

Liversidge Research Lecture

No. 11
1956

RECENT ADVANCES IN THE CHEMISTRY OF THE
AROMATIC COMPOUNDS

G. M. BADGER



The Royal Society of New South Wales



Professor Sir Geoffrey M. Badger
A.O., D.Sc. (Glas.), D. Univ., F. A. A.
Professor of Organic Chemistry
1955 - 1964

Sir Geoffrey Malcolm Badger

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SIR GEOFFREY MALCOLM BADGER 1916-2002

Geoffrey Malcolm Badger was born on 10 October 1916 at Port Augusta, South Australia. After secondary education at Geelong College, Geelong (Victoria), he studied at the Gordon Institute of Technology (Geelong) for three years, graduating with a Diploma of Industrial Chemistry. This qualification, together with a scholarship, enabled him to enrol directly into second year in the Faculty of Science at Trinity College, University of Melbourne. He graduated B.Sc. (1st. class Hons.) in 1937, and M.Sc. in 1938, working under Professor Bill Davies. He then proceeded to England to study at the University of London while holding a Finney Howell Research Fellowship at the Chester Beatty Research Institute, Royal Cancer Hospital, London, where he worked under the supervision of J.W.Cook on the synthesis of potential anti-tumour compounds. He graduated Ph.D. in 1940, and for the period 1942-1943 he was Research Chemist at ICI (Dyestuffs) Ltd., Manchester, where he worked on process development for the production of antimalarials as part of the war effort; this included synthetic studies on mepacrine methanesulfonate, and sulphamerazine. In 1943 he became Acting Temporary Instructor Lieutenant in the Royal Navy; this involved three months training at the University of Bristol and a week at the Royal Naval College at Greenwich. He then took up duties at HMS *Dauntless* in Inverkeithing near Edinburgh where he taught coastal and astronomical navigation to new naval officer recruits. He was in the Navy until 1946, and then was an ICI Research Fellow at Glasgow University with the status of Lecturer between 1946 and 1949. In 1949 he was appointed as Senior Lecturer at the University of Adelaide, and promoted to Reader in 1951. He was awarded the degree of D.Sc. at the University of Glasgow in 1949, and in 1955 he was appointed to the newly established Chair of Organic Chemistry at the University of Adelaide. Between 1954 and 1969 he was the single author of four books on chemistry, namely, 'The Structure and Reactions of Aromatic Compounds' (1954, reprinted 1957), 'The Chemistry of Heterocyclic Compounds' (1961), 'The Chemical Basis of Carcinogenic Activity' (1962, reprinted in Russian in 1966), 'Aromatic Character and Aromaticity' (1969, reprinted in Japanese and in Polish in 1971). As these titles indicate, his main research interest has been in the chemistry of aromatic compounds, but in the 1950s, at the height of the Phytochemical Survey spearheaded by CSIRO, he took a sidetrack into natural products chemistry (two papers). He relinquished his Adelaide Chair in 1964, with the title Professor Emeritus, to take up an appointment on the Executive of the Commonwealth Scientific and Industrial Research Organisation (CSIRO), but he returned to the University of Adelaide as Vice-Chancellor for the period 1967 to 1977. He then became Research Professor of Organic Chemistry, University of Adelaide. During 1979-1987 he was a Director of Western Mining Corporation.

Sir Geoffrey Badger has been very active in the organisation of Australian scientific and community affairs. He was President of the Royal Australian Chemical Institute (RACI), during 1964-1965; member of the Council (1964-7) - Secretary Physical Sciences (1968-72) - and President of the Australian Academy of Science (1974-1978); the first Chairman of the Australian Science and Technology Council (1977-1982); President of the Australian and New Zealand Association for the

Advancement of Science (ANZAAS) during 1979-1980; National Chairman of the Order of Australia Association (1989-1992); and a Member of the Australia Prize Committee (1990).

His time in the Royal Navy stimulated in him an interest in Captain Cook and the exploration of the Pacific Ocean. In more recent times this interest led to his role as Editor (and co-author) of the book "Captain Cook, Navigator and Scientist" (Australian National University Press, Canberra, 1971), and as sole author of the books, "The Explorers of the Pacific", (Kangaroo Press, Kenthurst NSW, 1988), and "Explorers of Australia", (Kangaroo Press, Kenthurst NSW, 2001).

Honours and Awards (Pre-2001)

- 1948 FRIC (Fellow of the Royal Institute of Chemistry)
- 1949 D.Sc., University of Glasgow
- 1950 D.Sc., *ad eundum gradum*, University of Adelaide
- 1950 H.G. Smith Medal, RACI
- 1952 FRACI (Fellow of the Royal Australian Chemical Institute)
- 1956 Liversidge Research Lecture, Royal Society of New South Wales
- 1958 Liversidge Research Lecture, Australian and New Zealand Association for the Advancement of Science
- 1960 FAA
- 1964 Abbott Lecture
- 1965 R.K. Murphy Lecture
- 1969 Fellow, Australian College of Education
- 1971 A.E. Leighton Medal, RACI
- 1974 Fellow, Australian Institute of Management
- 1974 W.D. Chapman Memorial Lecture and Medal of the Institution of Engineers
- 1975 Officer, Order of Australia
- 1978 Fellow, Australian Academy of Technological Sciences and Engineering
- 1979 Knight Bachelor
- 1980 D.Univ. Adelaide

- 1981 Medal, Australian New Zealand Association for the Advancement of Science (ANZAAS)
- 1985 'G.M. BADGER LABORATORIES': naming of the Organic Chemistry building, University of Adelaide

