Keep Going with Cyclooctatetraene!

Addison Ault

Abstract

This paper shows how some simple properties of cyclooctatetraene can indicate important ideas about the structure of cyclooctatetraene. Its heat of hydrogenation indicates no significant stabilization by delocalization of electrons, and its alternating carbon-carbon bond lengths are consistent with the presence of alternating “ordinary” single and double bonds. The nonplanar nature of cyclooctatetraene is conclusively indicated by the diastereotopic nature of the methyl groups in its dimethylcarbinyl derivative, illustrating one way that NMR can reveal subtle details of molecular structure. Finally, the Diels–Alder reaction provides a simple but elegant illustration of how reaction mechanisms can be deduced.

Keywords

Organic Chemistry; Aromaticity / Aromatics; NMR Spectrometry; Mechanisms; Pericyclic Reactions; Teaching / Learning Aids

Supplementary Materials

No supplementary materials available

Full Text

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Addison Ault
Department of Chemistry, Cornell College, Mount Vernon, Iowa 52314; *aault@cornell-iowa.edu*

The article by Cindy Samet (*1*) has inspired me to present some of the additional interesting properties of cyclooctatetraene. Although most of the properties of benzene are well known, many of the corresponding properties of cyclooctatetraene are less familiar. In this paper I summarize and compare some of these properties in order to show how they lead to quite different conclusions about the structure and reactivity of these molecules.

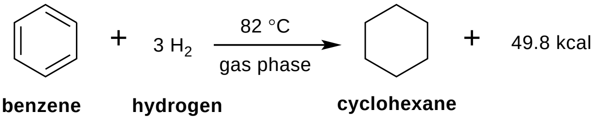
Experimental Criteria for Aromaticity

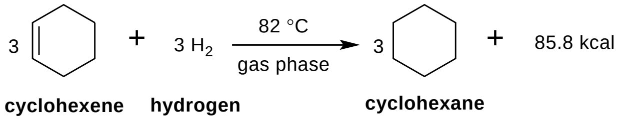
The term *aromatic* is now used to refer to neutral molecules or ions that exhibit a combination of the ground-state properties that characterize benzene. These properties are (i) relative thermodynamic stability, (ii) non-alternation of the lengths of the bonds in the ring, and (iii) the induction by a magnetic field of a diamagnetic ring current. While benzene shows extra stability, non-alternation of bond lengths, and a diamagnetic ring current, cyclooctatetraene shows quite a different set of characteristics. We therefore conclude that cyclooctatetraene is not aromatic.

Relative Thermodynamic Stability

One way by which the aromatic character of a substance can be established experimentally is to show that the substance is more stable than an appropriate reference compound.

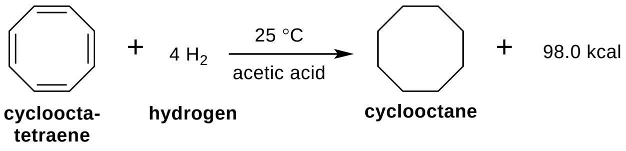
For example, the reduction of one mole of benzene to one mole of cyclohexane by catalytic hydrogenation releases 36 kcal less energy than the reduction of 3 moles of cyclohexene to 3 moles of cyclohexane:

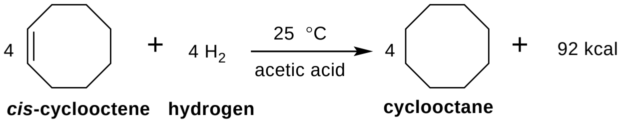




This comparison indicates that the three benzene “double bonds” are not equivalent to three “cyclohexene-like” double bonds. Apparently there is something special about three conjugated carbon–carbon “double bonds” in a 6-membered ring.

In contrast, when the heat of hydrogenation of 1 mole of cyclooctatetraene is compared to the heat of hydrogenation of 4 moles of *cis*-cyclooctene, the near equality of the enthalpy changes indicates that a system of alternating double and single bonds in an 8-membered ring is no more stable than an equal number of isolated double bonds in an 8-membered ring:

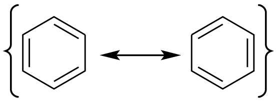




Non-alternating Bond Lengths

A second way by which the presence of aromatic character can be deduced experimentally is to show that the bonds of the ring system do not alternate in length.

