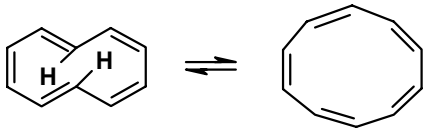
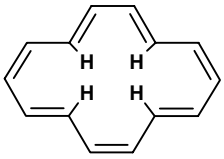
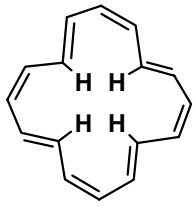
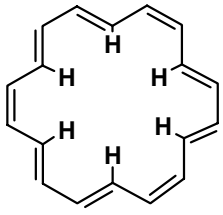
NMR EVIDENCE FOR AROMATICITY

Aromatic compounds, because the molecular orbitals permit the electrons to move in a circle around the whole ring, are strongly diamagnetic: they respond to a magnetic field with a "ring current" that produces a field through the center of the molecule opposing the applied field. The protons attached to the outside of the ring experience the tails of this magnetic field - in the same direction as the applied field. Thus aromatic compounds have chemical shifts lower than those of alkenes. The difference is small for benzene and not very convincing. What would be convincing is a proton in the center of the ring, experiencing the full strength of the diamagnetic ring current, at much higher field than alkenes. Physical organic chemists, eager to explore this test of the Huckel quantum mechanical approach to molecular orbitals, made the annulene molecules below and examined their chemical shifts. The molecules turned out to be conformationally flexible: the stabilization of the flat conformation by π interaction is offset by steric crowding of atoms inside the ring.

Superficially, this seems to have nothing to do with whether there are 4n or 4n+2 electrons in the ring. However, the Huckel theory predicts that rings with 4n π electrons will have two unpaired electrons. Such molecules are intrinsically magnetic or paramagnetic, and thus should respond to the field like a compass needle, making the field inside the ring larger than the applied field (chemical shift lower) and the field outside the ring smaller (chemical shift higher), exactly the opposite behavior of the diamagnetic 4n+2 systems. *The data below provide convincing evidence for the existence of both aromaticity and antiaromaticity* (only inside hydrogens are shown).

Structure	π Electrons	Temperature	Chemical Shift (# H's)	
	6	all	7.15 (all)	
	10	>- 160 C	5.67 (all)	
	14	+30 C	5.58 (all)	
		- 60 C	0.0 (4) 7.6 (10)	inside outside
	16	+35 C	6.73 (all)	
		- 120 C	10.34 (4) 5.40 (12)	inside outside
	18	+110 C	5.45 (all)	
		- 60 C	-2.99 (6) 9.28 (12)	inside outside