Biographical Sources

1. Best, R.J., *Discoveries by Chemists: A History of the Chemistry department of the University of Adelaide*, The University of Adelaide Foundation, 1987.
2. *Australian Men and Women of Science, Engineering and Technology*, compiled by Reed Reference Australia, in association with the Australian Academy of Science, and the Australian Academy of Technological Sciences and Engineering
3. Dr. George E. Gream, University of Adelaide.
4. Dr. Malcolm J. Thompson, Flinders University.
5. 'Who's Who in Australia 2000', Information Australia Group Pty Ltd, Melbourne.
6. Australian Academy of Science - a Science Education interview with Sir Geoffrey Badger by Professor R.W. Crompton - transcript of Video Histories of Australian Scientists [<http://www.science.org.au/scientists/gb.htm>]. A copy of the transcript was kindly provided by Dr. George E. Gream
7. 'Professor Sir Geoffrey Badger, Papers 1938-1997', Biographical Note, Adelaide University Library, MSS 11; A copy of the manuscript was kindly supplied by Dr. George E. Gream.

Obituary: C. Brice, "Sir Geoffrey Malcolm Badger AO, FRACI 1916-2002, *Chemistry in Australia*, 2003, **70**(1), 40.

Biographical memoir: I.D. Rae, "Geoffrey Malcolm Badger 1916-2002," *Historical Records of Australian Science*, 2009, **20**, 41-66.

Scientific Publications of G.M. Badger

Between 1939 and 1981 G.M. Badger had 232 publications, including several published Addresses at the University of Adelaide; he was sole the author of four books, and co-editor or co-author of two others.

**RECENT ADVANCES IN THE CHEMISTRY OF THE
AROMATIC COMPOUNDS***

G. M. BADGER

Department of Organic Chemistry, University of Adelaide, South Australia

Mr. President, Members of the Royal Society, Ladies and Gentlemen,

It is a great privilege and honour to be asked to give the Liversidge Research Lecture and I would like to express my thanks to the Council for giving me this opportunity to discuss the present status of aromatic chemistry, and indicate some future paths in research. The study of the aromatic compounds has never been seriously neglected, for it has not only posed many problems of academic and theoretical interest but, in addition, many such compounds are of great commercial importance.

It is not inappropriate that the Liversidge Research Lecture should be concerned with this topic in 1956, for this is the 100th anniversary of the discovery the first synthetic dyestuff, mauveine, by the youthful W.H. Perkin. Until this time the great reservoir of aromatic compounds in coal tar was unexploited: indeed, coal tar was considered a waste product or at the best as a source of pitch. In 1856, Perkin, showed that he could convert crude aniline to a commercially valuable product and the whole situation changed. Before long determined efforts were being made to separate the more abundant constituents on a large scale.

Various aromatic compounds had been discovered before this time. Some had been obtained from natural sources, from materials such as gum benzoin; and naphthalene had been separated from coal tar by Garden as early as 1820. Benzene was first described by Michael Faraday in 1825, but he obtained it from the liquid which separated from a compressed illuminating gas which had been prepared by the pyrolysis of fish oils. It was not until 1849 that C. Mansfield isolated pure benzene from coal tar. At this time fractionating columns had not been invented, and Mansfield had to carry out his distillations in an old-fashioned glass retort, with the thermometer in the liquid. As he isolated not only benzene but also toluene and pseudo-cumene, we can only admire his considerable patience and experimental skill. As he himself said (Mansfield, 1849):

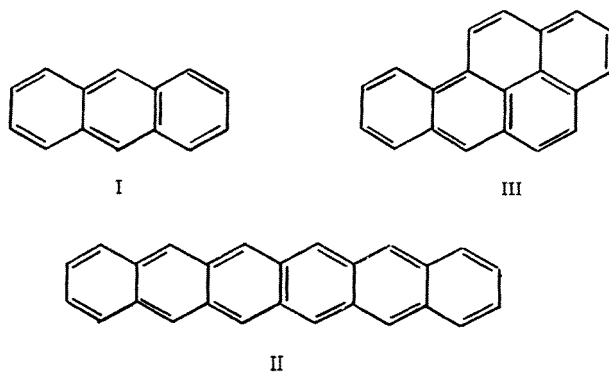
"It is perhaps the tedium of the methods necessary to effect a separation of mixed hydrocarbons from each other which has deterred experimental chemists from devoting their time to disentangling the oils here treated of: and perhaps to have conducted the innumerable distillations necessary for this purpose in a laboratory imperfectly furnished with gas and other conveniences, would have been a task too laborious to have been persisted in."

Aromatic compounds have often been distinguished from unsaturated aliphatic compounds by their stability and their tendency to undergo substitution rather than addition reactions. Benzene has long been regarded as the simplest of the aromatic

*Liversidge Research Lecture delivered to the Royal Society of New South Wales, July 12, 1956. Reproduced by permission of the Royal Society of New South Wales from *J. Proc. Roy. Soc. N.S.W.*, 1956, **90**, 87-99.

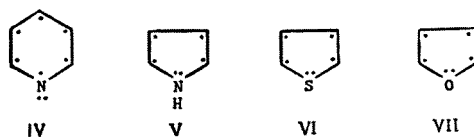
compounds, and it was formerly believed to be the parent structure of all aromatic compounds. Various heterocyclic analogues of benzene, such as pyridine and thiophen, were said to have "aromatic character". Such compounds certainly resemble benzene; but "aromatic character" is an uncertain term, for many polycyclic aromatic hydrocarbons differ very markedly from benzene in their general properties.