This has been shown to be true of benzene, a result that is consistent with the representation of benzene as a resonance hybrid of two equivalent contributing forms:

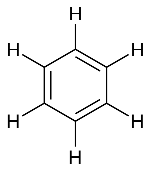


benzene
carbon–carbon bond length = 1.39Å

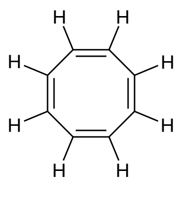
On the other hand, the ring bonds of cyclooctatetraene have been determined by electron diffraction methods to alternate in length, the longer bonds being similar in length to a typical carbon–carbon single bond (1.48 Å) and the shorter bonds being similar in length to a typical carbon–carbon double bond (1.34 Å).

Diamagnetic Ring Currents

A third experimental criterion for the presence of aromatic character is the induction by a magnetic field of a diamagnetic ring current. For example, the resonance of the 6 equivalent protons of the aromatic compound benzene appear in the proton NMR spectrum as a singlet at $\delta = 7.20$, whereas the resonance of the 8 equivalent protons of cyclooctatetraene appear at $\delta = 5.76$, or at essentially the same chemical shift as the resonances of the vinyl protons of cyclohexene and cyclooctene:



benzene
singlet at $\delta = 7.20$ in HNMR
deshielded by a diamagnetic
ring current



cyclooctatetraene
singlet at $\delta = 5.76$ in HNMR
typical vinyl chemical shift

The fact that the resonance of the benzene protons appears at lower field (smaller $\mathbf{H}_{ext}$) than those of vinyl protons implies that the aromatic protons are less shielded than typical vinyl protons. This deshielding effect is explained by the induction of a circulation of electron density in the π electron system in the aromatic compound. In any orientation of the aromatic ring with respect to the direction of the external magnetic field, $\mathbf{H}_{ext}$, the π electrons will circulate in such a way as to produce a small magnetic field that will oppose the external field.

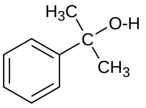
This effect, however, will be largest when the plane of the ring is perpendicular to the direction of $\mathbf{H}_{ext}$. The result is that the predominant shielding effect will be that which results from this particular orientation of the aromatic ring. This means that the net effect of the induced magnetic lines of force resulting from the circulation of the π electrons will oppose $\mathbf{H}_{ext}$ inside the ring but will augment $\mathbf{H}_{ext}$ outside the ring.

Because the protons of benzene are in the region of space where $\mathbf{H}_{shielding}$ augments $\mathbf{H}_{ext}$, they actually experience a deshielding effect; $\mathbf{H}_{ext}$ can be less for resonance to occur. Thus nuclei within or above or below an aromatic ring should be relatively shielded, whereas nuclei outside and more or less in the plane of the ring should be deshielded.

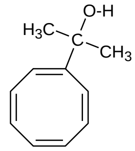
Since the induced circulation of π electron density in benzene creates a magnetic field that opposes $\mathbf{H}_{ext}$ inside the ring, it is called a *diamagnetic effect*. It is this diamagnetic effect that is characteristic of an aromatic system of π electrons.

The Shape of the Cyclooctatetraene Molecule

The planar nature of the benzene ring and the nonplanar nature of the cyclooctatetraene ring are indicated by the contrasting appearances of the proton NMR spectra of their dimethylcarbinol derivatives. Whereas phenyldimethylcarbinol shows a single peak in the methyl region of the proton NMR spectrum, the corresponding cyclooctatetraenyldimethylcarbinol shows two peaks.

