Richard Waack
The Dow Chemical Company
Framingham, Massachusetts

The Stability of the "Aromatic Sextet"

One of the triumphs of organic chemists during the last century has been the explanation of the unusual stability of the "unsaturated" cyclohexatriene[1] and similar molecules. Contrary to other unsaturated systems, cyclohexatriene was found extremely resistant to substitution reactions or skeletal change. The explanation was advanced—because of the pioneering ideas of chemists like Kekulé and Williamson and with the development of electronic theory of valence by Pauling, Robertson, and others—that cyclohexatriene was stabilized by resonance between two identical structures, the real molecule being of intermediate structure. Resonance was attributed to the "mobile" π-electrons, the σ-electrons remaining fixed in localized bonds. Aromaticity became synonymous with the aromatic sextet (1) (of electrons). Hückel's early application of his simplified molecular orbital method to monocyclic conjugated molecules led him to predict that this was only one of several electron groups which confer special stability on such a molecule (2). The extension of resonance to be the complete delocalization of the π-electrons over the whole molecule, with each electron moving in a molecular orbital, brings us to the modern concept of aromatic systems. Our aim in this discussion is to gain an understanding of the Hückel $4n + 2$ rule as it was developed within the framework of simple LCAO-MO theory.[2]

When carbon is hybridized to its trigonal sp^2 state, it can form three equivalent sigma bonds, leaving one p-orbital, containing a single electron, perpendicular to the plane of the three sigma bonds. The overlap of this p-orbital with an identical orbital on an adjacent carbon atom forms a π-bond. A conjugated system consists of a series of sp^2 hybridized carbon atoms linked together by sigma bonds and oriented in such a manner that the p-orbitals are all perpendicular to the plane of the molecule. The p-electrons are free to move over the entire carbon core system. This electron delocalization usually results in a lower total electronic energy, compared to the system in which each electron is assigned to a particular carbon atom or to a particular pair of carbon atoms. Our concern here is with monocyclic conjugated systems.

Chemical experiments have led to the rather surprising fact that monocyclic conjugated polyenes containing a certain number of π-electrons, e.g., 2, 6, 10, etc., are particularly stable. This favored π-electron configuration is given by the formula $4n + 2$, where n is zero or an integer. Benzene with six π-electrons was the first of these "aromatic" molecules encountered by chemists. More recent observations have revealed

that $4n + 1$ and $4n + 3$ electron molecules (radicals) tend to form a "more stable" system through the gain or loss of an electron to form the $4n + 2$ configuration. Physically, the aromatic system is one that can be written in at least two equivalent classical (Kekulé) structures; it is coplanar and its carbon-carbon bonds are of equal length, intermediate between single and double bonds. Chemically, aromaticity is distinguished by a preference toward substitution rather than addition reactions. Although the realization of the unusual stability of a cyclic system of π-electrons was of experimental origin, it can be shown following the principles of molecular orbital theory to be a theoretically predictable fundamental property of such systems. This was one of the substantial successes of the molecular orbital theory as developed by Hückel. It has recently been discussed briefly by Coulson (3) and by Longuet-Higgins (4), but it is such an outstanding example of the information obtained from straightforward molecular orbital calculations that it is worthwhile to discuss it here at greater length.

Let us consider a planar, cyclic system of sp^2 carbon atoms bound together by sigma bonds. The single electron in the p-orbital on each carbon atom is free to move throughout the potential field of the entire carbon core ring. This is shown in Figure 1.
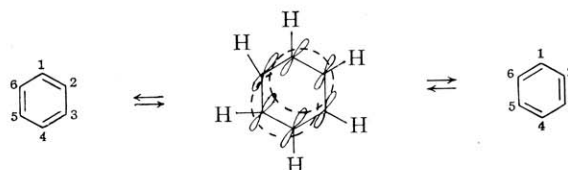

Figure 1. π-Electron system benzene.