Anthracene (I), for example, is a rather reactive substance which undergoes many addition reactions. It adds bromine and chlorine at room temperature. It reacts with oxygen in the presence of light to form a photo-oxide, and it readily adds maleic anhydride and other dienophiles in the Diels-Alder reaction. The dark green hydrocarbon, hexacene (II), has even less aromatic character for it is very unstable in light and air, and it reacts almost instantaneously with maleic anhydride. Moreover, although the cancer-producing hydrocarbon, 3:4-benzopyrene (III) does not readily undergo addition reactions, it is



exceptionally reactive in many substitution reactions. It is readily acetoxyated with lead tetraacetate, even at room temperature. It also couples quite readily, even with the moderately reactive *p*-nitrobenzene diazonium chloride, a reaction which was formerly believed to be confined to phenols, amines and, to a lesser extent, to ethylenic compounds.

In these circumstances it is idle to attempt to define an aromatic compound in terms of its properties or its "character", important though these may be. The only satisfactory way to distinguish an aromatic compound is by reference to its structure.

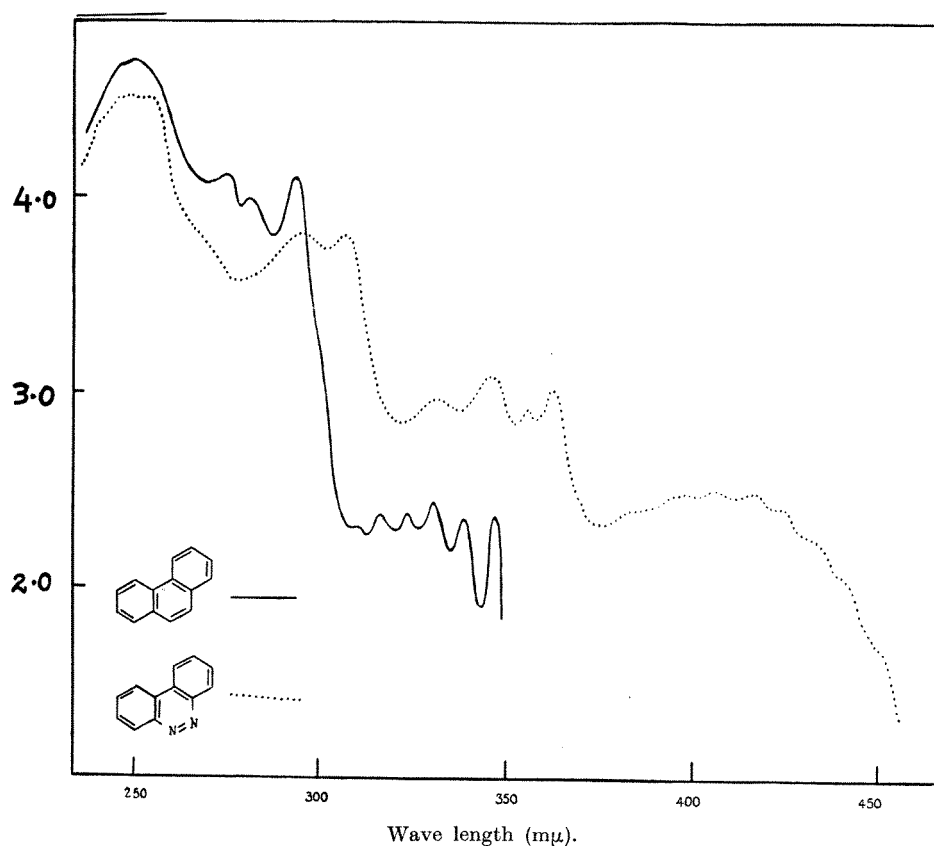


In benzene all the carbon atoms are in the trigonal state of hybridization, and by overlap in the usual way the various orbitals form the carbon-carbon and carbon-hydrogen sigma bonds. The remaining six $2p_z$ orbitals, which are vertical to the plane of the ring, interact laterally to form the π -bonds. This delocalization is the origin of the delocalization or resonance energy of the molecule and is now recognized as the cause of the peculiar stability of the compound.

Heterocyclic analogues of benzene have similar structures. In pyridine the nitrogen atom contributes one electron to the aromatic sextet, and the non-bonding "lone pair" of electrons is responsible for the basic character of the compound. The situation in pyrrole, thiophen and in furan is similar except that the heteroatom contributes two electrons to the aromatic sextet.

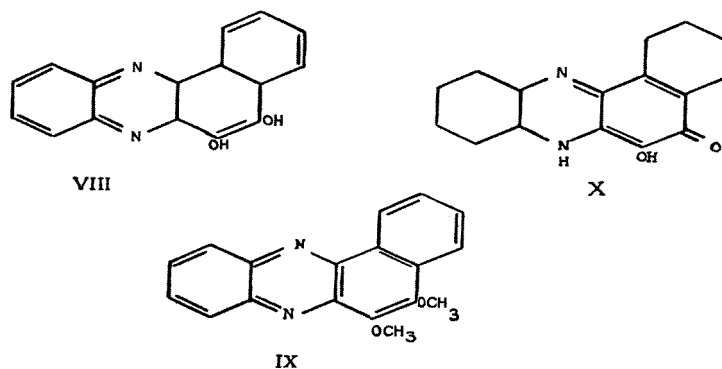
This similarity in electronic structure is amply confirmed by the ultraviolet absorption spectra, and particularly by the spectra of the polynuclear aza-hydrocarbons (Badger, Pearce and Pettit, 1951a; Badger and Seidler, 1954). Certain differences do exist, of course, but in many cases the resemblance between the spectrum of the hydrocarbon and those of its aza-hydrocarbon analogues is most marked. The chief electronic difference between the compounds is that the aza-hydrocarbons have two n -electrons not involved in bonding, and these compounds sometimes show a long wave length absorption in hexane solution which can be identified as an $n-\pi^*$ transition (Badger and Walker, 1956).

