Food for the Chemist

An Inaugural Lecture

GIVEN IN THE UNIVERSITY COLLEGE OF RHODESIA AND NYASALAND

Professor
S. H. Harper

OXFORD UNIVERSITY PRESS

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An Inaugural Lecture
given in the University College of
Rhodesia and Nyasaland
on 28 October 1960

by

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LONDON
OXFORD UNIVERSITY PRESS
1961

Oxford University Press, Amen House, London E.C.4

GLASGOW NEW YORK TORONTO MELBOURNE WELLINGTON
BOMBAY CALCUTTA MADRAS KARACHI KUALA LUMPUR
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PRINTED IN GREAT BRITAIN
AT THE UNIVERSITY PRESS, OXFORD
BY VIVIAN RIDLER
PRINTER TO THE UNIVERSITY

FOOD FOR THE CHEMIST

I HAVE been asked to deliver this inaugural lecture in order 'to admit myself to office by formal ceremony'. However, as the first Professor of Chemistry in this College it serves also to inaugurate the Chair of Chemistry and the Department of Chemistry in this University College of Rhodesia and Nyasaland.

This Chair, if it exists other than metaphorically, is already well worn, for I have been chair-borne during the past five years and the successful inauguration of this Chair and Department of Chemistry should be judged by deeds rather than words. When I came to reflect upon chairs I decided that bench-working organic chemists seldom sit down except for meals. We provide stools for our students which they rarely use! Some of you will have seen the famous drawing of Liebig's laboratory at Giessen in 1842, in which the students are standing or leaning against the benches, and only the laboratory steward is sitting down! Top hats and frock coats were the correct dress for the laboratory then, a far cry from the motley garb of the students of this College in the 1960's. One of the students depicted in this drawing is A. W. Hofmann, shortly to go to England to become the first Professor of Chemistry at the Royal College of Chemistry, the predecessor of my old Colleges, the Royal College of Science and the Imperial College of Science and Technology. I can carry this thread further, for I worked for my doctorate in what was later named the Hofmann Laboratory, and I was a member of the Hofmann Society, whose members were dedicated to the drinking of beer and the discussion of papers on organic chemistry. But to revert to Liebig's laboratory at Giessen; it has been said that 'a course of study was adopted which has in a measure

served as a model for all laboratories of instruction ever since. The student was thoroughly drilled in qualitative and quantitative analysis, prepared some organic compounds, and then carried out an investigation suggested by the professor in charge.' This is a precept as true today as a century ago.

However, I have digressed from my thesis that organic chemists only occupy chairs when drinking tea. This led me to consider the influence of food on chemists and the inspiration that it has provided. Whilst doing so I noticed that just a century ago (1860) the United Kingdom Parliament passed 'An Act for Preventing the Adulteration of Articles of Food and Drink' and thereby pioneered the road toward purer and better food. The passing of this first general pure food law in the world was commemorated appropriately in London last month, when food chemists, analysts, technologists, and administrators from many parts of the world reviewed the contributions of the past century to the advancement and dissemination of knowledge pertinent to the attainment and maintenance of purity and quality in foods. Although this line of thought of the inspiration that food has provided the chemist is devoid of sophistication, it seemed a theme that might be suitable for a lecture that is attempting the difficult, if not impossible, task of dealing with a technical subject in such a fashion as to survive the critical comments of my students and colleagues and yet be of interest to our guests here this evening, the cultural *élite* of this City.

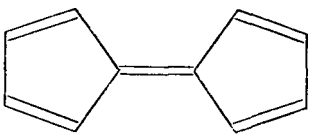
I could have started with Roger Bacon, medieval monk, the reputed discoverer of gunpowder and beloved of schoolboys, and proceeded to the decacyclic aromatic hydrocarbon, ovalene. However, I propose to dwell briefly on the recent discovery of a new type of compound which has

opened up a fresh field in the borderline between inorganic and organic chemistry and has attracted the attention of inorganic, organic, and theoretical chemists during the past decade.

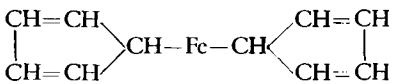
Some ten years ago chemists of the British Oxygen Company found that metallic iron, in the form of a synthetic-ammonia catalyst, reacted with *cyclo*pentadiene when the latter was passed as a vapour over the catalyst at 300° C.

$$2C_5H_6 + Fe \rightarrow C_{10}H_{10}Fe + 2[H]$$

The product was a yellow crystalline compound of the composition $C_{10}H_{10}Fe$; the first compound to be described containing only carbon, hydrogen, and iron. At about the same time workers in America treated the Grignard reagent from *cyclo*pentadiene with ferric chloride in an attempt to achieve oxidative coupling of *cyclo*pentadiene to the unknown hydrocarbon fulvalene, of interest because of its possible aromatic character.

