P. J. Garratt

AROMATICITY

AROMATICITY

PETER J. GARRATT
Department of Chemistry
University College London

A Wiley–Interscience Publication
JOHN WILEY & SONS
New York Chichester Brisbane Toronto Singapore

***Library of Congress Cataloging in Publication Data*:**

Garratt, P. J. (Peter Joseph), 1934–
  Aromaticity.

  "A Wiley-Interscience publication."
  Bibliography: p.
  Includes index.
  1. Aromatic compounds. 2. Chemical bonds.
I. Title.

QD331.G28 1986 547′.6 85-17816
ISBN 0-471-80703-6

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

AROMATICITY

E. HEILBRONNER: *On Mr. Binsch's slide the following definition is proposed: "A conjugated π-electron system is called aromatic if it shows neither strong first-order nor second-order double bond fixation." Now, could you point out a molecule, except benzene, which classifies as "aromatic."*

B. BINSCH: *Benzene is a perfect example!*

E. HEILBRONNER: *Name a second one.*

Jerusalem Symposia on Quantum Chemistry and Biochemistry, Vol. 3, *Aromaticity, Pseudoaromaticity, Antiaromaticity*, Israel Academy of Science and Humanities, 1971.

PREFACE

The classification of organic substances into aliphatic and aromatic compounds goes back to the early part of the last century. Its continued scientific justification arose from the finding that certain unsaturated radicals, such as C_6H_5, unexpectedly passed unchanged through a series of reactions carried out on these substances. Attempts to explain this behavior have provided one of the most fruitful areas for the interaction of theory and experiment known to organic chemistry, and this interaction continues to the present day. One of the initial major achievements of the application of quantum mechanics to large molecules, carried out by Hückel, was to provide not only an explanation for the stability of benzene but to predict other molecules which would be similarly stabilized. How these predictions were fulfilled and extended and how theory and experiment continue to interact in this area are the subjects of this text.

The text adopts a similar format to that I had used for a previous text in this area. It is aimed at final-year undergraduates and first-year graduate students and attempts to integrate theory and experiment. In order to improve readability, references have not been given except in the form of further reading at the end of each chapter. I hope that such provision, largely to reviews, will provide an easy and sufficient access to the primary literature for anyone seeking to clarify or develop the arguments used in the book.

The initial chapter provides an introduction both to the problem of aromaticity and to quantum theory; it may be omitted by those cognizant with the latter. The second chapter is pivotal to the rest of the text, expounding the theoretical and experimental differences between cyclobutadiene, benzene, and cyclooctatetraene. The following seven chapters describe the various types of compounds to which the attribute aromatic has been given; these chapters are each self-contained and, if the book is used as a teaching text, can be used or omitted to suit the instructor's taste. The penultimate chapter discusses the concept of homoaromaticity and related topological possibilities, an area which continues to provoke disputation, and the final chapter, after a cursory examination of the importance of aromaticity in the transition state, summarizes the conclusions of the preceding ten.

A number of people read the manuscript in whole or part during the course of its preparation. I would like to thank my students, Vahid Alikhani, Kate Baldwin, Alka Khurana, Stewart Mitchell, David Payne, John Porter, and Andrew Tsotinis, our visitors from Hannover, Uwe Matthies and Stefan Wolff, and my colleague Chris Cooksey, for reading and commenting on many or all of the chapters. Professor John Ridd read and gave me his expert advice on Chapter 3. I would also like to thank all of those who read and commented on the previous text and particularly Professor Peter Vollhardt, who translated and revised the previous German text with me. I am again indebted to Dr. Jim Parkin, but now also for his expert advice on word processing, a technique that allowed me to prepare my own typescript.

My friend and mentor, Professor Thomas Katz, initiated me into this area during a very happy period spent at Columbia University. It was sustained by the late Professor Franz Sondheimer, to whose memory I dedicate this book.

Acknowledgments. I thank Messrs Butterworths for permission to publish Figures 2.16 and 9.7; Professor R. McWeeny and Messrs Taylor and Francis for permission to publish Figure 2.14; and Pergamon Press for permission to publish Figure 4.19.

