that stoichiometric relationships between antigen and antibodies are not sufficient to explain immunologic reactions taking place at a solid interface, where aggregates are obtained which contain a few antigen molecules and a large number of antibodies. Such assemblies might be called Berthollides.

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124. The Structure of the Ferrocenyl-methyl Cation

Preliminary Communication[1])

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Summary. Using a modified Extended *Hückel* (S.C.C.) procedure the structure of the ferrocenyl-methyl cation has been calculated. The result is a structure (V) with about equal overlap population between all Fe—C bonds. The methylene group is bent towards the iron atom and both rings are tilted.

The best demonstration of the electron releasing effect of the ferrocenyl group is the isolation of stable salts like I [1e]. The diferrocenyl-methyl cation (I, R = ferrocenyl, R' = H) can be isolated as fluoroborate (X = BF_4) and recrystallized from methanol. The NMR. spectra of such ions (I) suggest that the molecule possesses for R = R' a plane of symmetry through the atoms 1 and 6 [1c] [2].

The exact structures of such ions are not yet known and still the subject of some debate [1]. This uncertainty is mostly due to differences in the interpretation of

I   II   III

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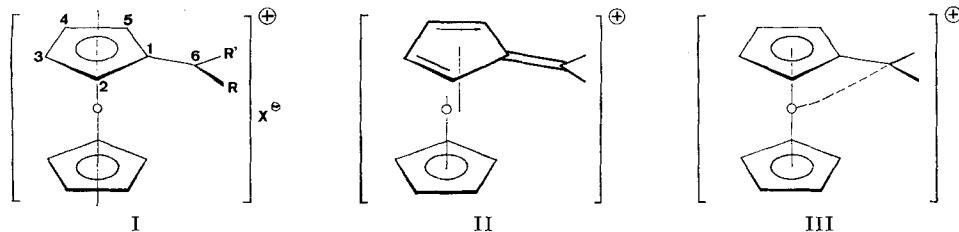
[1])   A full paper will be published elsewhere.

solvolysis experiments which may not give the answer to structural problems of the groundstate of the free ion. The observed rate enhancement due to the ferrocenyl group compared with that of the phenyl group and the stereospecificity of the reaction of solvolysis may be explained either by a structural model involving conjugation with the π-system (II) [1] [4] only, or by metal participation (III) [1] [3]. Some authors favouring metal participation have modified model III in several ways: they suggested that the fulvene part of the molecule was shifted (III a) [3], bent (III b) [1d] or that the lower ring was tilted (III c) [1d].

IIIa   IIIb   IIIc
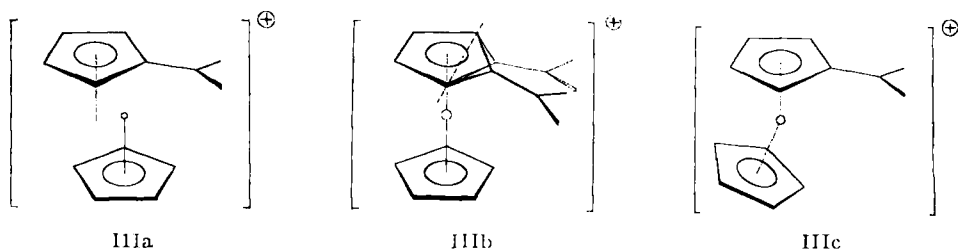
Consideration of the overlap integrals between the metal $3d$ and the $2p$ π-orbitals of the carbon atom 6 led *Hill & Richards* [3] to the conclusion that the model depicted in III a is reasonable. *Cais* [1e] and *Heilbronner* [5] find, using a HMO model, that the positive charge is dispersed over the whole molecule and that the fulvene moiety prefers bond alternation.

In this preliminary note we summarize the results obtained for the structure of the ferrocenyl-methyl cation using a self consistent charge (S.C.C.) procedure based on an Extended *Hückel* model [6].

To obtain the one electron H-operator, we take into account that the molecule may have an internal charge separation.

The diagonal elements H_{ii} of the H matrix are set equal to the valence state ionization potential (VSIP.) ε_{i_A} of orbital i at atom A. This potential depends on the net charge q_A of the atom A. For the relationship between q_A and ε_{i_A} we use the function given by *Zerner & Gouterman* [7] for C and Fe. For the VSIP. of hydrogen the values suggested by *Hinze & Jaffé* [8] were used. Since the ε_{i_A} values are given for three discrete net charges only, e.g. A^0, A^+, A^{++}, we have fitted a parabola through these points for interpolation.

The off-diagonal elements H_{ij} are calculated according to the *Mulliken-Wolfsberg-Helmholz* approximation [9]:

$$H_{ij} = K \cdot 0.5 \cdot S_{ij}(\varepsilon_i + \varepsilon_j) \text{ with } K = 1.75.$$

The overlap integrals S_{ij} are obtained according to *Ruedenberg, Roothaan & Jaunzemis* [10]. The basis set consists of *Slater* type orbitals (STO) with an exponent of 1.625 for C and 1.3 for H. The atomic orbitals for Fe are approximated as a linear combination of STO with the following exponents ζ_{kl} and coefficients c_{kl} [11].

