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Aromatic Compounds

**Organic Chemistry
Series Two
Volume 3**

**Consultant Editor
D H Hey FRS
Volume Editor
H Zollinger**

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Volume 3

Aromatic Compounds

Edited by **H. Zollinger**

Eidgenössische Technische Hochschule, Zürich



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International Review of Science

Organic Chemistry
Series Two

Consultant Editor
D. H. Hey, F.R.S.

Publisher's Note

The International Review of Science is an important venture in scientific publishing presented by Butterworths. The basic concept of the Review is to provide regular authoritative reviews of entire disciplines. Chemistry was taken first as the problems of literature survey are probably more acute in this subject than in any other. Biochemistry and Physiology followed naturally. As a matter of policy, the authorship of the Review of Science is international and distinguished, the subject coverage is extensive, systematic and critical.

The Review has been conceived within a carefully organised editorial framework. The overall plan was drawn up, and the volume editors appointed by seven consultant editors. In turn, each volume editor planned the coverage of his field and appointed authors to write on subjects which were within the area of their own research experience. No geographical restriction was imposed. Hence the 500 or so contributions to the Review of Science come from many countries of the world and provide an authoritative account of progress. The publication of Organic Chemistry Series One was completed in 1973 with ten text volumes and one index volume; in accordance with the stated policy of issuing regular reviews to keep the series up to date, volumes of Series Two will be published between the middle of 1975 and early 1976; Series Two of Physical Chemistry will be published at the same time, while Inorganic Chemistry Series Two was published during the first half of 1975. Volume titles are the same as in Series One but the articles themselves either cover recent advances in the same subject or deal with a different aspect of the main theme of the volume. In Series Two an index is incorporated in each volume and there is no separate index volume.

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Consultant Editor's Note

The ten volumes in Organic Chemistry in the Second Series of the biennial reviews in the International Review of Science follow logically from those of the First Series. No major omissions have come to light in the overall coverage of the First Series. The titles of the ten volumes therefore remain unchanged but there are three new Volume Editors. The volume on Structure Determination in Organic Chemistry has been taken over by Professor Lloyd M. Jackman of Pennsylvania State University, that on Alicyclic Compounds by Professor D. Ginsburg of Technion-Israel Institute of Technology, and that on Amino Acids, Peptides and Related Compounds by Professor H. N. Rydon of the University of Exeter. The international character of the Series is thus strengthened with four Volume Editors from the United Kingdom, two each from Canada and the U.S.A., and one each from Israel and Switzerland. An even wider pattern is shown for the authors, who now come from some sixteen countries. The reviews in the Second Series are mainly intended to cover work published in the years 1972 and 1973, although relevant results published in 1974 and 1975 are included in some cases, and earlier work is also covered where applicable.

It is my pleasure once again to thank all the Volume Editors for their helpful cooperation in this venture.

London

D. H. Hey

Preface

The majority of authors who treated various aspects of aromatic chemistry in the respective volume of Series One of the International Review of Science were, fortunately, also willing to contribute a chapter to Series Two. I am particularly grateful to these authors as the volume in Series One was, in general, well received by both book reviewers and the scientific community.

In some chapters the emphasis has been placed on aspects not discussed in Series One, as a careful and critical review of the whole subject was not possible in the first Series owing to limitations of space. Thus, the chapter on nucleophilic aromatic substitution in the present volume includes a discussion of substitutions involving aryne intermediates which were not mentioned in Series One. On the other hand, the nucleophilic addition-elimination mechanism is not discussed in this volume.

I am glad that a chapter on polymers containing aromatic nuclei could be included for the first time.

The chapter authors and I hope that the present volume fulfils its task in giving the reader a critical and comprehensive review of the advances which have taken place in aromatic chemistry during the past few years.