PETER GARRATT

AROMATICITY

CONTENTS

1

THE AROMATICITY PROBLEM

1.1. INTRODUCTION

One of the major achievements in chemistry during the nineteenth century was the formulation of an empirical theory of valency. This theory resulted largely from the study of organic compounds, the systematic investigation of which was begun in the early part of the century by Wohler and Leibig. Whereas the ionic theory of Berzelius explained much of the inorganic chemistry that was known at the time, Dumas and others clearly demonstrated that this theory was not successful in accounting for the behavior of organic compounds. Thus, although chlorine and hydrogen were of opposite nature in the system of Berzelius, chlorine could replace hydrogen in organic systems. Furthermore, as was pointed out by Laurent, in most cases such a *substitution* did not greatly affect the properties of the compound. A second important observation was that groups of atoms in organic molecules appeared to pass unchanged through complex series of reactions. These groups of atoms, such as CH_3 and CH_3CH_2, were called *radicals.* After a long and acrimonious argument between the proponents of the substitution theory and those of the radical theory, these theories were combined by Gerhardt, using the experimental results of Hofmann and of Williamson, into his "theory of types." In this theory, the hydrogen atoms of the parent system of the type were successively replaced by organic "radicals." Thus, methanol, CH_3OH, was of the water type, one of the hydrogens of H_2O having been replaced by the CH_3 radical. Dimethyl ether, CH_3OCH_3, was also of the water type, but in this case both of the hydrogens had been replaced by CH_3 radicals.

A second problem, which was resolved at about the same time, was the question whether atomic or equivalent weights should be used in the formulation of organic molecules. Berzelius had established excellent values for the atomic weights of many of the elements early in the century, but unfortunately his atomic weight for carbon was most seriously in error. Because of this, some chemists had come to favor equivalent weights, with carbon having the value of 6, for the composition of organic compounds. Complete confusion resulted, since, for example, H_2O_2 could be the formula of either water or hydrogen peroxide! However, at the Karlsruhe Conference in 1860, Cannizarro circulated a pamphlet that, although it did not lead to immediate agreement on a single system, had a profound effect on the conference participants. In this pamphlet, the Italian chemist summarized his previously reported results and explained how, by the use of Avogadro's hypothesis, a unique system of atomic weights could be obtained that was applicable to both organic and inorganic compounds. Most chemists accepted these findings, and molecular formulas were able to be established on which all could agree.

In 1857, just before the Karlsruhe Conference, Kekulé had recognized that by using the new atomic weights of Cannizarro, carbon appeared to be tetravalent in a number of its compounds. In his celebrated paper of 1858, Kekulé extended this view to all carbon compounds and also introduced the concept that the carbon atoms could be linked to one another. Similar views were put forward independently by Couper, who used a dotted line to represent a valency bond. These ideas were developed for other atoms, and it was concluded that each atom had one or more valencies. The belief that the formula now represented an arrangement of atoms began to be more commonly accepted, and structural formulas were introduced by Crum Brown. These structural formulas were then shown to require modification to express the three-dimensional nature of the molecules, and the concept of the tetrahedral arrangement of the carbon valencies was independently advanced by van't Hoff and Le Bel.

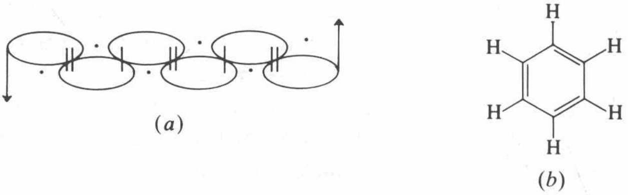
A number of carbon compounds, such as carbon monoxide, did not conform to the Kekulé–Couper theory of tetravalent carbon. The unsaturated hydrocarbons ethylene, C_2H_4, and acetylene, C_2H_2, were two further exceptions to the rule, and three serious explanations were put forward to account for the apparent lack of tetravalency of carbon in these systems. Couper proposed that carbon could be divalent as well as tetravalent, Kekulé suggested that some of the carbon valencies were unsatisfied, and Erlenmeyer proposed that the carbons were linked to each other with more than one valency. Benzene and the aromatic compounds raised further complications, since these molecules, unlike ethylene and acetylene, do not readily undergo addition reactions to give derivatives in which carbon is tetravalent. The paradox of benzene, unsaturated and yet inert, is the central theme of this book. The ramifications of this problem lead us far away from benzene, but it remains the aromatic compound par excellence and will be the subject of discussion in the rest of this and much of the two next chapters.

