

**BRIDGED  
AROMATIC  
COMPOUNDS**

**By Brandes H. Smith**

**ORGANIC CHEMISTRY: A SERIES OF MONOGRAPHS**

# BRIDGED AROMATIC COMPOUNDS

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*Brandes H. Smith*

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# **BRIDGED AROMATIC COMPOUNDS**

# ORGANIC CHEMISTRY

## A SERIES OF MONOGRAPHS

*Edited by*

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**Volume 1.** Wolfgang Kirmse. CARBENE CHEMISTRY. 1964

**Volume 2.** Brandes H. Smith. BRIDGED AROMATIC COMPOUNDS. 1964

*In preparation*

Donald J. Cram. FUNDAMENTALS OF CARBANION CHEMISTRY

Michael Hanack. CONFORMATION THEORY

Kenneth B. Wiberg. OXIDATION IN ORGANIC CHEMISTRY, PART A

## Preface

When first conceived this work was to cover the chemistry of bridged benzene rings, familiarly called the cyclophanes. Within a short time the work was expanded to include all bridged aromatic systems, the majority of which still are bridged benzene rings. The study of the bridged non-benzenoid aromatics is growing rapidly, particularly in the ferrocene area. Thus while this text may serve as an encyclopedia of cyclophane chemistry, it will be but a primer for bridged ferrocenes and other similar compounds.

There are several general reasons one might offer for studying the bridged aromatics but perhaps the most compelling reason is to be found in the geometry of the species. Generally, these species are of a definite fixed geometry with limited or restricted rotation about covalent single bonds. Some possess severely deformed bond angles and bond lengths. Although such rigidity and deformation of molecular character have evoked unusual behavior in several of these systems, the knowledge and the reasonable assurance of molecular configuration have permitted chemists more readily to devise and interpret experiments for studying the physical and chemical behavior of these molecules. This has been particularly true in explaining electrophilic substitution in the  $[m.n]$ paracyclophanes and ferrocenophanes, ultraviolet absorption bands in the cyclophanes, and certain electronic shielding effects manifested in the chemical shifts evident in the nuclear magnetic resonance spectra. There are many other curious phenomena which can be associated with the rigid or deformed molecular structures.

It may be that the chapter construction of this book permits or even encourages occasional overlap or repetition from one chapter to another. In most instances this has been done intentionally so that the reader may have specific data from previous chapters without resorting to a search.

The older literature, which is filled with reports of highly strained and yet improbable or impossible bridged systems, has been treated slightly and by no means completely in regard to content and references. Similar treatment has been given to some of the more recent and only slightly more credible reports. Conversely, the more accurate recent reports have been treated in considerable detail. In some cases the detail has been as nearly complete as in the original article. This is necessary to form proper foundations for subsequent or complementary topics. Other reports which are

equally revealing may have had no more than cursory treatment given them and a reference noted—not because these works are of lesser importance but because a discussion of them in detail would usually mean a repetition of much which had been previously presented. Lucid and full discussions of many of the points covered can be found in the original articles. The reader is urged to pursue these.

Since this book has been compiled and correlated from a multitude of individual, related—and sometimes apparently unrelated—studies, by far the greatest measure of appreciation from the author must go to those people who have provided him with the information needed to complete this work. Not only have a great many published reports been used to prepare the text, but many researchers have been kind enough to make available data which, at the time, were unpublished. Some of these subsequently have been published. Some will be found for the first time in this book. Without these data the work would be far less complete.

Many others have contributed in large or small measure to making this book a reality. The writer's interest in bridged aromatic systems can be traced to his association with Professor Alfred T. Blomquist, who has additionally served as a counselor on several phases of this writing. Librarians in several locations deserve special thanks for their toil in locating numerous and sometimes obscure references.

BRANDES H. SMITH

*Murray Hill, New Jersey*  
*November, 1964*

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13. D. J. Cram and L. A. Singer, Vol. 85, p. 1085 (1963), Table IV.
14. N. L. Allinger, L. A. Freiberg, R. B. Hermann, and M. A. Miller, Vol. 85, p. 1175 (1963), Tables VIII and IX.



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## Nomenclature\*

It is a naively simple observation, but still one that bears stating: for a reader to understand fully the contents of a book, he must know what the author is talking about. This in itself should be compelling reason enough for a chapter on the nomenclature of a specialized subject. But there is, in the area of the bridged aromatic rings, a further, deeper reason. There abound in this field varied systems, methods, and examples of nomenclature which have been used over the years before the existence of these species was established, as well as after. Most of these systems logically were created from existing systems for other classes of compounds such as the 1,4-disubstituted benzenes, the phenylenes, and so forth. Some others were cleverly devised by the chemist to suit his unique purposes. Examples are the tetroxaquaterenes of Brown and French (1) and the xylylenes of Brown and Farthing (2). This is not without precedent. The literature of the past and the present (and presumably the future) is filled with examples of proposed "trivial" names to be used for a single or several compounds. Frequently, but not always, this use of trivial names will occur after the author has bowed to the weight of convention and assigned the so-called systematic name.