$2C_5H_5MgBr + FeCl_3 \rightarrow ?$ 

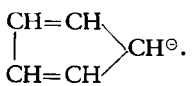
Instead, the same yellow iron-containing compound was obtained. Both groups of workers formulated it as



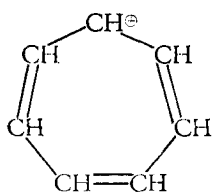
with an iron atom linking two *cyclo*pentadiene rings. This organo-iron compound attracted the attention of both inorganic and organic chemists because of its remarkable properties. It melts at 172° C and can be sublimed without

decomposition, it is steam-volatile, and is soluble in organic solvents. It is resistant to acids and to alkalis, but with oxidizing agents gives salts of a blue cation. The stability of this substance was in striking contrast to the failure of previous investigators even to prepare organo-iron compounds at all. These circumstances led several groups of workers in 1952 to doubt the correctness of this structure and to consider whether some alternative might better accord with the unique properties of this compound.

However, before we can follow this profitably we need to consider the nature of the *cyclo*pentadienyl anion, $C_5H_5^{\ominus}$, and radical, $C_5H_5\cdot$. Formally, the anion is the product of the abstraction of a proton from the methylene group of *cyclo*pentadiene; depicted as

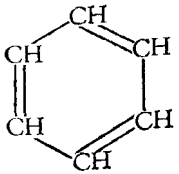


However, it does not behave as if it possessed ethylenic bonds and a localized negative charge. In fact, the *cyclo*pentadienyl anion satisfies Hückel's criterion for an aromatic system: that aromatic character is associated with a cyclic molecular orbital containing $4n+2$ electrons, in this case n being one. Indeed, the *cyclo*pentadienyl anion has been shown within recent years to possess aromatic properties.

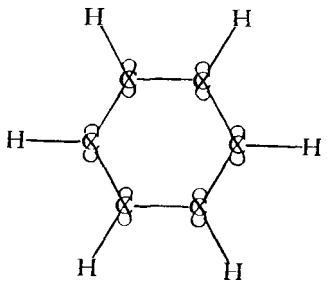


Together with the *cyclo*heptatrienyl cation, another recently

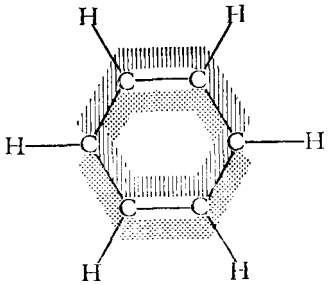
recognized aromatic system, and benzene, itself the classical example of the aromatic system, they constitute a trio all with n equalling one and so having a sextet of 'aromatic' electrons.



The classical Kekulé structure for benzene, depicting it as a *cyclo*hexatriene, has long been recognized as inadequate However, the development during the past thirty years of our knowledge of the electronic structures of molecules has enabled organic chemists to gain a more satisfactory insight into the special features of aromatic systems. Using the molecular orbital approach to their structures, in benzene the framework of carbon and hydrogen atoms is held together in a regular planar hexagon by electron pairs constituting sigma bonds.

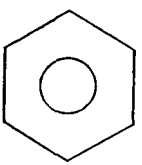


This leaves each carbon atom with a p-electron in a dumb-bell shaped orbital perpendicular to the plane of the ring. These orbitals become scrambled—they overlap—to give a continuous annulus above and below the ring:

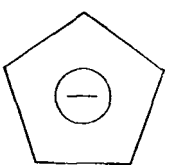


In fact, a structure that has been called a 'doughnut'—American style! The electrons in this molecular orbital, having the ring system as a nodal plane, constitute a sextet of *pi*-electrons—Greek style!

