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# Many faces of aromaticity

The IUPAC definition.[5] *The concept of spatial and electronic structure of cyclic molecular systems displaying the effects of cyclic electron delocalization which provide for their enhanced thermodynamic stability (relative to acyclic structural analogues) and tendency to retain the structural type in the course of chemical transformations. A quantitative assessment of the degree of aromaticity is given by the value of the resonance energy. It may also be evaluated by the energies of relevant isodesmic and homodesmotic reactions. Along with energetic criteria of aromaticity, important and complementary are also a structural criterion (the lesser the alternation of bond lengths in the rings, the greater is the aromaticity of the molecule) and a magnetic criterion (existence of the diamagnetic ring current induced in a conjugated cyclic molecule by an external magnetic field and manifested by an exaltation and anisotropy of magnetic susceptibility). Although originally introduced for characterization of peculiar properties of cyclic conjugated hydrocarbons and their ions, the concept of aromaticity has been extended to their homoderivatives (see homoaromaticity), conjugated heterocyclic compounds (heteroaromaticity), saturated cyclic compounds (σ-aromaticity) as well as to three-dimensional organic and organometallic compounds (three-dimensional aromaticity). A common feature of the electronic structure*

"I see no reasons to make changes. Aromaticity remains a fuzzy concept in the zoo of chemical models, ad all attempts to define it more clearly create more confusion than clarity" (G. Frenking, 2023)

Types of aromaticity
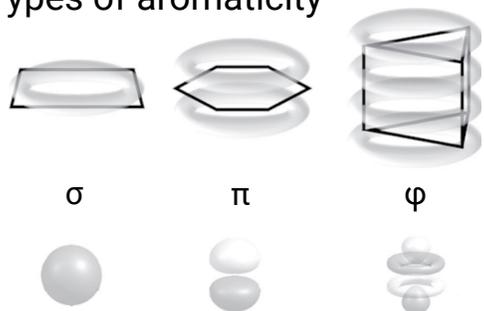
σ　　π　　φ

Suggested reading: *Nat. Chem.* **2022**, *14*, 585.

= Aromatic　　= Antiaromatic
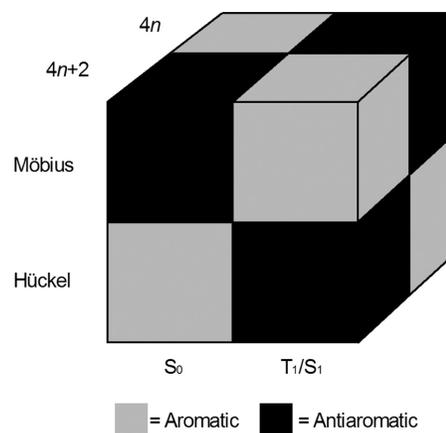
Energetic criterion

Energy decomposition analysis and aromatic stabilisation energies (kcal mol^{-1}):
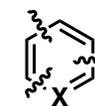
X	CH	N	P
ΔE_{int}	−513.3	−495.0	−464.7
ΔE_{Pauli}	1180.0	1356.2	1169.9
ΔE_{elstat}[1]	−540.4 (31.9%)	−563.0 (30.4%)	−517.1 (31.6%)
ΔE_{orb}[1]	−1152.8 (68.1%)	−1288.2 (69.6%)	−1117.5 (68.4%)
ΔE_{σ}[2]	−1045.2 (90.7%)	−1174.7 (91.2%)	−1016.2 (90.9%)
ΔE_{π}[2]	−107.7 (9.3%)	−113.5 (8.8%)	−101.3 (9.1%)
ASE	42.5	45.7	36.9

X	As	Sb	Bi
ΔE_{int}	−453.2	−440.0	−431.5
ΔE_{Pauli}	1120.4	1070.5	1044.0
ΔE_{elstat}[1]	−504.1 (32.0%)	−489.2 (32.4%)	−478.0 (32.5%)
ΔE_{orb}[1]	−1069.4 (68.0%)	−1021.3 (67.6%)	−995.5 (67.5%)
ΔE_{σ}[2]	−971.6 (90.8%)	−926.5 (90.7%)	−901.9 (90.6%)
ΔE_{π}[2]	−97.8 (9.2%)	−94.8 (9.3%)	−93.6 (9.4%)
ASE	34.9	31.1	29.4

Magnetic properties (NICS)

Magnetically induced current density in Bi_6^{2-} and $[\{CpRu\}_3Bi_6]^-$.
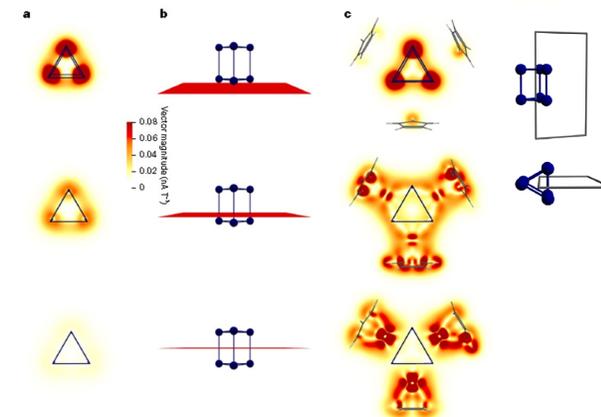
Aromaticity rules

TABLE 1 A historical overview of aromaticity rules

Year	Main contributor(s)	Contribution
1931	Hückel[11–14]	Hückel's (4N + 2) π-electron rule of monocyclic annulenes
1954	Platt[47]	Platt's ring perimeter model
1964	Heilbronner[48] and Herges[49]	4N π-electron rule for Möbius-type conformation of annulenes
1965	Breslow[50]	Antiaromaticity of 4N π monocyclic annulenes
1971	Wade[51]	2N + 2 cage electron rule for *closo* boranes
1972	Mingos[52]	4N + 2 valence electron rule for *closo* boranes
1972	Baird[28]	4N π-electron rule for the lowest-lying triplet state of annulenes
1972	Clar[53]	Π-sextet rule for benzenoid species
1978	Ovchinnikov[54]	Multiplicity of the ground state of large alternant organic molecules with conjugated bonds
1984	Glidewell, Lloyd[55]	Extension of Clar's rule to polycyclic conjugated hydrocarbons with even number of C atoms
2000	Hirsch[56]	2(N + 1)^2 rule for spherical aromatic species
2002	Jemmis[57]	Extension of Wade–Mingo's rule to fused boranes, the mno rule
2004	Ruiz-Morales[58]	Y-rule, an improvement of Clar's rule
2008	Soncini, Fowler[59]	A generalization of Hückel's (4N + 2)π rule and Baird's 4N π rule to higher excited states
2008	Rzepa[60]	Linking number rule as a generalization of Hückel's (4N + 2) π rule and Möbius' 4N π rule
2011	Poater, Solà[61]	2N^2 + 2N + 1 (S = N + ½) rule of open-shell spherical aromaticity
2013	Havenith, Nguyen, Ceulemans[39]	Rule for disk aromaticity
2014	Nguyen[36,37]	Rule for cylindrical aromaticity
2015	Zhao, Li[40]	6N + 2 rule of cubic aromaticity

Everything is relative; nothing is black and white, and numerous shades of grey exist. But it becomes clear that the change is required and it will come when there are enough anomalies challenging our currently accepted view of aromaticity.