Three-dimensional Aromaticity of Ferrocene

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The conjugated systems of ferrocene and related compounds were constructed using five equivalent 3d orbitals of iron and carbon $2p_z$ orbitals of the cyclopentadienyl or pentadienyl groups. Ferrocene with such a conjugated system was found to have positive resonance energy due to cyclic conjugation, and was characterized as a three-dimensional aromatic species.

Aromatic compounds have cyclic conjugated systems.[1,2] They are usually planar in geometry. In 1978, we showed that the concept of aromaticity can be extended to three-dimensional conjugated systems.[3,4] Graph-theoretical analysis identified tricarbonyliron complexes of olefins and *closo*-boranes as typical aromatics. Many compounds of this kind are in fact very stable, and undergo electrophilic substitution reactions.[5,6] Ferrocene is the most famous organometallic compound. However, its possible aromaticity has not been elucidated theoretically. In this paper, the author intends to resolve this problem by introducing a simplified bonding model of ferrocene[7,8] in combination with our graph theory of aromaticity.[1,2]

Theory

Ferrocene has strong covalent bonding between iron and cyclopentadienyl rings.[9,10] A large number of molecular orbital calculations have shown that the major bonding interactions between iron and rings involve a degenerate pair of iron 3d orbitals (d_{xz}, d_{yz}) and the π bonding orbitals of the rings.[9,10] Overlapping of these 3d orbitals with rings gives a three-dimensional conjugated system.

A convenient way of representing this situation is to use five equivalent hybridized 3d orbitals of iron as described by Powell[11] and by Pauling and McClure.[12] It was Herndon and Agranat who first constructed a Hückel-type molecular orbital model of ferrocene, using five equivalent 3d orbitals of iron.[7,8] We adopt their bonding model in what follows.

The directional character of five equivalent 3d orbitals is drawn in **1**, and overlap with $2p_z$ orbitals of two cyclopentadienyl rings generates a diagram which corresponds very closely to a staggered D_{5d} depiction of ferrocene with ten carbon–iron bonds given in **2**.[7,8] It is graphically shown in **3**, where five hybridized 3d orbitals of iron are represented by short horizontal lines. This indicates that the 3d orbitals can be treated formally as five hetero atoms. Eighteen valence electrons are then accommodated in this delocalized electron network.

The structure of ferrocene in the solid state deviates slightly from the staggered configuration.[13] However, in the gas phase it has an eclipsed configuration.[14] The rings are essentially free to rotate, and the configuration adopted in the crystal is susceptible to packing forces. No intrinsic barrier to internal rotation is predicted from the symmetry consideration of the occupied molecular orbitals.[9] The very low barrier observed may be attributable to van der Waals forces between the rings.[9] This allows us to take a staggered configuration of ferrocene for analyzing the degree of its aromaticity.

The resonance integral between each hybridized iron 3d and carbon $2p_z$ orbitals is set equal to that between two bonded carbon $2p_z$ orbitals. This is essentially the same approximation as adopted by Mingos to rationalize the stability of tricarbonyliron complexes of olefins.[15]

The Coulomb integral for iron 3d orbitals can be written as

$$\alpha = \alpha_c + h\beta_{c-c} \quad (1)$$

Here, α_c is the Coulomb integral for carbon $2p_z$ orbitals; β_{c-c} is the resonance integral between two bonded carbon $2p_z$ orbitals; and h is an appropriate constant. According to the widely accepted extended Hückel molecular orbital model, the Coulomb integral for iron 3d orbitals is -12.63 eV, which is slightly smaller than that for carbon 2p orbitals, -11.40 eV.[16] This implies that h might be positive in sign. However, the Coulomb integral for iron 3d orbitals is here set equal to that for carbon $2p_z$ orbitals. We dare adopt $h=0.0$ in order to have the iron 3d orbitals retain some electron-donating ability. This kind of treatment is required due to the neglect of iron 4s and 4p orbitals. Mingos adopted $h=1.0$ when he modeled conjugated systems of tricarbonyliron complexes of olefins using olefin π systems and only two of the iron 3d orbitals (d_{xz}, d_{yz}).[15] Our graph theory of aromaticity[1,2] was applied to the above bonding model of ferrocene pictured with $h=0.0$.

