Tetrahedron, 1958, Vol. 3, pp. 323–324. Pergamon Press Ltd., London

Paper Symposium on Aromatic Character

INTRODUCTION

by Sir ROBERT ROBINSON

THE designation "aromatic" was first applied to a group of natural products such as methyl salicylate (oil of wintergreen), anethole, (aniseed), safrole (sassafras), coumarin (Touka bean), and vanillin, etc., on account of their characteristic odours or flavours. When it was recognised that many of these substances were derivatives of benzene the classification acquired a structural significance and the "aromatic" series implied "benzene and its derivatives".

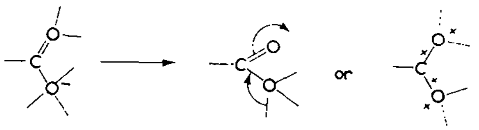
The scope of the definition was enlarged to include "polycyclic nuclei such as naphthalene, anthracene and phenanthrene" and a consideration of the essential common characters of these substances led to the extension to pyridine and its family and also to thiophene with furane and pyrrole by analogy.

At this stage the common "aromatic" molecular quality was sought and found in the possession of a stable nucleus which is readily formed and has a strong tendency to remain unchanged in chemical reactions. One illustration of this is the occurrence of substitution rather than addition reactions.

The next phase was the attempt to generalise the structural relations in the enlarged aromatic series in terms of valency theory, inevitably in the later stages on an electronic basis and finally with the help of the two usual wave-mechanical treatments.

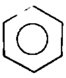
This has certainly led to a deeper, more satisfying, understanding of the nature of "aromatic" compounds in the wider sense but all the logical implications are not yet generally acceptable. There remains a contribution from the older systematics and this is approved by most organic chemists as a matter of convenience.

To take one example, the theoretical requirements for "aromaticity" are found in the carboxylion, $R{\cdot}CO_2^-$, because this is a stable group with a tendency to retain its type and there exists an electronic system, the formation of which is associated with a diminution of free energy. This may be crudely illustrated by the symbols:

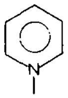


(—— = 2e, or $\overset{\times}{\times}$)

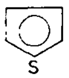
When the writer (with J. W. Armit in 1926) proposed the term "aromatic sextet" to denote a group of six electrons which by their presence and wave-mechanical interactions conferred a special stability on the molecular structure, the existence of similar groups such as that in the carboxylions was recognised. The "aromatic sextet" itself has proved a fertile conception, and it supplied an immediate explanation of such phenomena as the aromaticity of pyridine salts (the unshared electrons of the nitrogen atom not being involved in the sextet), the aromaticity of thiophene and pyrrole, and the stability of the anions derived from *cyclo*pentadiene derivatives.



benzenoid
sextet



sextet without
use of unshared
2e in nitrogen

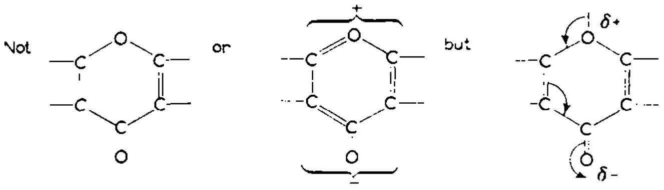


using 2e
lone pair in
S

using 2e left on
CH after ioni-
sation

Many more complex applications of the sextet have since been proposed, and among the more interesting are those in which electron transfer from one ring of a fused system to another is facilitated by the development of aromaticity in one or both nuclei.

In the anhydronium bases there is a similar compromise in the effects of opposing forces, neutralisation of electrical charges and tendency to aromaticity.



This was the first example to be proposed of hybridisation by conjugative electron displacement starting from a "classical" structure. The concept was by no means confined to γ-pyrones and especially the amides represent an even simpler case of hybridisation. The mis-called "resonance" theory, after an uneasy initial dynamic period, is now generally interpreted in the more static terms of hybrid molecules. It is hardly likely that an agreed definition of aromaticity will be evident in the papers of this Symposium, and it is hoped that discussion may ensue and reduce the area of disagreement, at least in the use of words. The present interest in the field is centred on more exact calculation on the one hand, and the discovery of new aromatic types on the other. It is hoped further contributions of an original nature will enable the theme to be developed in a significant manner in this Journal.