What Is Aromaticity?

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A brief review of the phenomenon of aromaticity is provided. The historical aspects of this property of molecules are covered, and contemporary views of aromaticity are described.

When chemists come across the terms *aromatic* and *aromatic character* it makes most of them think of benzene. Benzene is a unique and really rather strange hydrocarbon. If you had been taught only about aliphatic and alicyclic compounds and were then suddenly presented with the classic formula of benzene and asked to predict its chemical properties, you would almost certainly get them wrong.

Benzene

From this formula it is obviously an unsaturated compound. Such compounds undergo addition reactions, some of them with electrophiles and some with nucleophiles. You would probably suggest that it would readily add bromine, undergo polymerization by the Diels−Alder reaction, and be oxidized readily. Benzene does indeed react with electrophiles, but none too readily, and not to give addition products. It is not easily oxidized and does not normally participate in Diels−Alder reactions. You would probably be equally unsuccessful in predicting its physical (spectroscopic) properties.

Let us assume that, as good chemists, you accept the experimental evidence and agree that benzene really is stable in air, does not polymerize, and undergoes electrophilic substitution reactions. Then let us suppose that in your next examination you are asked to predict the properties of cyclooctatetraene, the next higher homologue of benzene.


Cyclooctatetraene

Not to be caught twice, you would suggest that, as a homologue, it would resemble benzene—it would not add bromine and would be stable to oxidation and to polymerization. And, of course, you would be wrong again. Cyclooctatetraene might well be called a superalkene; anything that ethylene can do it can do better and often with some extra complications as well.

The chemistry of completely conjugated cyclic polyalkenes is evidently not straightforward. A glib answer to the difference between benzene and cyclooctatetraene might well be "ah, but benzene is aromatic". What does this mean? For many people the answer is simple—benzene has a benzene ring, cyclooctatetraene does not.

Indeed, from the middle of the 19th century to the middle of the 20th century, *aromatic* was to all intents and purposes

synonymous with *benzenoid*. Although the term *aromatic* was used to describe the chemistry of benzene derivatives, it was not usually specified precisely whether this referred to structural features, *i.e.*, the presence of a benzene ring, or to its chemical properties, *e.g.* the tendency to undergo substitution rather than addition reactions. A compound either had or had not a benzene ring included in its structure and behaved accordingly.

Difficulties only began to arise when some hydrocarbons were recognized which had properties that were felt to be like those of benzene and "aromatic"—without any specific definition of this term—but whose structures were found not to include benzene rings. The first examples of such compounds were the azulenes.
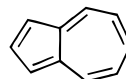
Azulene

Such compounds came to be called *non-benzenoid aromatic compounds*, but the fundamental concept of aromaticity was still not really defined. The name itself indicates a paradox.

Perhaps the fundamental problem was whether the terms aromatic and aromaticity are defined by structural features, which may include electronic features, or by the ability of a compound to undergo or, alternatively, to resist certain types of chemical reactions. In fact the term "aromatic" is remarkable in that during more than a century of use many different meanings and interpretations have been ascribed to it. Even more striking is the fact that this term is still commonly used by chemists, yet it has no firmly defined meaning, and, indeed, different persons may imply quite different things in using it.

Let us consider the origins of the term. It was used first in the early part of the 19th century to describe compounds which had aromatic odors (O.E.D. *aroma*: fragrance, sweet smell; subtle pervasive quality [Gk.]) and had been isolated from volatile plant oils, e.g., benzaldehyde (oil of bitter almonds), cymene (oil of caraway), methyl salicylate (oil of wintergreen), anethole (aniseed oil), and many others. The term also served to distinguish these compounds from other compounds, called fatty compounds (later, aliphatic compounds, *aliphatos*, Gk., fat) derived from fats.

It was soon noticed that many of these *aromatic compounds* contained relatively more carbon than the aliphatic compounds. In the 1860s Kekulé described them as "kohlenstoffreichere Verbindungen" (carbon-richer compounds). It also came to be recognized that these compounds were all in some ways derivatives of benzene.

In 1865 Kekulé set out the main differences between aromatic and aliphatic compounds as follows:[1]

"If we wish to give an account of the atomic constitution of aromatic compounds, we are bound to explain the following facts:

(1) All aromatic compounds, even the most simple ones, are relatively richer in carbon than the corresponding compounds in the group of fatty bodies (*i.e.*, aliphatic compounds).