Results and Discussion

All atomic orbitals forming the ferrocene conjugated system are numbered as shown in **3**. The Hückel-type secular determinant for it can then be written as

$$D(X) = \begin{vmatrix} -X & 1 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & -X & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & -X & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & -X & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 & -X & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & -X & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & -X & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & -X & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & -X & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & -X & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & -X & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & -X & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & -X & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & -X & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 1 & -X \end{vmatrix} \quad (2)$$

This determinant can be expanded into the characteristic polynomial $P(X)$ in this form:

$$\begin{aligned} P(X) &= (-1)^{15}D(X) \\ &= X^{15} - 20X^{13} + 155X^{11} - 4X^{10} - 600X^{9} \\ &\quad + 40X^{8} + 1245X^{7} - 160X^{6} - 1378X^{5} \\ &\quad + 300X^{4} + 760X^{3} - 240X^{2} - 160X + 64. \end{aligned} \quad (3)$$

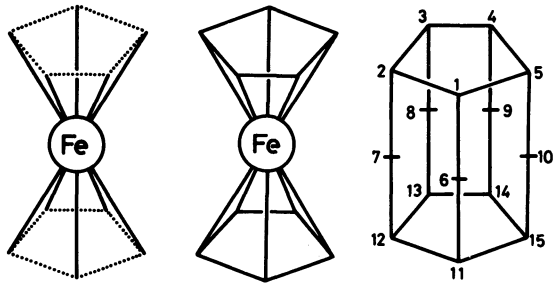
The corresponding reference polynomial $R(X)$ can be constucted graph-theoretically.[1,2] It is expressed as

$$\begin{aligned} R(X) &= X^{15} - 20X^{13} + 155X^{11} - 590X^{9} + 1155X^{7} \\ &\quad - 1112X^{5} + 460X^{3} - 60X. \end{aligned} \quad (4)$$

$R(X)$ has been interpreted as a characteristic polynomial for the olefinic reference structure.

Roots of the equation $D(X)=0$ or $P(X)=0$ represent the orbital energies of the ferrocene conjugated system **3**. They are given relative to α_c and in units of $\beta_{c\text{-}c}$. Total electron energy is equal to twice the sum of the energies of all occupied orbitals. It is $18\,\alpha_c+20.780\beta_{c\text{-}c}$ for this eighteen-electron system. Roots of the equation $R(X)=0$ represent the orbital energies which the ferrocene conjugated system would possess if it were hypothetically olefinic in nature. They are also given relative to α_c and in units of $\beta_{c\text{-}c}$. Total electron energy calculated for this reference structure is $18\alpha_c+20.527\beta_{c\text{-}c}$.

The energy difference between the ferrocene conjugated system and its olefinic reference structure is 0.253β, where β is the absolute value of $\beta_{c\text{-}c}$. This is our way of evaluating the resonance energy arising from cyclic conjugation.[1-4] It follows that the resonance energy of **3** is 0.253β. This positive value indicates that the ferrocene conjugated system is more stable than its olefinic reference structure by this amount. Positive and negative resonance energies represent aromaticity and antiaromaticity, respectively.[1-4] Accordingly, ferrocene is classified as an aromatic compound.



1 2 3

The resonance energy of ferrocene is comparable to that of benzene, 0.273β.[1,2] Considering that ferrocene is about twice as large as benzene, aromaticity of ferrocene, normalized with respect to the molecular dimension, is estimated to be about half that of benzene. In line with this ferrocene has been considered to be aromatic in its chemical behavior.[6,9,10] It is quite analogous in chemical reactivity to benzene. Furthermore, ferrocene is much more reactive toward electrophilic reagents than benzene. It rather resembles more reactive thiophene and phenol. In a previous paper,[17] we showed that more aromatic compounds are generally less reactive toward electrophiles. In this sense, ferrocene is chemically less aromatic than benzene. Theory and experiment thus agree qualitatively for the ferrocene conjugated system.