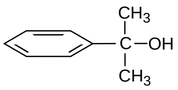


phenyldimethylcarbinol
coincident methyl singlets
enantiotopic methyl groups

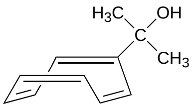


cyclooctatetraenyl-dimethylcarbinol
non-coincident methyl singlets
diastereotopic methyl groups

In the benzene derivative, the methyl groups have exactly the *same* chemical shift, and so they must be *enantiotopic*. This is consistent with the idea that the benzene ring is flat. In the cyclooctatetraenyl derivative, however, the methyl groups have *different* chemical shifts, and so they must be *diastereotopic*. The cyclooctatetraenyl ring therefore cannot be flat. A “tub” shape has been proposed for cyclooctatetraene:

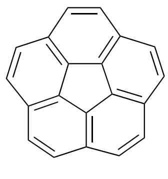


phenyldimethylcarbinol
coincident methyl singlets
enantiotopic methyl groups
ring is planar



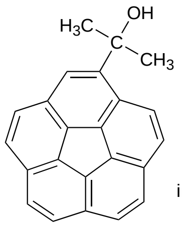
cyclooctatetraenyl-dimethylcarbinol
non-coincident methyl singlets
diastereotopic methyl groups
ring is "tub" shaped

It is interesting to see that this same “test” for planarity has been used more recently to establish the nonplanar nature of corannulene:



corannulene

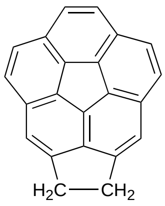
Although the 300-MHz proton NMR spectrum of corannulenyldimethylcarbinol shows only a single sharp peak for the resonance of the two methyl groups at room temperature, the same sample at −90 °C gives a spectrum that shows singlets at different chemical shifts for the two methyl groups (*2*).



corannulenyldimethylcarbinol
noncoincident methyl singlets at −90 °C
coincident methyl singlets at room temperature
diastereotopic methyl groups
molecule is “bowl”-shaped
inversion of the bowl is rapid at room temperature

These proton NMR spectra are explained by proposing that corannulene is not flat but has a “bowl” shape, which accounts for the noncoincident nature of the methyl resonances at the lower temperature, and that the barrier to “inversion” of the bowl is so low that this process is rapid (estimated to take place 200,000 times per second) at room temperature. Thus the diastereotopic methyl groups become chemical shift equivalent on the average at room temperature.

More recently, cyclopentacorannulene has been prepared and its proton NMR spectrum determined (*3*).

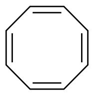


cyclopentacorannulene
AA′BB′ pattern for the four methylene protons
2 enantiotopic pairs of diasterotopic protons
molecule is “bowl”-shaped

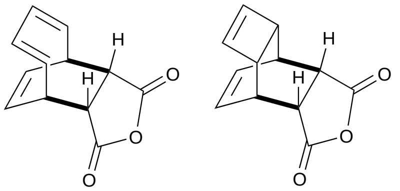
Again, the fact that the four methylene protons are not chemical shift equivalent indicates that the ring is not flat. Further, the fact that this nonequivalence persists to the highest temperature of observation, 135 °C, indicates that cyclopentacorannulene has a much higher barrier to inversion than does corannulene itself.

More Chemical Properties of Cyclooctatetraene

As a diene of sorts, cyclooctatetraene was expected to undergo Diels–Alder reactions. When maleic anhydride was used as the dienophile, however, the product obtained was not the product that might have been expected:

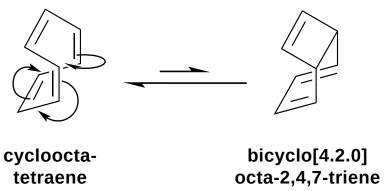


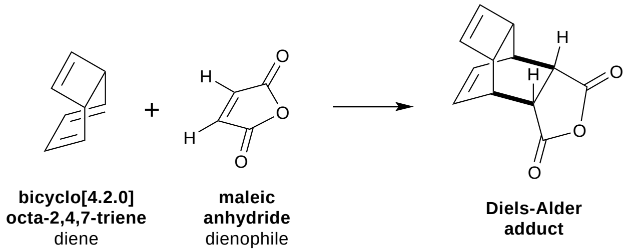
cycloocta-tetraene



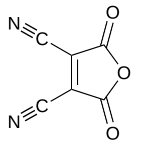
Diels-Alder adducts with maleic anhydride
not formed
formed