In view of the inadequacy of the classical valence-bond representations of these aromatic systems, new pictographs have been sought for, of which the hexagon with a circle inside is becoming widely adopted for benzene,

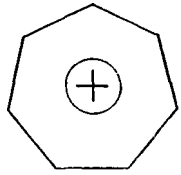


and correspondingly for the *cyclo*pentadienyl anion and the *cyclo*heptatrienyl cation. Some of you will have noticed this symbol for benzene in relief on the wall of the Department of Chemistry,



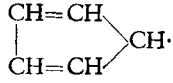
the hexagon being in fiery red to symbolize the source of

benzene in the carbonization of coal. The hexagon is surrounded with the alchemical symbols for the base metals of the Federation

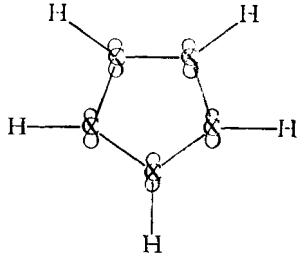


and in this context the circle has the added significance of representing the aromatic sextet of *pi*-electrons to the organic chemist of the 1960's and the noble metal gold to the alchemists.

Turning to the neutral *cyclo*pentadienyl radical, formally it is the product of the abstraction of a hydrogen atom from the methylene group of *cyclo*pentadiene.

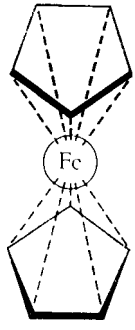


Like the anion the framework of carbon and hydrogen atoms is held together in a regular pentagon by sigma bonds, but in contrast to the anion only five *p*-electrons remain over.



Nevertheless, these five electrons overlap in a similar fashion to give an annular molecular orbital.

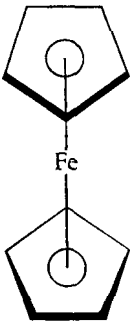
But to return to our iron compound, *biscyclo*pentadienyl iron. It was reasoned from the symmetry of the *cyclo*-pentadienyl radical that two such units might bond an iron atom between them in symmetrical antiprismatic fashion. The resulting 'sandwich' structure was given the name ferrocene.



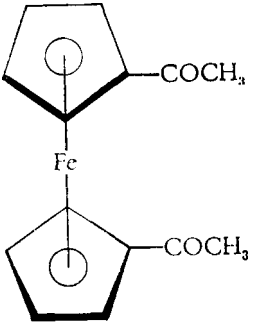
Although such a formulation was quite novel its correctness was quickly established. Its zero dipole moment, its diamagnetism, its single infra-red absorption band in the carbon–hydrogen stretching region, indicative of only one type of carbon–hydrogen bond, were consistent with this geometry. Full confirmation was provided by X-ray analysis of the crystals and by electron-diffraction analysis of the vapour, which demonstrated the centrosymmetrical nature and compact character of the molecule and established the interatomic distances as carbon–carbon 1·4 and carbon–iron 2·0 Å.

Despite the high degree of formal unsaturation, ferrocene is not catalytically hydrogenated and does not react with maleic anhydride, while its thermal stability and resistance to the action of acids are inconsistent with it being a polyolefin. In fact, ferrocene has typical aromatic properties. The hall-mark of aromaticity is the occurrence

of ring nuclear substitution reactions; ferrocene satisfies this criterion.



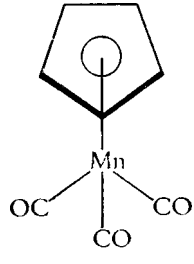
In the Friedel–Crafts reaction ferrocene gives a red crystalline diacetyl derivative, which has normal ketonic properties, and is oxidized by hypoiodite to a dicarboxylic acid, whose acid strength is similar to that of benzoic acid. Ferrocene is sulphonated and arylated.



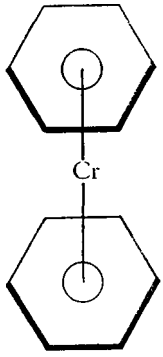
The typical substitution reactions of classical aromatic systems, such as nitration and bromination, are not observed as oxidation to the blue ferricinium cation supervenes, which is then resistant to the electrophilic reagent. However, these groups have been introduced indirectly

and the resultant nitro- and bromo-ferrocenes behave normally. But it would be out of place now to list all the counterparts of benzenoid compounds that have been prepared and studied.

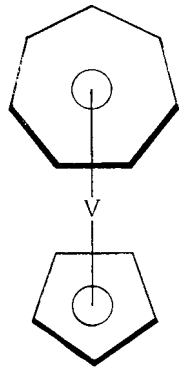
Once the novel structure of ferrocene had been elucidated it was recognized that it should be representative of a new class of compound, which presents a host of new problems for the inorganic chemist, in the variation of the metal and in the preparation of complexes containing other ligands, and because of their aromatic character are of special significance to the organic chemist. Successful search was then made for similar compounds derived from other metals, particularly the transition metals. Many such metallocenes are now known, including the chromium, manganese, cobalt, nickel, molybdenum, ruthenium, and osmium complexes. This search resulted in the development of better methods of preparation, one of which is the direct interaction of *cyclo*pentadiene with metal carbonyls. In this method the mixed vapours of *cyclo*pentadiene and the metal carbonyl are passed through a heated tube in a stream of inert carrier gas and the products condensed out in a cold trap. These reaction conditions give the *biscyclo*pentadienyl derivatives of chromium, iron, cobalt, and nickel directly.