Following the Hückel LCAO-MO method (5, 6) the energy of the molecular orbital of each π-electron for molecules composed of any number of sigma bonded carbon cores can be calculated. The energies of the π-molecular orbitals calculated for cyclic molecules composed of 3-, 4-, 5-, 6-, 7-, 8-, 9-, or 10-carbon atoms are represented schematically in terms of the empirical resonance integral, β[3], in Table 1. The number of molecular orbitals obtained is equal to the number of carbon atoms in the molecule. The energy scale increases in the upward direction. A positive energy is bonding, since β is negative and energy is released on forming a bond. The negative energy levels are called anti-bonding, as an electron in a negative energy orbital reduces the energy gained through the delocalization of the electrons. When an electron is in a zero orbital, it neither adds to nor decreases the π-

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[1] Benzene.
[2] Linear combinations of atomic orbitals—molecular orbital.

[3] β has been evaluated from thermochemical measurements of resonance stabilization to be of the order of 17 kcal/mol. 2β is the energy of the π bond in ethylene.

electron energy. This orbital is termed non-bonding. Each orbital can, following the Pauli exclusion principle, contain a maximum of two electrons. In Table 1 these are represented by arrows with the sense of the arrow indicating electron spin. The total π-electron energy for each molecule is obtained by putting the available p-electrons (one from each carbon atom) into the lowest energy molecular orbital etc. until no electrons are left. The total π-energy is the sum of the energies of the occupied orbitals times the number of electrons in each orbital.

Looking first at the 6-carbon-atom molecule, benzene, we see that all six π-electrons can be accommodated in the bonding orbitals. Also, each electron is paired, i.e., each orbital is doubly filled; therefore, benzene has a closed-shell singlet ground state. Looking at the five- and seven-membered rings, which of course represent cyclopentadienyl and cycloheptatrienyl free radicals, we see that each has an unpaired electron. The striking feature is that in the five-membered ring, the unpaired electron is in a *bonding* orbital. The lowest empty orbital available for another electron is this bonding orbital; thus, the addition of one more electron to this system increases the total π-bonding energy—at the same time forming a $4n + 2$ electron system. This accounts for the unusual stability observed for the cyclopentadienyl anion. In the seven-membered ring, the unpaired electron is in an *antibonding* orbital. The loss of this electron increases the total π-bonding energy—again forming a $4n + 2$ electron system. Thus, the remarkable stability observed for the cycloheptatrienyl positive ion is readily understood. Notice that in the $4n + 2$ electron system all the bonding orbitals are filled and each electron is paired with another of opposite spin.

With the three-membered ring[4] and the nine-membered ring,[5] the pattern repeats itself, the gain of an electron in an unoccupied bonding orbital or the loss of an electron from an antibonding orbital resulting in the more stable anion or cation having the "preferred" $4n + 2$ number of electrons. The ten-membered ring having just the number of electrons necessary to completely fill all its bonding π-molecular orbitals would have a closed shell singlet ground state. However, it has not yet been prepared and is expected to be highly destabilized by steric conflict between the internal hydrogen atoms (8). Naphthalene and azulene, in which the bridgehead bond is only a minor contributor to the total resonance stabilization, resemble such a ten carbon atom aromatic molecule. The point to remember is that the π-electron molecular orbitals of conjugated monocyclic molecules[6] varies with the number of carbon atoms such that $4n + 2$ number of electrons completely fill the *bonding* molecular orbitals and produce the largest electron delocalization (resonance) energy.[7]

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[4] Although the unsubstituted species is not known, the sym-triphenylcyclopropenyl cation has recently been prepared and found to have, as predicted, enhanced stability (7).

[5] As yet unknown.

[6] This also holds for polycyclics in which every carbon atom of the conjugated system is on the perimeter of the molecule.

[7] The delocalization energy is the stability gained through electron delocalization in excess of that of a comparable system of alternating single and double bonds. In terms of β it is calculated by summing the occupied energy levels of the molecule times the number of electrons in each energy level and subtracting 2β for each ethylene unit in one of its Kekulé structures. An odd electron localized on a particular carbon atom, as it must be in a Kekulé structure, has an energy of zero β as its contribution to the resonance energy of the molecule.