1.2. EARLY INVESTIGATIONS INTO THE STRUCTURE OF BENZENE

Benzene was discovered by Faraday in 1825 in the condensate obtained by compression of the gas generated by pyrolysis of whale oil. Faraday determined the composition, vapor pressure, and melting point (42°F). He deduced the correct molecular formula, which he expressed as C_6H_3, using the equivalent weights current at that time. The first synthesis of benzene was accomplished by Mitscherlich in 1833 by the decarboxylation of benzoic acid. Mitscherlich confirmed the correct molecular formula and subsequently synthesized a number of derivatives.

Benzene was recognized as the parent of a number of compounds, all of which contained the C_6H_5 radical, and this radical was shown to be inert, remaining intact throughout series of chemical reactions. Benzene did not fit into the Kekulé-Couper tetravalent theory of carbon and joined the unsaturated hydrocarbons ethylene and acetylene in providing difficulties for the theory.

The first satisfactory formula for benzene was put forward by Kekulé in 1865. In this formulation, the six carbon atoms of benzene were considered to be linked alternately by one or two valencies, which left eight valencies unsatisfied. Two of the unsatisfied valencies were then used to link the terminal carbon atoms to form a *cyclic system.* The six carbon atoms then had six unused valencies to which six monovalent hydrogens could be attached. This was originally illustrated by Kekulé as the structure shown in Figure 1.1*a* in which the ellipses represent the carbon atoms, the lines depict the bonds between the carbon atoms, the dots represent the points of attachment of the hydrogen atoms, and the arrows indicate the junction of the terminal carbon atoms. Subsequently, Kekulé modified these concepts and introduced the now familiar hexagon structure, with alternate double and single bonds (Fig. 1.1*b*).



(*a*) (*b*)

Figure 1.1. Structures for benzene suggested by Kekulé. For a description of structure (*a*) see text.

The hexagonal formula predicts that all six carbon atoms, but not the six bonds, are equivalent, and this prediction was confirmed by investigations carried out independently by Ladenburg and Wroblewsky. Wroblewsky prepared the five possible monobromobenzoic acids, using suitable blocking groups that could be subsequently removed, and he found that the 1,2 and 1,6, and the 1,3 and 1,5 derivatives were identical (Fig. 1.2). Thus, carbons 2 and 6 and carbons 3 and 5 are identical. Ladenburg had previously found that the three isomeric hydroxybenzoic acids gave the same phenol on decarboxylation and the same benzoic acid on reduction. The phenol was then converted to benzoic acid, which was shown to be identical with benzoic acid obtained by reduction. Thus, the carbon atoms at positions 1, 2, 3, and 4 are equivalent. The combination of these data with Wroblewsky's demonstrates that the six carbon atoms are equivalent to each other (Fig. 1.2).

These experiments now placed the requirement on any suggested structural formula of benzene that all the carbon atoms must be equivalent.

Ladenburg now protested that Kekulé's hexagon formula required *four*, rather than the *three* disubstituted products that had been prepared (Fig. 1.3). To counter this objection, Kekulé introduced the concept that there were two equivalent structures for benzene, Figure 1.4, which rapidly interconverted by a "mechanical motion." This mechanical motion is equivalent to the oscillation of the double bonds around the ring and the interchange between **1***a* and *b* renders the two 1,2-disubstituted derivatives in Figure 1.3 equivalent.

Although the "resonating" structures for benzene now appear to us as an example of Kekulé's intuitive genius, at the time it was introduced, the idea was considered a mere device to save the hexagon theory. Many other structures for benzene were proposed, such as the "para bonded" formula **2** by Dewar and Wislicenus and the "diagonal" formulas **3** and **4** by Claus. We now recognize that such formulas have stereochemical implications as three-dimensional structures, but this was not completely recognized at the