With the 5-membered heterocyclic systems the three main regions of absorption can generally be identified, but the resemblance is less marked particularly in the pyrrole and furan series. In these cases the electronegativity of the hetero-atom is high so that the 2p orbital is "contracted" relative to the carbon 2p orbitals, and the conjugation is restricted (Badger and Christie, 1956).

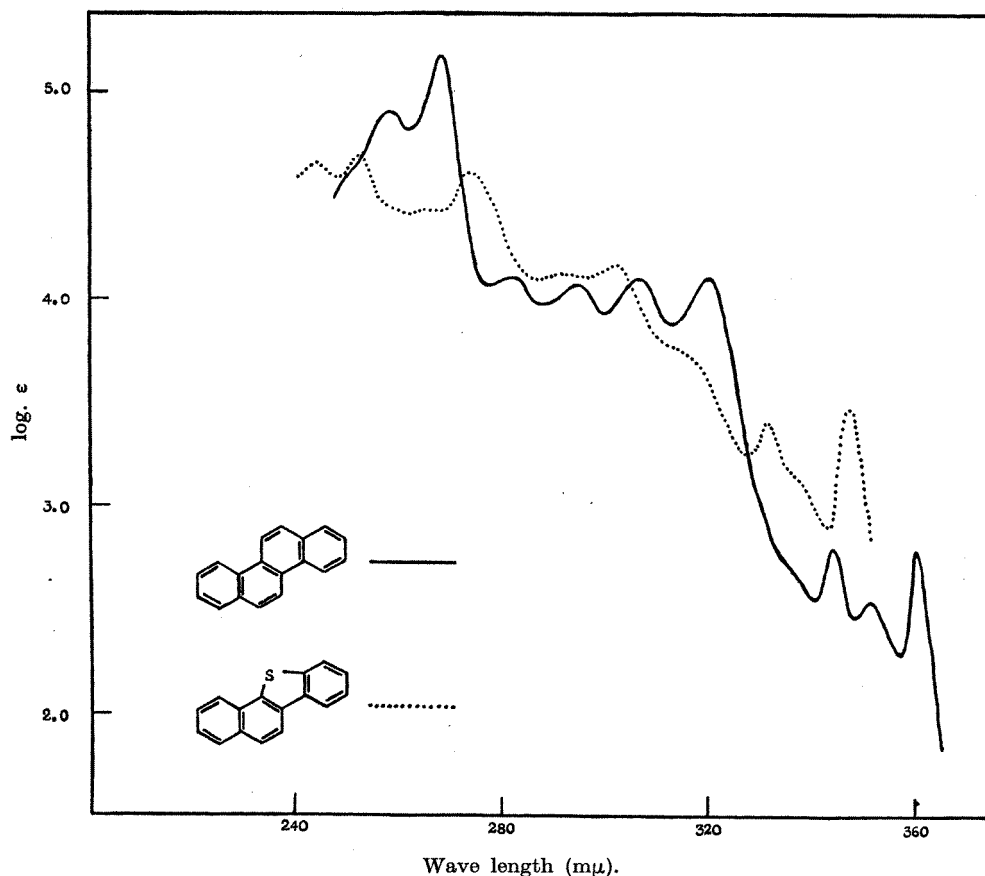


The heterocyclic systems also differ from benzene in their stability and in their reactivity, and a few rather less obvious differences become apparent in the polynuclear compounds.

As an illustration of this point it may be noted that 3:4-dihydroxy-1:2-benzophenazine (VIII) is a deep violet-blue substance quite unlike the yellow 3:4-dimethoxy-1:2-benzophenazine (IX). Such differences are not found among benzenoid compounds of the same type and the difference in this case is undoubtedly due to the fact that the dihydroxy-compound (VIII) exists predominantly in the quinonoid form (X) (Badger, Pearce and Pettit, 1951b).



Quinonoid structures of this type are of special interest in heterocyclic chemistry and they are of varying stability. Mild reduction of tetra-azabenzopentaphene gives an unstable red dihydride which probably has the structure (XI). The deep red 13:14-dihydro-5:8-diazopentaphene (XII) can be prepared synthetically and is sufficiently



stable for it to be isolated. The linear deep blue dihydride (XIII) of tetra-azapentacene, however, is excessively stable and has resisted all attempts to dehydrogenate it to the aromatic state (Badger and Pettit, 1951, 1952a, b).

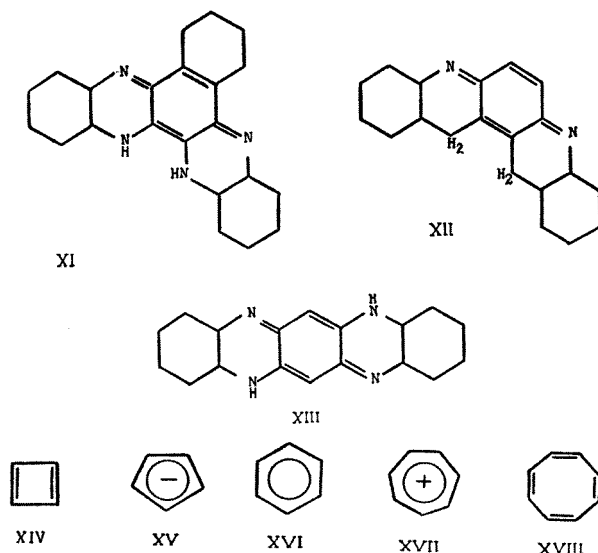
All these differences are, however, relatively minor in comparison with the overall similarity in electronic structures of the parent ring systems. Pyridine, thiophen, etc. may therefore be regarded as aromatic ring systems and we may define an aromatic compound as *a cyclic compound with a large delocalization or resonance energy, where all the*

annular atoms take part in a single conjugated system involving an even number of π -electrons.