Zürich

H. Zollinger

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1 The Controversial Notion of Aromaticity

I. AGRANAT and A. BARAK

The Hebrew University of Jerusalem



Hold thou the good: define it well:
For fear divine Philosophy
Should push beyond her mark, and be
Procuress to the Lords of Hell
Alfred Lord Tennyson¹

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1.1 INTRODUCTION AND GENERAL CONSIDERATIONS

1.1.1 Introduction

The present chapter, which is by no means comprehensive, will concentrate on the general problem of the definition of aromaticity, present and future, and on various aspects of delocalisation *vis-à-vis* aromaticity as revealed in the years 1972–1973. Emphasis will be given to the recent contributions of the Valence Bond theory and the rehabilitated HMO method to the notion of aromaticity. Contrary to the corresponding chapter in *Series One* of the *International Review of Science*², the present chapter does not attempt to survey the numerous experimental approaches to aromaticity. An explicit treatment of topological aspects of aromaticity are also not included. The title of the review has been rephrased so as to signify the controversial character of the notion and the lack of general agreement on the subject.

1.1.2 The state of the art of aromaticity

At the end of the review on aromaticity entitled 'Theoretical Aromatic Chemistry' in *Series One* of this review², the author expressed the hope that a universal definition of aromaticity will emerge that will allow simple, qualitative, as well as significant comparison between molecules. The studies of the notion of aromaticity during the period covered in the present chapter certainly did not fulfil this hope. The status of aromaticity may be compared with the motion of a pendulum, swinging to and fro between two extremes: the highly glamorous position of a well-defined, indispensable, general concept and the disreputed position of an outdated, vague, confusing and futile term which should be eliminated from the vocabulary of the chemist.

The aromaticity controversy reached its peak at the International Symposium devoted to the topic 'Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity' held in Jerusalem in the spring of 1970³. The role of the devil's advocate was played by Heilbronner who argued, from a pragmatic point of view, against the usefulness of the notion of aromaticity⁴. Bringing the arguments *ad absurdum*, he ironically coined the term *schizo-aromatic* for molecules that may be aromatic or non-aromatic depending upon the type of measurements made^{4–6}. Bergmann and Pullman, in concluding the symposium, led the opposing conception, maintaining that aromaticity is useful and will continue to be employed as long as we know the inherent limitations of this notion⁷.

The discussion in the Third Jerusalem Symposium prompted (or provoked) Labarre, Lloyd and Binsch to reveal explicitly their views (perhaps also their feelings) on the definition of aromaticity, in special articles devoted to the topic^{8–10}. They expressed various degrees of antagonism to the notion of aromaticity, but suggested solutions of their own to the impasse (*vide infra*).

Clues as to the opposite trend in the state of the art of aromaticity have been provided in the recent appearance of the following favourable signs: an elementary review by Breslow on the nature of aromatic molecules in the popular and prestigious organ *Scientific American*¹¹, a review on anti-aromaticity by the same author¹² and an advanced textbook entitled *Aroma-*

ticity by Garratt¹³. Aromaticity, in Breslow's account for laymen¹¹, refers to the exceptional stability of certain ring-shaped organic molecules. Whether a given system is aromatic, non-aromatic or anti-aromatic depends on how many of its electrons are delocalised. Breslow does not ignore the reality that aromaticity is a word with many meanings¹². Such regrettable imprecision is a cause for caution, although it is hardly a reason to disregard the word. Breslow adopts the common energetic definition that a compound is aromatic if cyclic delocalisation of π -electrons stabilises it relative to an analogous model compound without cyclic delocalisation¹². Likewise, a cyclic conjugated system is considered to be anti-aromatic if its π -electron energy is higher than that of a suitable reference compound which is not cyclically delocalised. Thus aromaticity is a particular aspect of bonding whereas anti-aromaticity is a particular aspect of anti-bonding. In both cases the definition assumes that there are ways of assigning the total energy of a given molecule to various compartments, one of which reflects the result of cyclic delocalisation of its π -electrons¹². Garratt put forward the following definition¹³: aromatic compounds are cyclic systems which exhibit a diamagnetic ring current and in which all of the ring atoms are involved in a single conjugated system. Garratt realises that this definition is open to criticism; on the other hand, it allows both for the formal definition of an aromatic system and also provides a physical property which the experimentalists can determine¹³.