Apparently cyclooctatetraene reacts by way of the intermediate formation of a ring-closed isomer that is produced by an electrocyclic isomerization:



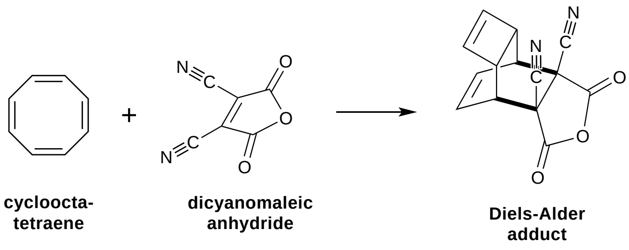


Evidence to support this interpretation was provided by a study of the reaction of cyclooctatetraene with the extremely reactive dienophile dicyano-maleic anhydride (*4*):

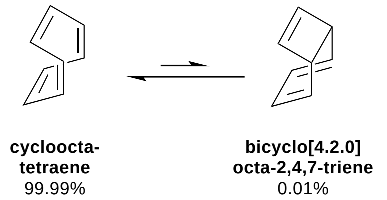


dicyanomaleic anhydride

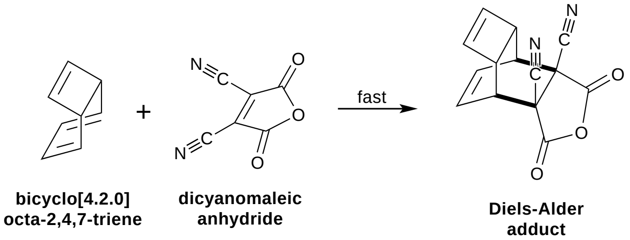
The study showed that the rate of reaction of cyclooctatetraene with this extremely reactive dienophile approached a constant maximum value as the concentration of the dienophile was increased.



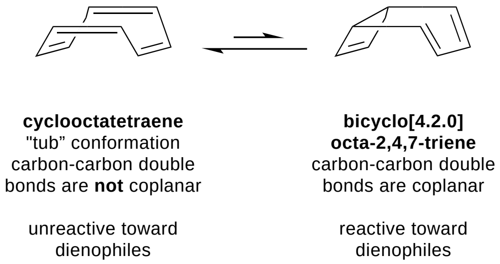
At high concentrations of the very reactive dienophile, the rate must come to depend upon a process that does not involve the dienophile, and this process most likely is the electrocyclic isomerization reaction



electrocyclic isomerization reaction
rate-limiting at high anhydride concentrations



As a result of this study, the concentration of the ring-closed isomer in equilibrium with cyclooctatetraene is estimated to be about 0.01%. The ring-closed isomer must therefore be much more than 10,000 times more reactive in the Diels–Alder reaction than cyclooctatetraene itself. Presumably this is because the diene double bonds in the ring-closed isomer are much more nearly in the coplanar conformation required for reaction than are the double bonds of cyclooctatetraene itself, which exists in a tub conformation:



An alternative path, the “ordinary” Diels–Alder reaction with cyclooctatetraene followed by electrocyclic isomerization to the observed product, can also be ruled out by the requirements for conservation of orbital symmetry.

Summary

We have summarized the way in which simple properties of cyclooctatetraene can indicate important ideas about the structure of cyclooctatetraene. Its heat of hydrogenation indicates no significant stabilization by delocalization of electrons, and its alternating carbon–carbon bond lengths are consistent with the presence of alternating “ordinary” single and double bonds. The nonplanar nature of cyclooctatetraene is conclusively indicated by the diastereotopic nature of the methyl groups in its dimethylcarbinyl derivative, illustrating one way that NMR can reveal subtle details of molecular structure. Finally, the Diels–Alder reaction provides a simple but elegant illustration of how reaction mechanisms can be deduced.

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