Fe $4s$: $\zeta_{10} = 25.38, c_{10} = -0.02078; \zeta_{20} = 9.75, c_{20} = 0.07052;$
$\zeta_{30} = 4.48, c_{30} = -0.1744; \zeta_{40} = 1.40, c_{40} = 1.0125.$

Fe $4p$: $\zeta_{21} = 10.6, c_{21} = 0.00241; \zeta_{31} = 4.17, c_{31} = -0.00818;$
$\zeta_{41} = 0.51, c_{41} = 1.00003.$

For the calculation of the $3d$ orbitals of Fe the double ζ method [12] was used with the following exponents ζ_{kl} and coefficients c_{kl}:

$$\zeta_{32} = 5.35, c_{32} = 0.5366; \zeta'_{32} = 1.80, c'_{32} = 0.6678.$$

As start the H-matrix is calculated on the basis of an assumed charge distribution. The diagonalization of this matrix is followed by a *Mulliken* population analysis. This leads to a new set of net charges which in turn yield a new H-matrix. This process is repeated until the charge difference between two steps is smaller than 0.02 electron units. For reasons of numerical stability we have introduced a damping function.

We started our calculation with a geometry derived from ferrocene (D_{5d}), replacing a H atom by a CH_2 group. To keep computing time within justifiable limits in exploring the multidimensional potential surface the following restrictions were introduced: all C–H distances (1.1 Å) and the C–C distances (1.4 Å) of the lower ring in I were kept constant; a plane of symmetry passing through the metal atom, C(1), and C(6) was assumed. We varied the distances between the two rings, keeping their distance to the Fe atom equal, until a position of minimum total energy was reached. We obtained 3.25 Å for the distance between the two rings, *i.e.* the same distance as observed in ferrocene [1b]. Displacing the iron along the z-axis from its central position between the two rings (see IV) leads to a destabilization if the distance between the two rings is kept at 3.25 Å.

We shifted the fulvene moiety along the x-axis and varied the angles α, β and γ independently as shown in IV. These calculations lead to the structure shown in V.

IV   V
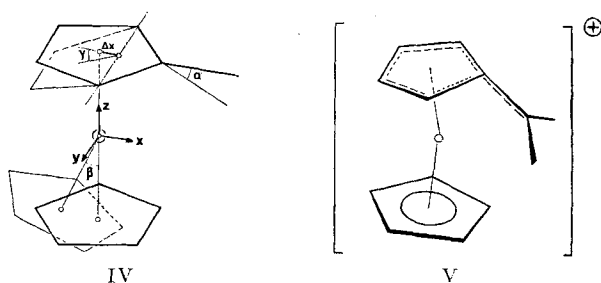
The calculated values are: $\alpha = 40°$, $\beta = 10°$, $\gamma = 0°$, $\Delta x = 0.1$ Å. Introduction of bond alternation into the fulvene moiety (C–C = 1.5 Å, C=C = 1.34 Å) decreases the total energy by 0.4 eV. We believe the value of $\alpha = 40°$ may be somewhat too large.

The resulting structure can be thought of as a fulvene part bound to the iron cyclopentadienyl unit in such a way that all Fe-C-overlap populations are about equal (see table). The structure of the ferrocenyl-methyl cation is essentially due to the interaction of the filled nonbonding $3d_{z^2}$ orbital of the iron with the empty π^* orbital of the fulvene moiety. The $3d_{z^2}$ orbital is thus lowered in energy while the π^* orbital of the fulvene is destabilized. Mixing of the lowest antibonding orbital with the metal orbitals results in a weakening of the C(6)–C(1) bond which facilitates the bending of C(6) towards the iron.

Net charges of V

atom	1	2	3	4	6	Fe
charge	0.063	0.033	0.022	0.022	0.065	0.50

Reduced overlap populations of V

bond	1–2	1–6	1–Fe	2–3	2–Fe	3–4	3–Fe	6–Fe
	0.834	1.124	0.046	1.145	0.066	0.865	0.079	0.078

In the final structure about half the positive charge is located at the iron atom and the other half distributed uniformly over both rings (see table). For comparison the charge at the iron atom in ferrocene is calculated to be $+0.3$. This result compares favourably with *Mössbauer* experiments [13]. Another interesting result of these calculations is that planar structure (III) should have a triplet groundstate (1.4 eV difference between highest occupied and lowest unoccupied MO) [14] while the bent structure (V) should have a singlet ground state. Some experiments carried out by *Cais et al.* [15] may be explained in this way.

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125. A Semi-Empirical Model of the Energy Barrier of Proton Transfer Reactions[1]

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Summary. The energy barrier in proton transfer reactions is described by a *Johnston*-type equation (1) ($n =$ order of bond to be broken). The barrier model is discussed in terms of free energies. The V_i values are free energies of ionic cleavage in aqueous solution of the X–H and Y–H bonds; they are computed from eqns. (4c) and (4d). The values of p_1 and p_2 affect curvature

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