1.1.3 Destroying the tower of Babel of aromaticity

Is aromaticity an out-of-date or an up-to-date concept? Is aromaticity a myth or a reality? Labarre and Crasnier open their critique of the notion by asking and discussing these cardinal questions, before venturing upon defining and measuring aromaticity⁸. One cause of the present confusion lies in Kekulé's original poor choice of the word for the fundamental new concept. The trend of overlooking what was being measured and defined has continued since. A second difficulty proceeded from the fact that aromaticity has at least two meanings, basically different: the chemist's meaning (a compound is aromatic if its chemistry is like that of benzene), and the physicist's meaning (a compound is aromatic if it has a low ground-state enthalpy). The undermining of the word aromaticity began with the discovery of molecules which were physically but not chemically aromatic. The new concepts derived from aromaticity, which were introduced in order to bridge the gap between the two definitions — pseudo-aromaticity, quasi-aromaticity, anti-aromaticity, non-aromaticity, homo-aromaticity, pseudo-anti-aromaticity, super-aromaticity, spiro-aromaticity — resulted in complete confusion.

The fact that aromaticity has been a typically organic concept led to great difficulties when confronted with inorganic ring systems. This applies in particular to Hückel's rule and to resonance energy. In the field of inorganic ring systems, the separation between σ and π levels vanishes. The concept of resonance energy cannot readily be extended to the general field of ring systems, because its calculations, even in the simplest inorganic cyclic molecules, are strongly dependent on the chosen degree of accuracy and on the personal selection of standards. This difficulty has been felt even on the level

of pure organic chemistry. The bond alternation criterion and Binsch's first- and second-order double bond fixation criterion are also not necessarily applicable to inorganic chemistry. Furthermore, it is not legitimate to compare the aromaticity scale obtained by the ring current concept with those based on the resonance energy and on reactivity factors.

Labarre and Crasnier's main criticisms against the use of the word aromaticity are as follows: if aromaticity is postulated to be an intrinsic, mysterious, non-observable characteristic of the so-called aromatic compounds, it becomes obvious that all there is to do is to collect the various answers provided by this myth to each of the external perturbations and nobody can say whether the aromaticity scales so obtained will be consistent or not. Moreover, each individual may create a picture of myth which is convenient for him. Accordingly, aromaticity is not a scientific word but an aesthetic one.

A case against Kekulé's fundamentally necessary assumption that a cyclic molecule cannot be aromatic if it is not planar is also argued. Under certain conditions, e.g. delocalisation due to a $2p$ - $3d$ overlap, planarity is no longer a *sine qua non* for the aromaticity of the molecule.

Benzene seems to be the worst standard for the study of aromaticity. It is a highly symmetrical and very exceptional molecule; it belongs to the D_{6h} point group and its actual structure in the liquid state is locally the same as in the solid state. The specific properties of π delocalised ring systems seem to depend on their symmetry point group. Thus, a comparison of the aromaticity of pyridine (C_{2v}) with that of benzene (D_{6h}) is meaningless. All the approaches to the myth aromaticity would become perhaps more powerful if the concept of group symmetry was present in their developments.

Labarre and Crasnier conclude that the word aromaticity must be extirpated from the scientific literature, not only because it means nothing from a scientific point of view (not being an observable property), but chiefly because it too often hides a dangerous imprecision about what is being measured and why. Moreover, the use of the word restricts the freedom of scientific reasoning. The time has come when the tower of Babel of aromaticity must be destroyed. The way to avoid the confusion will be a theoretical one: when the theory permits to predict quantitatively the experimental signs of aromaticity, it will be possible to approach the unique entity. In the meantime, a scientist using a given experimental approach should try to define and to measure whatever is measurable by his technique, in the hope that the data will eventually fit into a unified concept and a unified theory.

1.1.4 An alternative nomenclature of cyclic conjugated systems?

Lloyd and Marshall emphasised the remarkable contrast between the high frequency and the avidity with which the word aromatic is used and the indeterminacy of its meaning. They compared the present attitude towards aromaticity with a medieval theological disputation and saw the need for a reformation (or a counter-reformation). They suggested that because of the confusion and lack of common consent as to its meaning, it would be better if the use of the term aromatic were discontinued (save perhaps with its general and original connotation of 'perfumed'), and that it should pass into

the realm of the historian of chemistry. Instead, Lloyd and Marshall proposed the following alternative approach to the nomenclature of cyclic conjugated polyolefins, based on a differentiation between three factors: structural features, ground-state properties and chemical reactivity^{9,14-15}.

