

The Circle Symbol for Aromaticity

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Question

What is the origin of the circle symbol for aromaticity?

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Answer

The use of a circle enclosed within a hexagon to represent the “aromatic sextet” of benzene was first introduced by the British chemists, James Wilkins Ait and Sir Robert Robinson (figure 1), in a paper published in 1925 (1). Just as the fundamental role played by the electron pair or duplet in the electronic formulation of molecular structures merited its own distinct symbol in the form of a straight line connecting two atoms, so these authors felt that a planar ring or sextet of electrons imparted sufficiently distinctive properties to certain organic molecules so as to also merit a unique symbol of its own (1):

The circle in the ring symbolizes the view that six electrons in the benzene molecule produce a stable association which is responsible for the aromatic character of the substance.

Though this proposal predates the rise of the delocalized molecular orbital approach to aromaticity and our current σ/π distinctions (2, 3), these authors further hinted that their theory of the aromatic sextet and its accompanying symbol did not “require any particular assumption in regard to the position of the electrons or their orbits in space.”

While occasionally mentioned in passing in advanced monographs the period 1925-1959 (4), the circle symbol appears to have had no impact on introductory organic textbooks (5). Indeed even Robinson himself seems to have abandoned it, as it does not appear in his famous 1932 resume of his version of the electronic theory of organic chemistry (6) nor in Michael Dewar’s 1949 update of Robinson’s system, though the latter does show the delocalized π -orbitals on benzene



Figure 1. Robert Robinson (1886-1975).

and makes occasional use of dotted lines to indicate electron delocalization in various transition states and intermediates (7).

Only in the late 1950s and early 1960s did the circle symbol finally make an appearance in the introductory organic textbook and most notably in the 1959 edition of the highly popular text by Morrison and Boyd, where it was used not only for benzene but also for naphthalene, anthracene, phenanthrene and other polycyclic aromatics (8). By this point all connection with Robinson’s original proposal seems to have been lost and the symbol’s reemergence as a textbook icon appears instead to have been a by-product of the increasing popularity of the delocalized MO approach to the description of π -electron systems. Even then, its textbook usage has been variable, with some books, such as the 1965 text by Roberts and Caserio, rejecting

it as “quite uninformative and even misleading” when it comes to electron counting, while yet others have followed the lead of Morrison and Boyd and have applied it to cyclic π -systems in general, as well as consistently employing it in equations representing their chemistry (9).

Finally, it should be noted that there continues to be debate over the exact meaning of the symbol. While several of the above textbooks have used it to denote cyclic π -electron delocalization irrespective of electron counts, some advanced monographs restrict its use only to those monocyclic π -systems which obey the Hückel $4n+2$ rule for aromaticity, thus allowing for 2, 6, 10, etc. π -electron systems (10), whereas yet others restrict it, in keeping with Robinson’s original intent, to monocyclic systems containing only six π -electrons (11). This latter usage is perhaps the most precise and the most defensible. Just as the line always represents a 2c-2e bond, and the “Y” symbol used in boron hydride structures always represents a 3c-2e bond, so the circle may be thought of as representing a special kind of 6c-6e bond. Just as the 3c-2e symbol eliminates (by definition) the need for resonance using only 2c-2e bonds in certain species and reduces the number of required resonance structures in others, so the 6c-6e circle symbol eliminates (by definition) the need for resonance in certain monocyclic species, such as benzene, pyridine, the cyclopentadienyl anion, etc, and reduces the number of required structures in yet others. Thus naphthalene has three major resonance structures using only 2c-2e bonds, but just two using the circle symbol, each of which consists of one hexagon with a circle and one with two localized (albeit conjugated) double bonds.

Literature Cited

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2. E. Hückel, “Quantentheoretische Beiträge zum Benzolproblem. I,” *Z. Physik*, **1931**, 70, 204-286; “Quantentheoretische Beiträge zum Benzolproblem. II,” *Z. Physik*, **1931**, 72, 310-337; “Quantentheoretische Beiträge zum Problem der aromatischen und ungesättigten Verbindungen. III. Benzolproblem,” *Z. Physik*, **1932**, 76, 628-648.
3. E. Hückel, *Grundzüge der Theorie ungesättigter und aromatischer Verbindungen*, Verlag Chemie: Berlin, 1938.
4. W. A. Waters, *Physical Aspects of Organic Chemistry*, Van Nostrand: New York, NY, 1936, p. 411.
5. Thus the symbol does not appear in the popular American texts by Conant (1932), Whitmore (1937), Wheeland (1949), Fieser and Fieser (1950), Noller (1951) or Cram and Hammond (1959).
6. R. Robinson, *Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions*, Institute of Chemistry: London, 1932.
7. M. J. S. Dewar, *The Electronic Theory of Organic Chemistry*, Oxford University Press: Oxford, 1949.
8. R. T. Morrison, R. N. Boyd, *Organic Chemistry*, Allyn and Bacon: Boston, 1959. These authors originally used broken lines for the circle. In later editions this was replaced by solid lines.
9. J. D. Roberts, M. C. Caserio, *Basic Principles of Organic Chemistry*, Benjamin: New York, NY, 1965, p. 234. A more recent example involves the texts by McMurry (1996), who rejects the symbol as ambiguous, versus Solomons (1992), who uses it extensively.
10. G. M. Bader, *Aromatic Character and Aromaticity*, Cambridge University Press: Cambridge, 1969 and P. J. Garrett, *Aromaticity*, McGraw-Hill: London, 1971.
11. E. Clar, *The Aromatic Sextet*, Wiley: London, 1972.

Do you have a question about the historical origins of a symbol, name, concept or experimental procedure used in your teaching? Address them to Dr. William B. Jensen, Oesper Collections in the History of Chemistry, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 or e-mail them to jensenwb@ucmail.uc.edu