 830
 in pericyclic reaction, 745
- Trefoil knot, 67
- Triethylborane and radical
 generation, 269
- Trifluoromethyl radical geometry, 266
- Trig (in Baldwin's rules), 274
- Trimethylene diradical, 336
- Tri-*n*-butyltin hydride (Bu₃SnH), 271
- Triphenylene Clar notation, 211
- Triphenylmethyl cation, 475
- Triphenylmethyl radical, 256, 257
 and magnetic susceptibility, 258
- Triplet manifold, 793, 794
- Triplet state, 278, 792
 of methylene, 278
- Triplet-triplet absorption, 795
- Tritium (³H), 782
- Triton (³H⁺), 414
- Trityl, 475. *See also* Triphenylmethyl
- Twist boat
 cyclohexane, 124
cis-1,4-di-*t*-butylcyclohexane, 132
- Twist conformation of cyclopentane, 128
- Twistane, 163, 170
- Twisted alkene, 165
 and chirality, 858
- Twisted excited state, 820
- Twisted π system and Möbius MO
 theory, 765
- u* (unlike), 84
- ul* (unlike), 84
- Unichiral, 85
- Unimolecular process, 255, 805
- Unimolecular reaction, 309, 318, 343, 372, 450, 472, 683, 731
- Unnormal addition, 589
- UV-vis region of the electromagnetic
 spectrum, 787

- ν (vibrational energy level), 787, 798
 V (characteristic volume), 339
Vacuum UV, 818
Valence bond configuration mixing (VBCM), 513
Valence bond (VB) theory, 24, 35, 240
 and resonance, 189
 and resonance energy, 237, 240
Valence isomerization, 726
Valence isomers, 167, 701, 726
Valence shell electron pair repulsion theory (VSEPR), 36
Valley-ridge inflection point (VRI), 370
van der Waals radius, 5, 6
 and non-bonded interactions, 6
 of deuterium relative to hydrogen, 383
van der Waals strain, 121, 139
 and $A^{(1,2)}$ strain, 122
 and $A^{(1,3)}$ strain, 122
 and annulenes, 217
 and axial substituent, 129
 and butane gauche conformation, 150
 and limits to molecular stability, 160
 and *syn*-pentane interaction, 122
 and UV-vis absorption, 821
van der Waals surface area (A_w), 7
van der Waals volume (V_w), 7
Variable hybridization
 and acidity, 45
 and carbanion stability, 45
 and electronegativity, 37
 and geometry, 37, 39
 and J_{13C-H} , 41
 and p character, 37
 and s character, 37
 CH_2Cl_2 , 39
 CH_3Cl , 40
 CH_3F , 40
 cyclopropane, 40
 hybridization index, 37
 hybridization parameter, 37
Variable transition state theory in elimination reactions, 664
Variational principle, 176–178, 236, 239
VB theory, 24, 25
VBCM, 513
Velocity of a reaction, 342
Vertical excitation, 821
Vertical excited state, 819, 820
Vertical plane of symmetry (σ_v), 59
Vertical transition, 796, 847
Vibrational energy level, 372, 787
 and electronic states, 793
Vibrational relaxation, 794
Vicarious nucleophilic aromatic substitution, 530
Vicinal dihalide dehalogenation, 665
Vinyl alcohol acidity, 419
Vinyl carbanion, 212
 hybridization, 311
 reactive intermediate, 653
Vinyl cation, 532, 609, 612, 613, 615
Vinyl halide
 dehydrohalogenation, 653
 electrophilic addition, 585
 nucleophilic vinylic substitution, 533
Vinyl radical, 256
 in addition of HBr to propyne, 611
Virtual experiment, 339
Vitamin D₃, 720, 721
Vitamin E, 69
Von Richter reaction, 530
VRI, 370
VSEPR theory, 36
 and electronegativity, 36
 and variable hybridization, 37
 methylene, 279
 V_x (Benson electronegativity), 23
Wagner–Meerwein rearrangement, 492
Wagner–Meerwein–Whitmore rearrangement, 492
Walden cycle, 495
Walden inversion, 337, 494, 671
Wavelength
 and energy of light, 789
 and specific rotation, 87
Wavy line stereochemical descriptor, 58
Wedge outline in Maehr convention, 75
Westheimer method, 135
Wheland intermediate, 330, 520
Winstein–Holness equation, 360
Wolff rearrangement, 288
Woodward–Hoffmann rules
 atom transfer reaction, 750
 cheletropic reaction, 749
 cycloaddition, 739
 electrocyclic reaction, 705
 general selection rule, 755
 pericyclic reaction, 755
 sigmatropic reaction, 718, 724
X (excess acidity function), 433
Xanthate ester pyrolysis, 682
Xanthone, polarity of electronically excited states, 817
XeF₂, 581, 611
Xi-bond, 58
ξ-bond, 58
m-Xylylene, 798
Y in Grunwald–Winstein equation, 477
Yang cyclization, 836
Ylide elimination mechanism, 635
Y_{OTs} scale of solvent ionizing power, 477
Yukawa–Tsunoo equation, 399
Z, 76
Z scale of solvent polarity, 339
Zero point energy (ZPE), 373, 382
Zig-zag conformation, 154, 234
Zimmerman rearrangement, 828
ZPE, 373
Zusammen, 76
Zwitterionic structures and electronically excited states, 820