(a) The terms arenes, aryl and benzenoid will be used to denote structural features, namely the presence of a benzene ring. Presently, the term arenes is defined as the generic name of monocyclic and polycyclic hydrocarbons¹⁶. Lloyd and Marshall propose that arenes should be specifically restricted to benzenoid hydrocarbons. The unambiguity of the word benzenoid (compared with aromatic) is self evident.

(b) The terms Hückel, anti-Hückel (or counter-Hückel) and non-Hückel systems will be used to refer to ground-state properties. These terms will replace what is probably the most general present-day usage of aromatic, anti-aromatic and non-aromatic, respectively, namely the energetic criterion.

(c) The terms regenerative or meneidic will be used to refer to chemical reactivity, namely the tendency of an unsaturated molecule to react by substitution rather than addition. The word regenerative is descriptive of the process which takes place — the original electronic system is regenerated after being temporarily lost in the transition state; the word meneidic is of Greek origin (from *menein*, to stay, persist, remain; and *eidōs*, type, form). Both words imply Armit and Robinson's characterisation 'the tendency to retain the type'. Thus benzene normally behaves as a regenerative or meneidic system whereas ethylene does not. These two terms need not necessarily be confined to electrophilic substitutions. However, for convenience, they should be restricted to substitutions at sp^2 -hybridised centres and to substitutions through association (S_A reactions) wherein a new bond is formed before the old bond breaks. The 2,3-dihydro-1,4-diazepinium salts, previously denoted as quasi-aromatic, and obviously not Hückel compounds, are examples of regenerative or meneidic systems.

The three factors which form the basis of the alternative nomenclature had all at different periods been regarded as criteria for aromaticity but are not always compatible.

1.1.5 Sharpening the definitions, but without obsession¹⁰

Binsch poses the provocative question whether aromaticity should be considered an exercise in chemical futility. He realises how ill-defined the concept is, but he forcefully rejects the idea that aromaticity should be eradicated from the chemical terminology. The shortcomings of aromaticity are typical of the general crisis in chemistry.

Binsch considers all attempts to force aromaticity into a narrow theoretical straitjacket as futile. Instead, he considers the following approaches (which are partly incompatible and partly interconnected): formal definitions, physical properties, magic rules and experimental criteria.

Binsch argues that even if the term aromaticity is reserved exclusively for compounds containing a benzene ring, complications may arise. The formal classification schemes presuppose the existence of discontinuities whereas chemistry is based on similarity and contiguousness. The formal definition of

aromaticity remains useful especially for didactic purposes, as long as it is not fixed too sharply.

Two attempts of interpreting aromaticity in terms of physical properties, based on energetics and structure, have been considered. The energetics approach was confronted with the difficult problem of choosing the correct reference structure and with the impossibility of making a measurement on a hypothetical molecule. The classical resonance energy failed as a quantitative measure of aromaticity. The salient characteristics of aromaticity are more closely related to the change in π -electron energy associated with the transition from acyclic to cyclic systems. The new definition of a specifically cyclic resonance energy (*vide infra*) eliminates most of the discrepancies between theory and experiment. However, the reference structure is still a fictitious entry. The more empirical and intuitive information creeps into a theory of aromaticity, the more satisfactory it becomes to the chemist, whereas a serious attempt at a rigorous theoretical definition must ultimately be lethal to the whole concept. Two other objections were raised: if aromaticity is interpreted exclusively on ground state energetics, it does not *per se* apply to the chemical reactivity. Furthermore, resonance energy is a global property of a molecule and thus chemically meaningful for highly symmetrical structures, but uninteresting for less symmetrical structures.

The structural approach, on the other hand, is based on a molecular property that is rarely ambiguous, can frequently be measured accurately and has an absolute meaning independent of a reference compound. More important, the information obtained consists of a whole matrix of interatomic distances, not only of a single number. Sharpness of definition can be gained only at the expense of chemical information content.