(2) There are a large number of homologous substances among the aromatic compounds as there are among the fatty substances.

(3) The most simple aromatic compounds contain at least six atoms of carbon.

(4) There is a certain family likeness among all the aromatic substances and their derivatives; they all belong to the group of "aromatic compounds".

(5) In situations where vigorous reactions take place, a portion of the carbon is often eliminated, but the resultant product contains at least six atoms of carbon. Decomposition usually stops with the formation of these products, except when the organic groups are completely destroyed.

These facts justify the supposition that all aromatic compounds contain a common group, or, it may be said, a common *nucleus* consisting of six atoms of carbon. In this nucleus a more intimate combination of the carbon atoms takes place—this is the cause for the aromatic bodies being relatively rich in carbon.

As a result, the term aromatic was appropriated, apparently unintentionally, to convey a structural meaning, namely a *derivative of benzene*, rather than its hitherto purely descriptive meaning.

No sooner had Kekulé put forward these ideas than Erlenmeyer suggested that the concept of *aromaticity*, if used at all, should be based on chemical properites and refer to compounds which had similar chemical behavior rather than to compounds which had common structural features.[2] (In fact Erlenmeyer suggested that the use of the term aromatic should be discontinued). Thus, from the very beginning there was disagreement and confusion about the meaning of the term aromatic, a confusion which continued but was usually satisfactorily dealt with by being ignored.

At about the same time the structure of benzene was established by a number of chemists, including Couper, Kekulé, Loschmidt, and the so-called Kekulé formula, with three conjugated double bonds in a six-membered ring, was adopted. It was fully appreciated that this formula was inadequate to explain the chemistry of benzene and that an average of the two possible cyclohexatriene structures was somehow involved, although not explained.
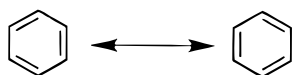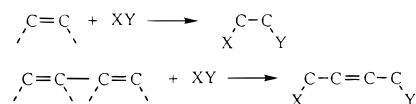

Alternative formulations for benzene were proposed, including one with six "extra bonds" directed toward the center of the ring.


In 1890, Bamberger, who preferred this type of formula, suggested that the special properties of benzene were associated with the fact that benzene had *six* "potentielle Valenzen" and that aromatic character was associated with this particular number.[3] This represents a foreshadowing in pre-electronic terms of the later concept of the aromatic sextet of electrons.

The next major step came in 1899, with Thiele's application of his theory of "residual affinities" or "partial valences" to the structure of benzene.[4] He had used this concept to describe addition reactions of alkenes and also to explain conjugate addition in conjugated dienes:

Thiele applied these ideas to the structure of benzene and suggested an alternative formulation which very much anticipates the inscribed circle formula:
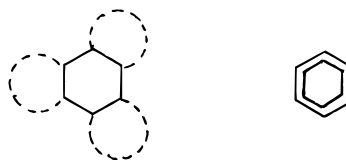
He also specifically commented that in benzene "the three single bonds cannot be distinguished from the three double bonds".

The first specific connexion of aromaticity with the presence of six electrons marks one of the major steps forward in the story and this originated in St. Andrews in the early 1920s. Armit and Robinson stated that compounds which are generally regarded as aromatic are characterized by "reduced unsaturation and the tendency to retain the type" (*i.e.*, to undergo substitution rather than addition reactions).[5] They added "the explanation is obviously that six electrons are able to form a group which resists disruption and may be called the aromatic sextet".[5] They also suggested the inscribed circle (poached egg) formula for benzene:


In addition they recognized that six presented a particularly favorable group of electrons and that the totally different chemical nature of cyclooctatetraene indicated that a group of eight electrons was not favored in the same way.[5]

The development of quantum mechanics in the 1920s led to the modern era of aromaticity which was initiated by the publication of Hückel's rule in 1931.[6] Hückel suggested that "amongst fully conjugated, planar, monocyclic polyolefins, only those possessing $(4n+2)$ π-electrons, where n is an integer, will have special stability". Since then a variety of more refined theoretical treatments have been made but will not be discussed here. Hückel's treatment is a simplification of the truth and has been extensively questioned, but, whatever its theoretical shortcomings it generally works, and it has had an enormous influence on organic chemistry. In recent years, some authors (e.g., Shaik, Hiberty, and Vollhardt) have suggested that this approach puts the cart before the horse and that the delocalization of π-electrons in benzene

follows from the symmetric nature of the σ-framework, but this view is not accepted by some other chemists. It is always possible that it is not a horse/cart but a chicken/egg situation. Much work has been inspired and initiated as a result of considerations of the concept of aromaticity.