Table 1. π-Electron Molecular Orbitals of Monocyclic Conjugated Polyenes

		3	4	5	6	7	8	9	10
Number of π-Electrons		4n+3	4n	4n+1	4n+2	4n+3	4n	4n+1	4n+2
Where n =		0	1	1	1	1	2	2	2
Number of Electrons to form 4n+2		Lose 1	Gain or Lose 2	Gain 1	0	Lose 1	Gain or Lose 2	Gain 1	0

The four-membered ring and the eight-membered ring each contain $4n$ π-electrons. As before, we put the available p-electrons into the π-molecular orbitals. The result is that the lower energy orbitals are all doubly occupied. The highest occupied π-orbital which in this case is the doubly degenerate[8] non-bonding orbital, can accommodate four electrons, but only two electrons remain to occupy these *two* energy levels. The most favored distribution is one electron in each orbital with their spins parallel, i.e., a triplet state. Very close in energy are three singlet states, one in which the electrons are opposed in spin but in different orbitals and two where they are opposed in spin and in the same orbital. The result of these four close-lying electronic states is that these $4n$ molecules do not possess a closed shell ground state in the planar delocalized configuration. Molecules not having closed shell ground states are known to be very reactive or unstable.

These $4n$ π-electron molecules may be stabilized by losing two electrons, thus producing the di-cation or gaining two electrons to form the dianion. In this manner they form a closed shell and acquire the $4n + 2$ electron configuration. The gain of two electrons to form the *planar* dianion has been observed for cyclooctatetraene (9). Further correspondence between theory and experiment has also been shown (10).

There is another way this unstable situation can be relieved. The calculation of the π-electron molecular orbitals assumed two things; a planar molecule, and that the electrons were delocalized (i.e., free to move over the entire molecule). If the electrons were to become localized, to form a system of alternating single and double bonds, this energy level scheme would no longer apply and the molecule might become more stable. This has proved to be the case for the eight-carbon ring cyclooctatetraene, which exists in a puckered form consisting of alternating single and localized double bonds, thus having a closed shell ground state. Also because of the localization of the electrons, cyclooctatetraene has only a small fraction of the resonance energy (3–4 kcal) (11) that would be expected from the π-electronic energy levels calculated above, assuming planarity and delocalization. Furthermore, its chemical reactivity is that of a typical unsaturated system and not that of an aromatic system, i.e., cyclooctatetraene readily undergoes addition reactions (12).

The four-membered ring, cyclobutadiene, has as yet resisted all efforts toward its preparation. The simple MO treatment, as depicted here, predicts a triplet ground state for cyclobutadiene (13), but more comprehensive theoretical treatment (14, 15) predicts that if it is prepared, its most stable form will be rectangular having alternating single and double bonds (i.e., localization of the π-electrons as in cyclooctatetraene). Its first electronically excited state would be the square shape triplet (16). Such an intermediate has been observed in the attempted preparation of tetraphenyl-cyclobutadiene (17). This may be interpreted as a triplet ground state as predicted by the simple MO calculations (18), or that the observed species is the first excited state of the rectangular ground state.

This ground state, it is suggested, is vibrationally unstable, so cyclobutadienes may be capable of only transient existence in an excited state (4, 16). The theoretical predictions of stable cyclobutadiene-transition metal complexes (19) has been verified by isolation of several such complexes.

The fundamental theory of $4n$ π-electron molecules has been discussed by Craig (20). He concludes that in such "pseudoaromatic" molecules the notion of resonance is of dubious significance, and they are expected to show marked unsaturation and unequal bond distances.

The enhanced stability of $4n + 2$ π-electron molecules is not expected to continue *ad infinitum* as the ring size increases. As the rings become very large, theory indicates that the most stable configuration is that of alternating bond distances, regardless of the number of π-electrons (21). The large monocyclic polyenes that have been prepared thus far, e.g. $C_{18}H_{18}$ (22) and $C_{30}H_{30}$ (23), are reported to be more stable than their acyclic counterpart, but they do not have aromatic stability. The physical evidence is as yet inconclusive, as their UV spectra are indicative of bond alternation, whereas their NMR spectra indicate aromaticity in the sense of being able to sustain an induced ring current(21).