This definition leads us to consider whether certain 4-membered, 5-membered, 7-membered, and 8-membered rings may resemble benzene and possess aromatic structure (XIV-XVIII).

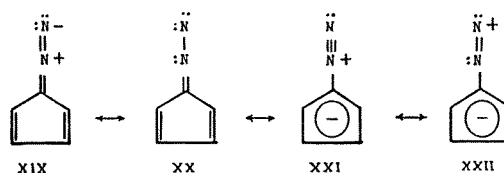
*cyclo*Butadiene (XIV) is unknown, having resisted all attempts at synthesis, and in any case the structure would involve a very considerable distortion of the trigonal-hybrid bond angles.

*cyclo*Octatetraene (XVIII), at the other end of the series, is a well known compound, but all the experimental evidence indicates that the molecule is puckered, and that the bonds approximate to alternate single and double bonds. For aromatic stability and high resonance energy the molecule would have to be planar, in which case the bond angles would be 135° compared to the 120° required for sp^2 hybridization. It seems that this angular strain is sufficient to counteract the stabilizing influence of resonance.

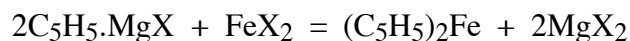


The 5-membered ring system, *cyclopentadiene*, is not aromatic, having a resonance energy of only 3 kcal/mole; but its anion (XV) has a structure closely resembling that of pyrrole and is aromatic. Indeed it is the increased stability which results which explains why *cyclopentadiene* forms salts with alkali metals, whereas ordinary saturated carbon atoms do not.

The anionic structure (XV) can also exist in certain substituted *cyclopentadienes*, such as diazocyclopentadiene. This is a stable red compound quite unlike diazomethane. As Doering and DePuy (1953) have pointed out this compound may be considered as a resonance hybrid of the four contributing structures (XIX-XXII), which explains its aromatic stability.



The 5-membered ring system also occurs in ferrocene and related compounds (Pauson, 1955b). Ferrocene was first prepared by the action of ferric chloride on *cyclopentadienylmagnesium bromide* (Kealy and Pauson, 1951). The ferric chloride was reduced to the ferrous state and reacted further according to the equation:



Subsequently it has been shown that ferrocene may also be formed by the direct action of *cyclopentadiene* on iron at 375°.

It is an extremely interesting compound. It is soluble in all common organic solvents and crystallizes in large orange needles. It is stable to water, to 10% sodium hydroxide, and to boiling concentrated hydrochloric acid. It is volatile above 100° at atmospheric pressure and the vapour is stable to at least 450°. It is not hydrogenated over platinum oxide and it does not react with maleic anhydride. Moreover it undergoes the Friedel-Crafts reaction. With acetyl chloride it gives a red diacetylferrocene, which has been oxidized to ferrocene dicarboxylic acid.

All these properties suggest that ferrocene must have an aromatic structure, and this is supported by other data (Woodward, Rosenblum and Whiting, 1952). For example, the first dissociation constant of the di-acid is very close to that for benzoic acid. Moreover, the infra-red absorption spectrum gives the C-H stretching frequency at 3067 cm⁻¹ (3.26μ) in the region typical for aromatic C-H bonds; the acetylferrocene gives a carbonyl stretching frequency of 1675 cm⁻¹ (5.97μ) almost identical with that given by acetophenone, 1668 cm⁻¹ (5.93μ).

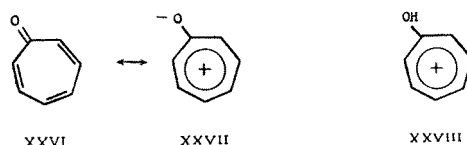
Many analogous compounds with other metal atoms have also been prepared, and these vary considerably in stability. In addition diindenyliron (XXIV) has been prepared. A "sandwich" structure (XXIII) was suggested for ferrocene, and this has been confirmed by X-ray analysis of the crystal structure and by other means; but the exact fashion in which the two rings are bonded to the iron atom is still under discussion. According to one view the bond is formed between a *d*-orbital of the metal and the π-orbitals of the ring as a whole, all the carbon atoms being bonded equally to the metal atom (Moffitt, 1954). All the transition elements have an available *d*-orbital and it may be noted that ferrocene-like compounds have now been prepared from all of them. On the other hand, the same "sandwich" structure occurs in *dicyclopentadienylmagnesium* which cannot involve bonding of this type, and the bonding in this case may have considerable ionic character.

According to the alternative theory there is simultaneous bonding of all six-π-electrons from *cyclopentadiene* anions leading to three dative covalent bonds between each ring and the metal (Fischer and Pfab, 1952). This theory has been adversely criticised; but it does suggest that similar sandwich-like compounds with unchanged aromatic systems, such as benzene, are possible. When such compounds were looked for they were found, for Fischer has recently reported the preparation of dibenzenechromium(0), and dibenzenemolybdenum(0) (Fischer, 1956).

In addition to these compounds there is also the group of substances in which only one *cyclopentadienyl* ring is linked to a metal atom to which groups such as CO are

attached. A particularly interesting example is dicyclopentadienyldiiron tetracarbonyl, the structure of which has been recently established (Hallam, Mills and Pauson, 1955).

Further research is clearly necessary to determine the nature of the metal-carbon bonds in all these compounds, and especially to determine the degree of ionic character in the analogous compounds involving other metal atoms. A comparison of the strengths of carboxylic acids derived from ferrocene analogues involving different metals would be useful. A study of the exchange reaction using the radioactive isotope corresponding to the metal concerned (e.g. ^{60}Co with dicyclopentadienylcobalt) might also give information of value.