The resonance energy of a ferrocene-like conjugated system is a function of the h value defined in Eq. 1. It is maximized when h=0.3—0.4, and then takes the value of 0.296β. As far as h is larger than −0.5 but smaller than 1.5, the resonance enrgy stays positive in sign. This indicates that the system stays aromatic. Thus, not only tricarbonyliron complexes of olefins[3] but also ferrocene-like compounds

are highly delocalizable iron-organic systems with a considerable degree of aromatic stabilization.

Someone may depict ferrocene as a combination of two cyclopentadienide ions and one ferrous ion, attributing its aromaticity to the former ions. However, this model is not realistic at all. The resonance energy of the cyclopentadienide ion is 0.317β.[1,2] The resonance energy of ferrocene is much less than twice the resonance energy of this ion. Perturbation by the central iron atom is so great as to remove any simple prediction of aromaticity based on the cyclopentadienide ions only.

The resonance energy of open ferrocene,[18] *i.e.*, bis-(pentadienyl)iron, **4**, can be estimated according to the same procedure. Its conjugated system is similar in shape to that of ferrocene, but two C–C bonds are lacking. For simplicity, this open ferrocene is again assumed to take a staggered configuration. There still are three orientational isomers. They are pictured in **5**, **6**, and **7**. There of course is a possibility of facile rotation of the ligands in solution or in the gas phase.[18]

For isomer **5**, the two types of polynomials are

$$P(X) = X^{15} - 18X^{13} + 126X^{11} - 444X^{9} + 849X^{7} - 882X^{5} + 464X^{3} - 96X \quad (5)$$

and

$$R(X) = X^{15} - 18X^{13} + 126X^{11} - 436X^{9} + 783X^{7} - 698X^{5} + 266X^{3} - 32X. \quad (6)$$

For isomer **6**, the two types of polynomials are

$$P(X) = X^{15} - 18X^{13} + 126X^{11} - 442X^{9} + 832X^{7} - 8X^{6} - 832X^{5} + 36X^{4} + 408X^{3} - 44X^{2} - 76X + 16 \quad (7)$$

and

$$R(X) = X^{15} - 18X^{13} + 126X^{11} - 436X^{9} + 784X^{7} - 704X^{5} + 276X^{3} - 34X. \quad (8)$$

For isomer **7**, the two types of polynomials are

$$P(X) = X^{15} - 18X^{13} + 126X^{11} - 442X^{9} + 839X^{7} - 12X^{6} - 864X^{5} + 44X^{4} + 450X^{3} - 48X^{2} - 92X + 16 \quad (9)$$

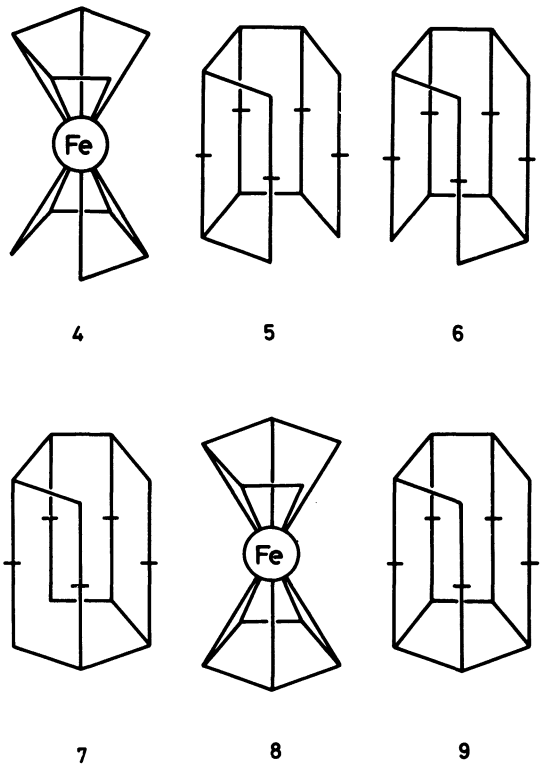
and

$$R(X) = X^{15} - 18X^{13} + 126X^{11} - 436X^{9} + 785X^{7} - 708X^{5} + 280X^{3} - 36X. \quad (10)$$