The parallelism of the energetic and structural approaches makes chemical sense. Compounds predicted to be anti-aromatic by the energetic criterion, are prone to suffer second-order double-bond fixation. The two approaches are complementary. The emphasis on energetics is likely to produce a deeper insight into the physical origin of certain effects whereas structural consequences provide more detailed unambiguous information.

Most of the experimental work in the area of aromaticity derived its motivation from various attempts to explain aromatic character by simple magic rules. Among these are the aromatic sextet, Hückel's rule, Craig's rules and the Woodward-Hoffmann rules. With respect to Hückel's rule, two points are noteworthy: the inference of special stability in planar monocyclic hydrocarbons with $(4q + 2)\pi$ electrons was arrived at by a leap of the imagination, stimulated by the analogy to atomic systems, but this analogy cannot be derived. The dramatic differences in properties between Hückel and anti-Hückel systems in small rings diminish with increasing size.

Hückel's rule is a special case of the Woodward-Hoffmann rules which make general statements about energetically favourable or unfavourable orbital interactions in cyclic arrays. The terms aromatic and anti-aromatic are now also applied to transition states and to electronically excited states. Binsch questions the wisdom of the urge to generalise. He maintains that the goal of elevating the importance of orbital interactions to an all-encompassing principle can only be achieved at the expense of doubtful simplifications. Moreover, qualitative rules are often very difficult to quantify.

The most frustrating aspect of most theories of aromaticity is the fact that they cannot be subjected to direct quantitative experimental tests. This difficulty may be removed by explicitly defining aromaticity in terms of certain observables. A very popular experimental criterion of aromaticity relies on magnetic phenomena of conjugated molecules. But ring current effects, e.g. in the annulenes, should not be taken as an experimental proof of aromaticity. Although the ring current criterion goes parallel with the energetic and structural criteria for monocyclic systems, this parallelism does not hold in certain polycyclic systems.

In conclusion, Binsch realises that the problem of aromaticity has not been solved. By gaining in generality, aromatic character grows steadily more diffuse and qualitative, until chemical intuition becomes the only test of its validity. On the other hand, the attempts to reduce aromaticity to an observable, result in definitions that are too narrow to be acceptable. At present, we cannot afford to renounce the term aromaticity. Being just a name, we are at liberty to continuously adapt its meanings to the changing needs for conceptualisation. Attempts to sharpen the definitions must continue, but should not become an obsession¹⁰.

1.2 ASPECTS OF DELOCALISATION

1.2.1 The revival of the HMO method. Hess and Shaad's REPE and related approaches

It is well known that the HMO method failed to predict correctly aromatic or anti-aromatic character in cyclic conjugated hydrocarbons. A striking illustration of this failure is the Hückel delocalisation energy of the notorious pentalene, which is higher than that of benzene. Dewar and de Llano have recently applied a more refined approach based on the Pariser-Parr-Pople (PPP) SCF MO method, which gave very good predictions on aromaticity¹⁷. Dewar's resonance energy (DRE) was defined as the difference between the calculated π energy and the sum of bond energy terms¹⁸⁻²². This difference vanishes for acyclic polyenes, is significantly positive for aromatics and is significantly negative for anti-aromatics. In computing resonance energy, Dewar used double and single bond energies appropriate to non-aromatic systems instead of those for non-conjugated systems in the reference compound. In essence, the DRE is a measure of the extra stabilisation (or destabilisation) associated with a ring system compared with the corresponding open-chain compound which contains the same number of conjugated carbon atoms²¹. It turned out that it was this change in reference rather than the switch to a more sophisticated computational method which was crucial²². Dewar noted that for acyclic polyenes (which by definition can exhibit neither aromatic nor anti-aromatic character) both the effective energy of the carbon-carbon double bonds and the effective energy of the carbon-carbon single bonds are constant^{17,20}. Thus, conjugation has the same energetic consequences (per bond) in all non-aromatic systems²⁰.

Hess and Schaad have found that with a proper reference structure, analogous to Dewar's, the simple HMO method can make accurate predic-