This brings us to the 7-membered ring system. The parent compound, *cycloheptatriene*, has a small resonance energy and is clearly aliphatic. The *cation*, however, has six π -electrons and as the distortion from the sp^2 valency angle of 120° is small, this system (XVII) must be said to have an aromatic structure. The *cycloheptatrienylium* (or tropylium) ion has been prepared by Doering and Knox (1954; see also Dewar and Pettit, 1955) who found it to be a stable cation. Once again the C-H stretching frequency occurs in the infrared at 3020 cm^{-1} (3.32μ), a figure which is similar to that for other aromatic compounds.

The same ring system occurs in tropone and in tropolone (Pauson, 1955). Tropone may be given the structure (XXVI), but it is better represented as the hybrid of this structure together with (XXVII) in which the positive charge is equally shared by all the annular carbon atoms. This latter structure emphasises its relationship to the tropylium ion (XVII), and it also explains the basicity of the compound, for tropone readily forms stable salts with acids to give the cation (XXVIII).

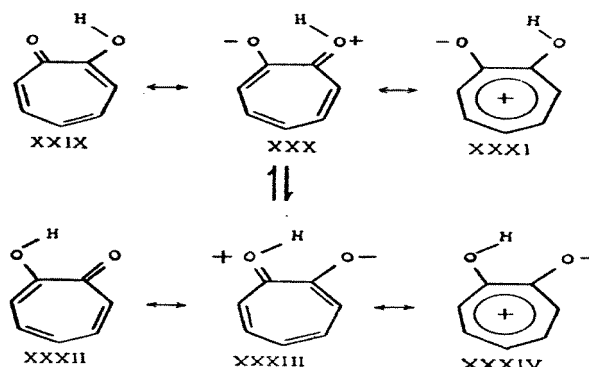
The hydroxy-derivative of tropone, which is known as tropolone, has been very extensively studied (Dewar, 1945; Johnson, 1951). It is best regarded as a resonance hybrid of the three structures (XXIX-XXXI), but it undergoes very ready tautomerism to the resonance hybrid represented by structures (XXXII-XXXIV).

Tropolone shows all the properties of an aromatic substance. It has a resonance energy of 29 kcal./mole. The ring system is a regular heptagon with an average C-C bond length of 1.40 \AA (Robertson, 1951), and the carbon-hydrogen stretching vibration occurs in the infra-red spectrum at 3050 and 3015 cm^{-1} in agreement with other aromatic compounds (Koch, 1951). It undergoes a number of substitution reactions: it can be nitrated, nitrosated and brominated; and it couples with diazonium salts.

It is also of some interest that this stable aromatic system has been identified in a number of natural products: in stipitatic acid; in puberulic acid; in purpurogallin; in the thujaplicins; and in colchicine (Pauson, 1955).

These recent advances in the chemistry of non-benzoid aromatic hydrocarbons are interesting and important; but we cannot neglect the benzenoid compounds, which still pose many problems. Many aromatic compounds can be produced from petroleum by

various pyrolytic processes, but the main source is still coal tar, from which several hundred substances have already been isolated. In spite of the great volume of work which



has been carried out in this field it is surprising how little we really know about the mode of formation of the aromatic constituents of coal tar. The complete system is exceptionally complex, and it is necessary to consider several isolated aspects of the problem before any understanding can be reached.

When coal is heated in the absence of air it begins to decompose at about 300°. Between 300-450° it gives a "primary" tar which consists mainly of paraffins, cycloparaffins, olefins and phenols. This "primary" tar is believed to be formed by splitting off various fragments and side chains from the main coal structure, and it is noteworthy that it contains only small quantities of aromatic hydrocarbons (Vahrman, 1952).

Tars from Durham Holmside Coal

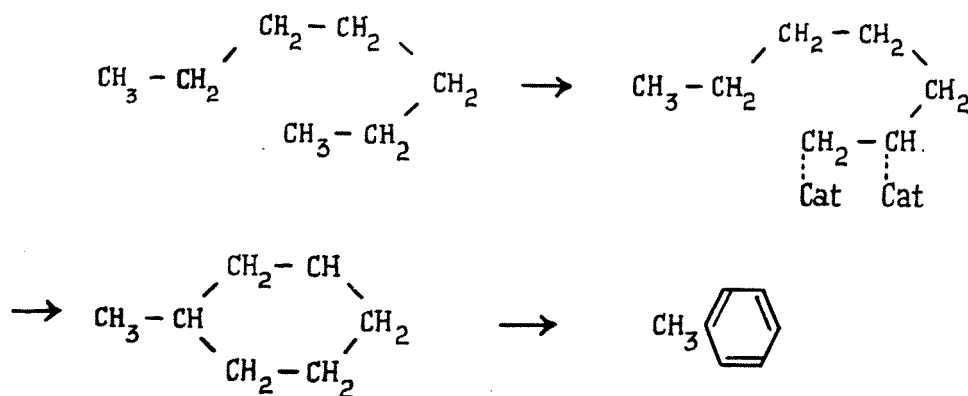
Carbonization Temperature	Carcinogenic Activity
450°	+
560°	+++
1250°	++++

In ordinary gas-works or coke-oven practice, however, much higher temperatures (of the order of 900-1200°) are involved and the "primary" tar is converted into a "secondary" tar. This secondary tar, which is the normal "coal tar", contains many different aromatic ring systems, and the problem is to determine how each is formed. It is only at these higher temperatures that compounds such as anthracene and the higher polycyclic aromatic hydrocarbons are formed. In this connection it is significant that tar obtained at 450° is only very weakly cancer-producing, and that the cancer-producing constituent (presumably 3:4-benzopyrene) is largely formed between 450° and 560°, there being only a slight increase in the amount formed between 560° and 1250° (Kennaway, 1925).