A prime example is provided by the way that this has led to a great deal of work on cyclic polyenes other than benzene. At the end of the 19th century, chemists wondered whether or not these cyclic polyenes would have "aromatic" properties resembling those of benzene. This inspired attempts to synthesize its higher and lower homologues, cyclooctatetraene and cyclobutadiene.


Cyclooctatetraene   Cyclobutadiene
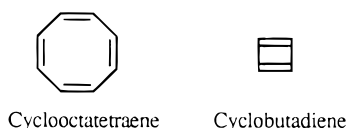
Willstätter preprared cyclooctatetraene in 1911−1913, by a tedious synthesis starting from the alkaloid ψ-pelletierine, extracted laboriously from pomegranate bark.[7] The product proved to be very unlike benzene, polymerizing readily and easily undergoing addition reactions. This lack of "aromatic" properties surprised most organic chemists at the time for there was a general expectation that cyclic systems of formal alternate double and single bonds would behave like benzene. In order to reationalize their surprise, for more than 30 years some chemists questioned the work and the structure of the product. Most objections were based on what appeared to the objectors to be the close similarities between the properties of Willstätter's product and those of styrene. In 1945 the Western Allies found that during the Second World War a simple synthesis of cyclooctatetraene, from acetylene, had been devised in Germany and that it had been produced in substantial amounts.[8] The authenticity of the original product was vindicated, and the original synthesis was repeated and found to be correct in all particulars.

One of the longest running sagas of organic chemistry was the attempted preparation of cyclobutadiene, a molecule with a deceptively simple structure. First attempts were described in 1894;[9] many others followed, and it was not until 1965 that a sample was eventually obtained and trapped *in situ* by reaction with dienophiles.[10]

With the benefit of hindsight this inaccessibility appears to be totally reasonable. Its high chemical reactivity, which prevented its obtention, is entirely consistent with its being a 4π-electron system and a highly strained molecule.

Although Hückel's work appeared in 1931, it was rather overlooked by many organic chemists for nearly 20 years, partly, no doubt, because of the intervention of the Second World War. In the 1950s there was an explosion of work based on the ideas it presented, in particular to prepare the appropriate compounds to test its validity.

Perhaps foremost among such work was the preparation and investigation, especially by Sondheimer and his colleagues, of a series of larger ring conjugated polyenes, now described as *annulenes*, and the recognition that [14]annulene and [18]annulene indeed had properties that could allow them to be classified as aromatic.[11] In addition to cyclic polyenes, cyclopolyenynes were also prepared and shown to have properties appropriate for conjugated (4n+2) π-electron systems.

[14]annulene   [18]annulene

trisdehydro[18]annulene
(a cyclooctadecahexaenetriyne)
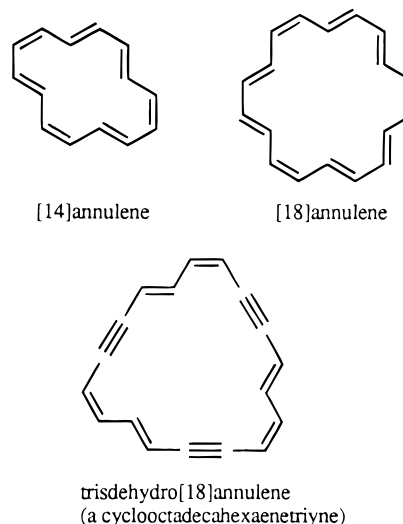
Removal of a proton from cyclopentadiene to provide a cyclopentadienide anion

cyclopentadienide ion

or removal of a hydride ion from cycloheptatriene to provide a cycloheptatrienium, or tropylium, cation

cycloheptatrienium **or** tropylium cation
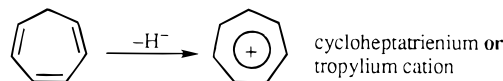
should provide ionic species in which six π-electrons could be delocalized around the rings, *i.e.*, they should be "aromatic".