In summary, the calculation of the π-electron molecular orbitals for planar monocyclic conjugated polyolefins gives an explanation for the observation that the $4n + 2$ number of π-electrons forms a highly stable aromatic molecule. The aromatic stability results from the molecule having its *bonding* molecular orbitals completely filled, thus forming a closed shell ground state. Odd numbered conjugated molecules (which must be radicals) not having this number of electrons tend to stabilize by gaining or losing electrons to attain the $4n + 2$ number, which produces a closed shell and the greatest π-resonance energy. In the $4n$ π-electron molecule, electron delocalization results in a degenerate ground state and so is not expected to enhance its stability. The most favored molecular structure for $4n$ molecules is one of alternating non-conjugated double bonds.

Finally we point out that treatment of aromaticity by the earlier valence bond method predicts aromatic stability for $4n$ systems, and it does not account for the enhanced stability of the ions of $4n + 1$ systems; it is thus not in harmony with the experimental facts.

Bibliography

COULSON, C. A., "Valence," Oxford University, Amen House, London E. C. 4, **1952**.

CARTMELL, E., AND FOWLES, G. W. A., "Valency and Molecular Structure," Academic Press Inc., New York, **1956**.

Literature Cited

(1) ARMIT, J. W., AND ROBINSON, R., *J. Chem. Soc.*, **127**, 1604 (1925).

(2) HÜCKEL, E., "Grundzuge der Theorie Ungesättigter und Aromatischer Verbindungen," Verlag Chemie, Berlin, **1938**, pp. 71–85.

(3) COULSON, C. A., "Chem. Soc. Symposia," Bristol, **1958**, The Chem. Soc., London, Spec. Pub. 12, pp. 91–93.

(4) LONGUET-HIGGINS, H. C., "The Kekulé Symposium, London, 1958, Theoretical Organic Chemistry," Butterworths Scientific Pub., **1959**, pp. 12–13, 17.

(5) HÜCKEL, E., *Z. Physik.*, **70**, 204 (1931); 76, 628 (1932).

(6) COULSON, C. A., AND LONGUET-HIGGINS, H. C., *Proc. Roy. Soc.* (London), **191A**, 39 (1947).

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[8] Having two levels of equal energy.

(7) BRESLOW, R., AND YUAN, C., *J. Am. Chem. Soc.*, **80**, 5991 (1958).

(8) MISLOW, K., *J. Chem. Phys.*, **20**, 1489 (1952).

(9) KATZ, T. J., *J. Am. Chem. Soc.*, **82**, 3784 (1960).

(10) COULSON, C. A., *Tetrahedron*, **12**, 193 (1961).

(11) TURNER, R. T., ET AL., *J. Am. Chem. Soc.*, **79**, 4127 (1957).

(12) RAPHAEL, R. A., in "Non-Benzenoid Compounds," Ginsberg, D., Ed., Interscience, New York, **1959**, pp. 465–74.

(13) ROBERTS, J. D., STREITWEISER A., AND REAGEN, C. M., *J. Am. Chem. Soc.*, **74**, 4579 (1952).

(14) SHIDA, S., *Bull. Chem. Soc. Japan*, **27**, 243 (1954).

(15) LENNARD-JONES, J. E., AND TURKEVITCH, J., *Proc. Roy. Soc. (London)*, **A158**, 297 (1937).

(16) COULSON, C. A., "Chem. Soc. Symposia," Bristol **1958**, The Chem. Soc., London, Spec. Pub. No. 12, pp. 97–100.

(17) FREEDMAN, H. H., *J. Am. Chem. Soc.*, **83**, 2195 (1961).

(18) WAACK, R., Unpublished work.

(19) LONGUET-HIGGINS, H. C., AND ORGEL, L. E., *J. Chem. Soc.*, 1969 (**1956**).

(20) CRAIG, D. P., *Proc. Royal Soc.*, (London), **A202**, 498 (1950); *J. Chem. Soc.*, 3175 (**1951**); *J. Chim. Phys.*, **49**, 143 (1952); *Kekulé Symposium*, London, pp. 20 (**1958**).

(21) LONGUET-HIGGINS, H. C., AND SALEM, L., *Proc. Roy. Soc.*, (London), **259A**, 445 (1960).

(22) SONDHEIMER, F., AND WOLOVSKY, R., *Tetrahedron Letters*, **3**, 3 (1959).

(23) SONDHEIMER, F., WOLOVSKY, R., AND GAONI, Y., *J. Am. Chem. Soc.*, **82**, 755 (1960).