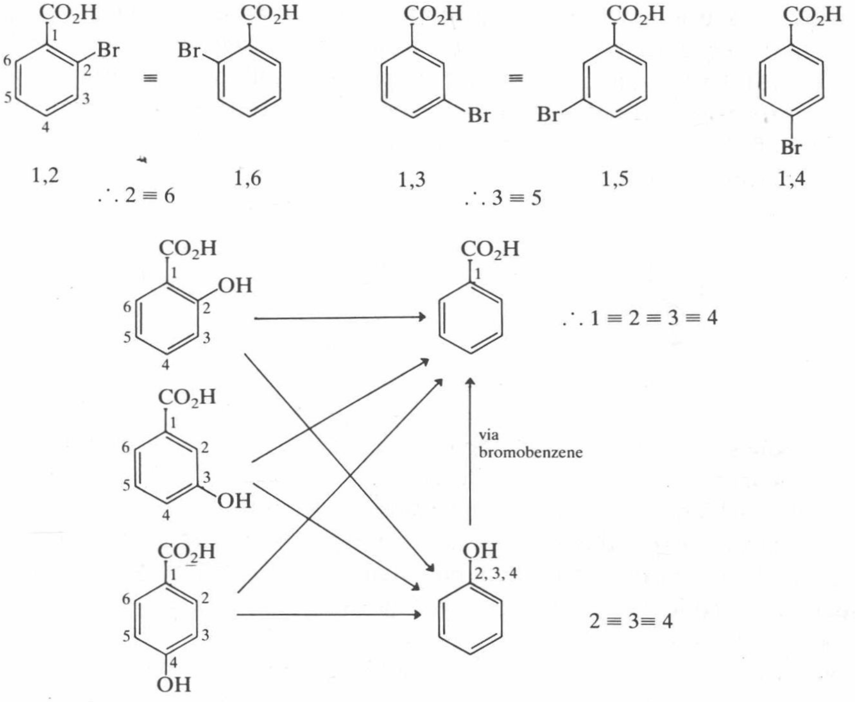


Figure 1.2

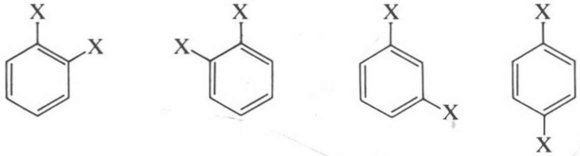
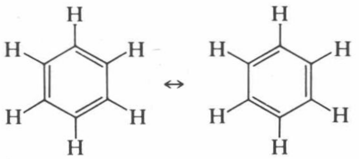


Figure 1.3. The four possible disubstituted benzenes assuming the static Kekulé hexagonal structure.



a **1** *b*

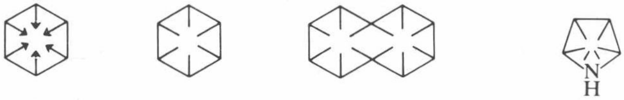
Figure 1.4

time. Ladenburg, however, also proposed formula **4** for benzene and subsequently recognized the three-dimensional properties of "Ladenburg's prism" (**5**). Ladenburg believed that the prism formula was consistent with the observation that only one ortho disubstituted benzene was known, but van't Hoff demonstrated that the prism formula requires that enantiomeric "ortho" forms should exist.

2 **3** **4** **5**

Figure 1.5

Kekulé's formulation continued to provide conceptual difficulties for many workers. Lothar Meyer and Armstrong independently proposed a model in which the six unused valencies were directed toward the center of the hexagon (**6**); this formula was adopted by Baeyer (**7**). Bamberger extended this type of formula to naphthalene (**8**) and to heterocyclic systems, such as pyrrole (**9**). Bamberger recognized that in these systems *six* unsatisfied valencies are required for each ring, and he clearly considered that this arrangement must provide a stabilized inert system.



6 **7** **8** **9**

Figure 1.6

These structural theories for benzene are a remarkable achievement of nineteenth-century chemistry, but they do not explain the lack of reactivity of benzene and related aromatic systems. It is difficult to understand why either the Kekulé structure or those with unsaturated valencies should not readily undergo addition reactions. The Dewar, Claus, and Ladenburg structures, when translated into three-dimensional forms, are unacceptable. Dewar's structure **2** would indicate that two carbons are different from the other four, besides having the stereochemical implications shown in formula **10**. The diagonal formula **3** of Claus is not translatable into three-dimensional terms with reasonable bond angles (Fig. 1.8). A number of these structures will be discussed further in Chapter 3 as valence isomers of benzene.