The cyclopentadienide anion had in fact been described by Thiele in 1901.[12] The salt spontaneously inflamed in air, in this no way resembling benzene but, on the other hand, behaving in a not unreasonable way for a reactive carbanion. But away from air and moisture the cyclopentadienide salt was fully stable, as predicted by Hückel's rule; this had also been commented upon earlier and the stability ascribed to its having an aromatic sextet.[13]

The cycloheptatrienium cation had also been prepared but unintentionally and unwittingly in 1891.[14] This totally escaped recognition until 1954, when its preparation was repeated and its structure proved.[15] It satisfied what was expected of it in being stable and diatropic, but, not surprisingly as a cation, it did not undergo typical aromatic electrophilic substitution reactions.
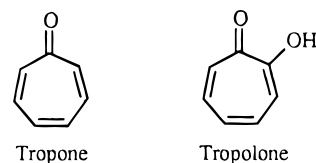

Tropone   Tropolone

Prior to the rediscovery of the tropylium ion, other cycloheptatriene derivatives, namely tropone and tropolone, were prepared and thought to be examples of dipolar derivatives of the cycloheptatrienium ion with positive charge on the seven-membered ring and a negative charge on the carbonyl oxygen atom. This is now regarded as being an unsatisfactory interpretation of their structure, tropone being a fairly normal nonplanar unsaturated ketone and tropolone

an extended or vinylogous β-diketone and carboxylic acid, with a push−pull electronic system linking the carbonyl and hydroxyl groups and **not** involving the C(1)−C(2) bond:
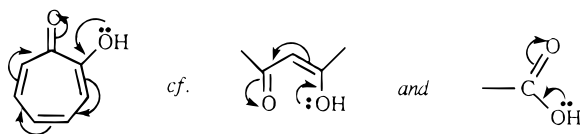
All the above examples are ones where bench chemistry has been directly inspired by Hückel's rule. The rule has also been followed by many other theoretical studies of aromaticity using ever more refined and sophisticated theoretical methods.

The highly important Woodward−Hoffmann rules can also be regarded as having their origins in concepts of aromaticity. In 1939 Evans and Warhurst put forward the concept that the stabilization of cyclic polyenes which derives from circuits of $(4n+2)$ π-electrons might also be applied to cyclic transition states,[16] drawing a comparison between the structure of benzene and that of the transition state of a Diels−Alder reaction:
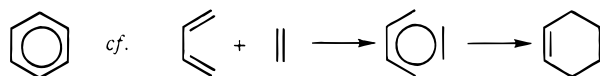

Other pericyclic reactions can be regarded similarly, in terms of aromatic transition states.

There are many other studies in which aromaticity is of vital importance, including applications in applied chemistry. Technologically there is much interest in organic conductors, and aromatic systems and an understanding of their nature are playing a large role in this field, especially compounds having stacked polycyclic rings. Literally more vitally, electron-transfer is being more and more recognized and studied as a vital part of biological processes, and the role of aromatic polypyrroles as in chlorophyll, haem, vitamin B_{12}, etc., excites much interest and involves their aromatic nature.

I was invited to personalize this section by showing how an interest in concepts of aromaticity had inspired some of my own chemical work. One obvious instance is that, inspired by W. Baker, one of the pioneering masters of the field, I became interested in the whole concept and from this resulted three books that I have written, two on non-benzenoid aromatic compounds and one on the more general concept of aromaticity.[17]

It also directly prompted much of my research activities. In the early 1950s various chemists, many of them American, were busily producing new "aromatic" derivatives of cycloheptatriene, including the compounds then thought to be dipolar derivatives.

I thought it was time that Britain made some contributions, and in 1955 we prepared the first unquestionably dipolar "aromatic" compound, a dipolar derivative of the cyclopentadienide ion:[18]

Pyridinium cyclopentadienylide
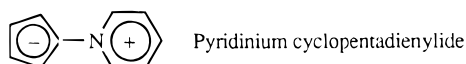
This compound showed the aromatic properties expected of it, both chemically and spectroscopically, and, unlike tropone,

it really was a zwitterionic non-benzenoid aromatic compound, dipole moment = 13.5D.