Dehydrogenation and cyclodehydrogenation

The cyclization of paraffin hydrocarbons to aromatics was first described by Norton and Andrews in 1886, who obtained a small amount of benzene by passing hexane through a hot tube. In recent years it has been shown that the process is catalyzed by various

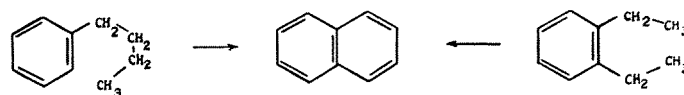
oxides, which may be supported on alumina or used in the pure state, and it has now been rather extensively studied (Moldawskii and Kamuscher, 1936). Under these catalytic conditions, at temperatures of 450-600°, paraffins and olefins containing six or more carbon atoms are converted into aromatic compounds. It seems that three distinct stages are involved: the dehydrogenation of the paraffin to the corresponding olefin; the cycloisomerism of the olefin to a hexahydrobenzene; and thirdly the dehydrogenation to the aromatic hydrocarbons (Steiner, 1950). (Of course if the initial material is a suitable olefin or cycloparaffin, only one or two of the stages may be required). In this way *n*-hexane and hex-1-ene give benzene; *n*-heptane and 2-methylhexane give toluene; and *n*-octane gives *o*-xylene together with ethylbenzene and some *m*- and *p*-xylene.



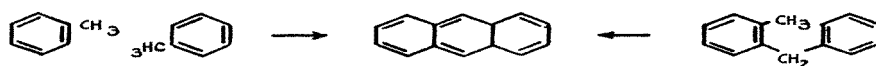
Reactions of this type must clearly occur at the high temperatures involved in the coal gas-coal tar process, and the surface of the coke may well be of considerable importance. Many of the simple benzenoid compounds may therefore be formed in this way.

It is possible that similar cyclization-dehydrogenation reactions may also account for some of the polycyclic aromatic products. Several reactions of this type have been studied experimentally, and the following examples serve to indicate the type of cyclization which can occur (Hansch, 1953).

n-Butylbenzene has been converted into naphthalene in quite high yield by heating with chromium oxide catalyst at 500°; and naphthalene is also obtained from *o*-diethylbenzene with a zinc oxide-calcium oxide on alumina catalyst at 600°. Cyclopentene also gives naphthalene.



Anthracene has been formed by the pyrolysis of toluene, and it can be obtained in quite reasonable quantity by heating *o*-benzyltoluene with lead oxide.



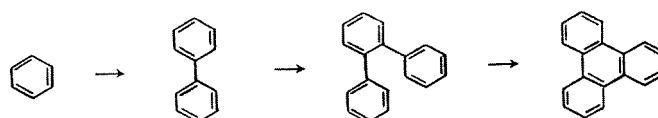
Similarly the pyrolysis of 1-benzyl-2-methylnaphthalene yields 1:2-benzanthracene.



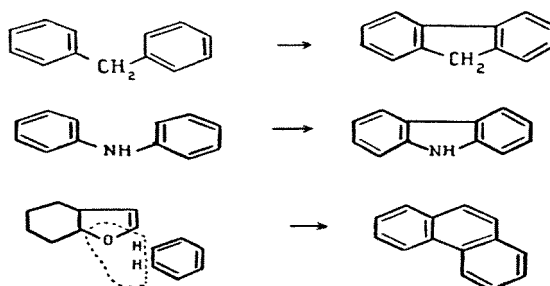
Using processes of this type it is possible to account for the formation of a great many substances from simple paraffins. *n*-Decane is converted into many different aromatic compounds by heating on a chromia-alumina catalyst and these can all be accounted for by a combination of cyclization and cracking reactions (Hansch, 1953).

Aromatic ring systems are relatively stable even at high temperatures, but they do condense with elimination of hydrogen to form more complex ring systems and this reaction must also occur during coal carbonization processes at the high temperatures involved.

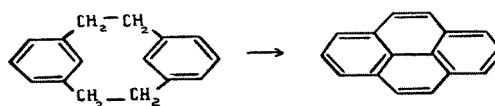
Benzene can be converted to diphenyl by passage through a red hot tube or by passing over a red hot wire. 1: 2-Diphenylbenzene has also been reported, together with the *m*- and *p*-isomers; and triphenylene has been isolated in small amount. A series of condensations leading to triphenylene and similar compounds would therefore seem not unreasonable (Kinney and DelBel, 1954).



On a somewhat similar scale, the following condensation of compounds which occur in low temperature tar to compounds which occur in high temperature tar, would also seem to be important (Mantel and Hansen, 1953).

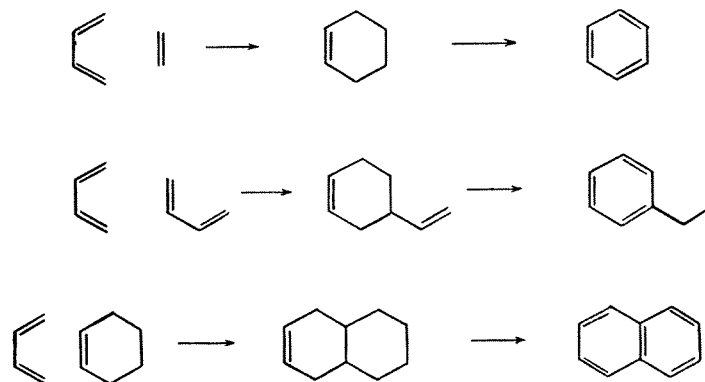


An especially interesting laboratory dehydrogenation of this type (which however was brought about with palladium) has been reported by Baker *et al.* (1951) and may serve as a model for the formation of pyrene (see below).



Diene synthesis.