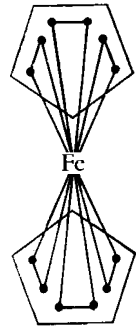
At lower temperatures, or in the liquid phase, chromium, iron, cobalt, molybdenum, and tungsten form *cyclo*pentadienyl metal carbonyls. These are interesting compounds with structures that have been termed 'piano-stools', and are a hybrid of the metal carbonyls and the metallocenes. These, too, undergo typical aromatic substitution in the five-membered ring. 'Sandwich' structures in which one or both *cyclo*pentadienyl rings have been replaced by benzene rings have also been prepared; the first being dibenzene-chromium, and the molybdenum, tungsten, and vanadium derivatives are now known.



Theoretical chemists quickly turned their attention to the electronic structures of these novel compounds. However, they appear not to have reached agreement on the precise nature of the bonding, particularly in the transition metal *biscyclo*pentadienyls. As we have seen the key feature is the 'sandwich' structure with the central metal atom symmetrically bonded to each ring; a situation that cannot be accounted for by classical valency concepts. It has been generally assumed that in ferrocene, bonding occurs through the iron atom, with its twenty-six electrons, striving to attain the inert gas structure of krypton of thirty-six



electrons. Woodward and his co-workers at first associated five *pi*-electrons with each ring, that is a *cyclo*pentadienyl radical, and interaction of these with the uncharged iron atom built up its electron shells to that of krypton. Fischer and his co-workers associate three pairs of *pi*-electrons with each ring, that is a *cyclo*pentadienyl anion, which interact with a ferrous iron atom forming six co-ordinate bonds, distributed round the iron atom in a trigonal antiprism.



Moffitt, however, deduces that there is only a single covalent bond between an uncharged iron atom and each ring as a whole. Four *pi*-electrons would then remain in each ring, without taking part in the bonding. For all

these theories the mathematical elaboration of the orbital hybridizations that are necessary is complex and barely understandable to the non-specialist chemist, let alone to the layman. Fischer's theory has the merit, through invoking a sextet of *pi*-electrons, of emphasizing the aromatic character of the rings and, furthermore, it enabled Fischer to predict the existence of dibenzenechromium and subsequently to prepare it for the first time.

Nevertheless, whatever theory of bonding finally gains general acceptance it must account for the shape and dimensions of the molecule, and its physical and chemical properties. In addition the theory must satisfy certain stereochemical requirements. We have seen that in the crystalline state ferrocene has the centrosymmetrical structure, with the rings in 'staggered conformation' fixed relatively to each other. However, there is strong evidence that in the vapour phase and in solution there is free rotation of the rings relative to each other. The electron diffraction pattern of the vapour at 400° C is only consistent with a freely rotating molecule. There is also evidence from consideration of the numbers and nature of various polysubstituted ferrocenes that there is rotational freedom. To illustrate this take the case of a disubstituted ferrocene. If the rings are fixed there will be five isomers, the homoannular 1:2 and 1:3, and the heteroannular 1:1′, 1:2′, and 1:3′. If there is free rotation then there will be only three isomers, the 1:2, 1:3, and 1:1′. Only three isomers of this type of compound are known. Optical and geometrical isomerism will also occur in suitably substituted ferrocenes.

Lest I have created the impression that the interest in ferrocene and related compounds is purely academic, let me add that already they have proved of technical interest as a motor and jet fuel additive.

Ladies and gentlemen, I have used this device of the inspiration of food for the chemist to bring to your attention one of the many new and stimulating developments in chemistry that are continually taking place. It serves to illustrate too that the old water-tight compartments of inorganic and organic chemistry have disappeared and how the whole armoury of chemistry can be brought to bear on a research problem. I hope that what I have served you has not been too indigestible and perhaps has even had a touch of piquancy about it. Nevertheless, it is time to return to reality and, in conclusion, I invite you to join us for real sandwiches and, taking the word out of the Principal's mouth, coffee!

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