The resonance energies are then calculated to be -0.189β for **5**, -0.160β for **6**, and -0.071β for **7**. This clearly shows that open ferrocene must be slightly antiaromatic and reactive in nature. In accord with this, open ferrocene is a relatively less tractable material, which readily decomposes to dipentadienyl and ferromagnetic iron byproducts.[18] It decomposed on attempted sublimation.

Wilson *et al.* determined the actual geometry of a tetramethyl derivative by X-ray crystallography,[18] and the structure was found to correspond closely to a geometry intermediate between **6** and **7**. It is not unlikely that this structure is chosen as a result of packing forces in the crystal. It is far from the most antiaromatic isomer **5**. By the way, **6**, represents the conjugated system of **4**.

Cyclopentadienyl(pentadienyl)iron, **8**, comes between ferrocene and open ferrocene. This semi-open



4 5 6

7 8 9

ferrocene has not been prepared yet. If this compound is assumed to have a staggered configuration, **9**, the following two polynomials are obtained:

$$P(X) = X^{15} - 19X^{13} + 140X^{11} - 2X^{10} - 516X^{9} + 18X^{8} + 1023X^{7} - 70X^{6} - 1089X^{5} + 134X^{4} + 580X^{3} - 112X^{2} - 120X + 32 \quad (11)$$

and

$$R(X) = X^{15} - 19X^{13} + 140X^{11} - 508X^{9} + 953X^{7} - 887X^{5} + 358X^{3} - 46X. \quad (12)$$

The resonance energy is then calculated to be 0.048β. Semi-open ferrocene is thus predicted to be essentially nonaromatic and olefinic in reactivity. Therefore, this compound may not be stable.

Comparing the resonance energies of ferrocene, semi-open ferrocene, and open ferrocene, we note that the resonance energy decreases in this order. This fact suggests that the cyclopentadienyl rings may play a key

role in stabilizing ferrocene-like conjugated systems. As we have seen, ferrocene is far from being an ionic species in the form of ferrous dicyclopentadienide. Its pentagonal substructures are firmly incorporated in the three-dimensional conjugated system. However, they still seem to be crucial to aromatic stabilization. It is quite possible that the electron-rich pentagonal rings are responsible for most part of the resonance energy.

Concluding Remarks

Our graph theory of aromaticity[1,2] is mathematically exact, in the sense that no parametrization is used in the framework of the theory. Its predictive capability depends solely on the validity of the bonding model employed. The bonding model adopted above for ferrocene and related compounds is fairly rough with omission of iron 4s and 4p valence orbitals. We believe that this bonding model is still practical enough to account for the aromatic origin of stabilization since it takes account of the predominant effect of iron 3d orbitals. At present, the resonance energy cannot be estimated for ferrocene of D_{5h} symmetry.

Our choice of Hückel parameters may not be based on physically sound grounds. However, the obtained resonance energies are consistent with chemical stabilities of the compounds. As has been referred to, the resonance energy of ferrocene is rather insensitive to the h value in Eq. 1. It is also fairly insensitive to the resonance integral between carbon $2p_z$ and hybridized iron 3d orbitals. Let this resonance integral be denoted by $k\beta_{c\text{-}c}$. The resonance energy of ferrocene is calculated to be 0.352β for $h=0$ and $k=0.8$ and 0.331β for $h=0$ and $k=0.5$. This further supports our view that ferrocene is basically aromatic in a thermodynamic sense. This compound can now be characterized as another example of three-dimensional aromaticity. This way of reasoning would become a new guiding principle in the field of organometallic chemistry, and would aid in developing simplified bonding models for a variety of complex organometallic compounds.

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