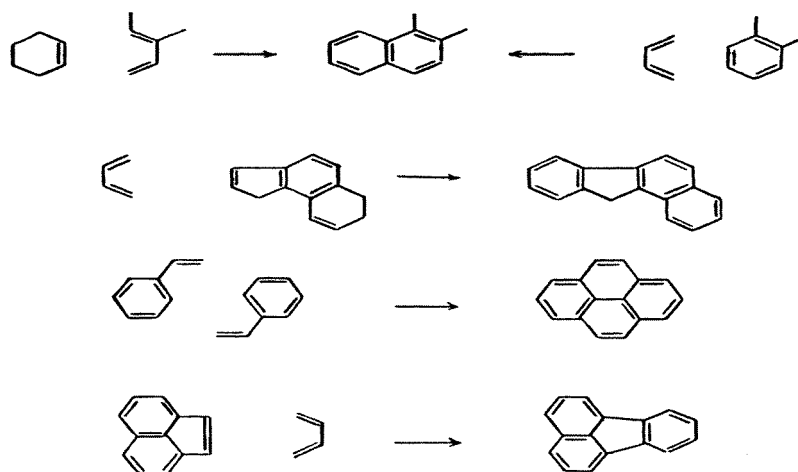
All the reactions mentioned in the preceding section involved cyclization or condensations such that the end product has the same number of carbon atoms as the starting material. As reactions of this type are catalysed by a variety of substances it seems likely that it is predominantly a surface reaction and that there is little or no contribution from vapour phase reaction.



Nevertheless reactions do seem to occur in the vapour phase as exemplified by the Weizmann process for the formation of aromatics by the thermal cracking of petroleum in empty or packed tubes at 630-680° (Weizmann *et al.*, 1951). Under these conditions it has been suggested that the fundamental process must involve an initial cracking of the material to small molecules such as acetylene and butadiene and that re-synthesis occurs by diene addition. The following examples indicate the nature of the synthesis, and there is every reason to expect that reactions of this type may also be of significance in the formation of coal tar.

It is significant that the Weizmann process leads to relatively larger amounts of styrene and ethylbenzene in the "xylene" fraction, whereas the catalytic cyclization of *n*-octane mentioned previously leads mainly to *o*-xylene, although ethylbenzene is also formed in small amount.

Similar diene syntheses have also been postulated for the formation of polycyclic compounds, as exemplified by the following, but it must be admitted that the evidence is scanty.

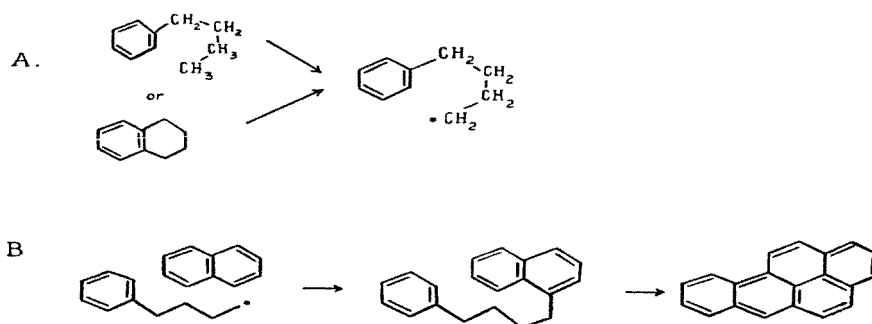


Some experiments on the polymerization of acetylene by pyrolysis have also been reported and, indeed, the original experiments of Berthelot (1866) in this field are of great importance in the history of organic chemistry. It is a pity that some of these have not been repeated in recent years as we now have available many new experimental techniques. Nevertheless Berthelot did obtain benzene, styrene, and some other compounds. Zelinsky did repeat the experiment under slightly modified conditions in 1923, and he identified benzene, toluene, *p*-xylene, styrene, indene, naphthalene, fluorene and anthracene among the products. *cyclo*Ocatetraene has since been discovered among

the products of the thermal polymerization of acetylene, but it is produced in much larger amount by the Reppe process which involves the use of a catalyst.

Unfortunately no attempt has been made to identify compounds in the higher boiling fractions and these may well be important for Kennaway (1925) has found that the tar produced by the pyrolysis of acetylene is cancer-producing, and the presence of 3:4-benzopyrene may be inferred from the fluorescence spectrum of the tar.

3:4-Benzopyrene has a characteristic fluorescence spectrum which enables it to be identified in very complex mixtures. Chromatography and absorption spectroscopy have also been used for this purpose and this cancer-producing hydrocarbon has now been identified in coal tar, in the atmospheric dust of cities, in domestic soot, in the soot in the chimney of a smoked sausage factory, in processed rubber, in commercial carbon black and in cigarette smoke (Cook *et al.*, 1933; Waller, 1952; Goulden and Tipler, 1949; Falk *et al.*, 1951; Falk *et al.*, 1952; Cooper, Lindsey and Waller, 1954). Its mode of formation is therefore of great importance. As a working hypothesis the following scheme may be suggested for the pyrolytic formation of 3:4-benzopyrene.



A somewhat similar scheme has been suggested for the formation of benzopyrene by the action of aluminium chloride on tetralin. In view of its widespread occurrence in human surroundings the mode of formation of this very powerful carcinogen is of very great importance, and work is being directed towards the solution of this problem.

With regard to the general problem of the formation of aromatics, we may safely say that the pyrolytic processes are exceptionally complex. There is little doubt that reactions similar to all those which I have described occur, at least to some extent, in the formation of coal tar, and possibly in the formation of the tarry matter in soot and similar materials; but little is known about the relative importance of these processes.

Earlier in this lecture I indicated that aromatic chemistry has always attracted the attention of chemists. I have tried to tell you about some of the problems which have been studied in recent years, and some which are at present under investigation. I hope you will agree that there are many extremely interesting problems still awaiting solution.

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