We also very naively thought that it would be nice to prepare some azatropylium derivatives, but instead we got side-tracked into a much more interesting class of compounds that had seven-membered ring cations but did not have complete cyclic conjugation, the 2,3-dihydro-1,4-diazepinium salts:[19]
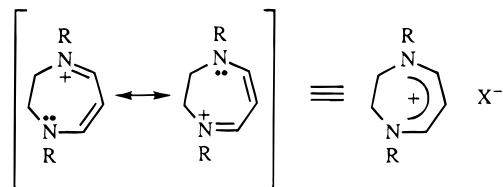
The conjugated vinamidinium system of six π-electrons in many ways closely resembles benzenoid compounds; they have even been described sometimes as quasi-aromatic compounds. These compounds have provided us with more than 40 years of both fun and interesting chemistry, forever turning up unexpected but highly entertaining chemistry, and are still continuing to do so.

As an example, although the conjugation in the ring is not completely cyclic, this conjugated system behaves in many ways just like a clasical aromatic system, in regards to its stability, spectra, structure, and chemistry. Although cations, they very rapidly undergo electrophilic substitution, *e.g.*, halogenation, nitration. They do many other interesting things not directly associated with aromatic behavior, but this is not relevant here.

From the foregoing discussion it may be seen that "aromaticity" has provided, still provides, and will continue to provide stimulation for both organic and theoretical chemists.

All chemists use the term "aromatic" widely, yet different individuals still have differing ideas and feelings of exactly what they mean by it, the one unifying basis for these ideas being that an aromatic compound is "like benzene". But how and in what way? As mentioned earlier, historically there have been two different approaches, one based on structure, the other on properties, as embodied in the early suggestions of Kekulé and Erlenmeyer.

Structural features could concern atomic or electronic structure. It is commonly tacitly assumed that aromatic molecules are cyclic, so this provides one unifying feature. The use of the term *non-benzenoid aromatic* implies that the structural unit is not limited to a six-membered ring. From Hückel's theory all cyclic conjugated polyenes having $(4n+2)$ π-electrons might be classified as aromatic (and those having $4n$ π-electrons as antiaromatic). This would provide a structural definition but not necessarily a guide as to whether or not they resembled benzene−and many of them do not to any appreciable extent. Other factors, for example steric, may supervene and render the system very unlike benzene. So this type of terminology and definition does not necessarily bring together compounds of similar chemical properties which bench chemists might regard as aromatic.

It is appropriate to consider what typifies benzene as an aromatic compound. Largely for historic reasons, the

properties which had until recently been taken primarily into consideration were chemical properties, such as

thermal stability
resistance of the ring to oxidation
electrophilic substitution, rather than addition, reactions
modifying effects on substituent groups

The problem with any criterion based on chemical properties is that it embraces a very wide range of different reactions and types of reaction, and different compounds may resemble benzene in some ways but may differ in other, and it is effectively impossible to lay down any precise criterion. An excellent example of the problem is provided by the cyclopentadienide anion, as mentioned earlier.

Thermodynamic stability is another possible basis, and it has been proposed that cyclic conjugated systems may be considered to be aromatic if cyclic delocalization makes a negative contribution to their heat of formation.[20] Once again there are problems in providing uniform standards. These include the difficulty often involved in obtaining reliable data and in finding suitable reference compounds with which they may be compared. Furthermore, although delocalization may be an important factor in contributing to the overall stability of a conjugated cyclic polyene, other contributing factors may sometimes nullify or override its effect as, for example, steric factors do in the case of [10]annulene. In addition, criteria based on thermodynamic stability may not necessarily provide the same answer as those based on chemical reactivity.

The criteria presently most favored are based on physical evidence for delocalization of π-electrons, in particular the equalizing of lengths of bonds which form the ring, and the induction of ring currents when such molecules are exposed to magnetic fields. Complete cyclic delocalization of π-electrons in a homocyclic ring should lead to all the bonds being of equal length, as in the case of benzene, where all the bond distances are 1.397 pm. But even here care is needed. Substituents in a ring cause divergencies in bond lengths, as may crystal forces. These divergencies are usually of limited extent but may sometimes be quite appreciable. Even so, measurements of bond distances do provide excellent information on the extent of electron delocalization in molecules, but on occasions there still remains a subjective contribution to the assessment.

Similarly ^{1}H-NMR spectra can provide valuable information, with cyclic $(4n+2)$ π-electron systems giving rise to diatropic ring currents and $(4n)$ systems giving paratropic ring currents which lead, respectively, to deshielding and shielding effects on exocyclic protons attached to the ring. Some 30 years ago a suggestion was made that "we can define an aromatic compound......as a compound which will sustain an induced diamagnetic ring current".[21] But does this diatropicity necessarily correlate with what is felt in chemical terms to be aromaticity? On the whole, modern practice defines molecules as diatropic, paratropic, or atropic, and the further jump to describing them as aromatic, antiaromatic, or non-aromatic is thereby carefully avoided. It has also been pointed out that, because other factors may affect chemical shifts, diamagnetic susceptibility exaltation is a better criterion.[22,23] The following definition has been proposed:[23] "Compounds which exhibit significantly exalted diamagnetic susceptibility are aromatic. Cyclic delocalisation

Chart 1
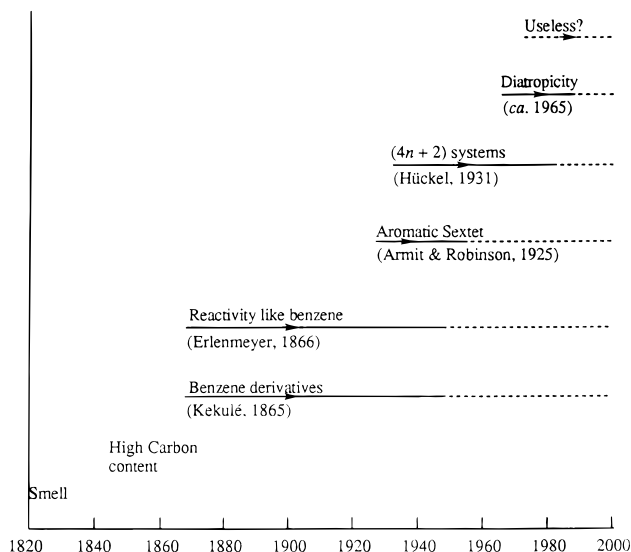
may also result in bond length equalisation, abnormal chemical shifts and magnetic anisotropies, as well as chemical and physical properties which reflect energetic stabilisation."

In the foregoing text we have been looking at various different properties which have come to be associated with aromaticity—stability, chemical reactivity, physical structure, and magnetic properties. The often unstated factor underlying all these observations is "does it or does it not resemble benzene". The decision often becomes increasingly complex as information multiplies. Evidence from different aspects may be mutually conflicting, and, even when it is relatively consistent, the final decision may depend upon the predisposition of the investigator rather than on firmly defined criteria.

Binsch has commented:[24] By gaining in generality aromatic character grows steadily more diffuse and qualitative until we are ultimately left with chemical intuition as the only test of its validity. On the other hand attempts to reduce aromaticity to an observable seem to result in definitions that are too narrow to be acceptable to the chemist.

He added that this is not an atypical state of affairs in chemistry.

Maier, in a review,[25] provided Chart 1 illustrating the changes of meaning and interpretation which have been associated with the terms "aromatic" and "aromaticity" in more than a sesquicentenary of use. He concluded the review by asking the question "Is the expression 'aromatic' actually useless?" The article is written in German, and the answer supplied is "jein".

Wherever the terms **aromatic** and **aromaticity** go in the future—out of the window, to glorious heights, or (and perhaps more likely) if they remain as cozy, not too readily demarcated concepts, the debt that chemistry presently owes to them is huge, for the intellectual debate and, perhaps even more important, for the amount of chemistry, especially practical but also theoretical, which they have stimulated is enormous and can never be overrated. The subject continues to thrive and have applications undreamed of by the early

workers, and there are almost certainly new aspects just waiting to appear and for you or me or someone else to notice them. The very uncertainty involved in the concept provides a stimulus and excitement which would be lacking if there were a cut-and-dried and simple explanation which answered all our queries.

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