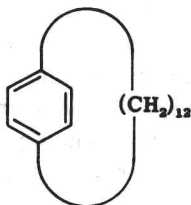
It seems at least advisable, if not imperative, to review these variations in order that the reader may be better prepared and acquainted with the cast of characters he is to meet later, both in this book and in any of the original references he may choose to seek out. However, lest the same reader

\* The new system of nomenclature which is used throughout this book (and which is described later in this chapter) for bridged aromatic species other than bridged benzene rings is a provisional one only. A proposal describing it has been submitted to the Committee on Organic Nomenclature of the Division of Organic Chemistry, American Chemical Society, for its consideration. This proposal has received favorable comment by the above Committee and a Subcommittee, of which the author is a member, has been formed to refine the proposal for acceptance by the Committee before its submission to the Society. At the time this book went to press, final action by the Committee had not been taken. The reader thus is cautioned in his use of the method as further revisions and refinements may be made.

be dismayed that he is to encounter a bewildering array of names based on many different systems, let him be assured that in the body of this work an effort has been made to adhere to a single system whose aim it is to unify the nomenclature of these bridged structures. This system will be described later in detail. Deviations to other systems are made for purposes of illustration or to allow those who would refer to the original work to have the necessary guide.

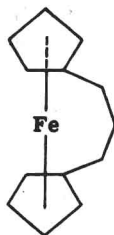
### Polymethylene or Disubstituted Aromatic System

In this system the parent ring is considered to be the disubstituted aromatic. Though it usually has been applied to benzene it is by no means restricted in this manner. The 1,2 bridges, being *ortho*, are trivial, which limits the system to the 1,3 and 1,4 positions for the benzene nucleus and to comparable positions in other aromatics such as naphthalene, ferrocene, thiophene, etc. For example, by this method compound (I) would be called



(I)

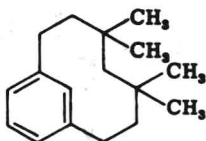
1,4-dodecamethylenebenzene and (II) would be 1,1'-trimethyleneferrocene.



(II)

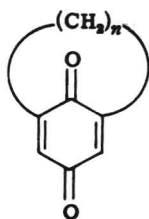
To use this system on simple bridged aromatics all one needs to know is

the numbering scheme of the aromatic ring. The introduction of substituents into the bridge quickly makes matters more complex by adding primes to the position numbers of bridge substituents. These bridge numbers, then, may very well be duplicates of those identifying the bridge attachments to the aromatic nucleus. Thus (III) would be 1,3-(3',3',5',5'-tetramethyl-

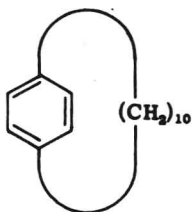


(III)

heptamethylene)benzene. If one now adds the further complications of substituents in the aryl nucleus and the possibility of multinuclear bridged structures, the system becomes both highly complex and unwieldy. Yet it had persisted up to a few years ago. Two simple examples from the literature are those of Prelog and Wiesner (3) and Cram *et al.* (4, 5) These are (IV) and (V), respectively, and are called polymethylenebenzoquinones and 1,4-decamethylenebenzene.



(IV)

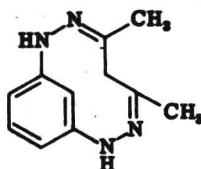


(V)

### Phenylene System

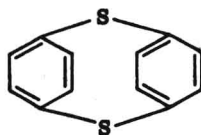
A second alternative for a nomenclature system is to consider the bridge of the bridged species to be the parent moiety and the aromatic ring to be the substituent which is "bridging." For example, in such a system (V) would become 1,10-(*p*-phenylene)decane. Being a reverse sort of method, and not calculated to draw attention to the ring which is being bridged,

it has been used seldom. Examples of its use are from Wieland *et al.* (6) who called (VI) a *m*-phenylenehydrazine derivative, from Parekh and Guha



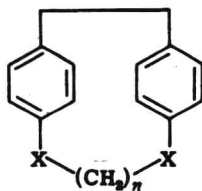
(VI)

(7) who called (VII) *p,p'*-diphenylenedimonosulfide, and from Fuson and



(VII)

co-workers (8, 9) on (VIII), which went unnamed but which was referred to as containing *p*-phenylene units.

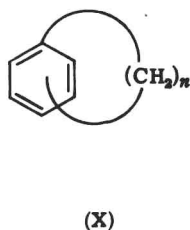
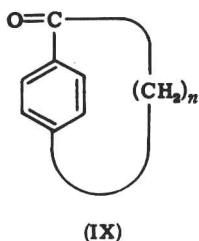


(VIII)

### Benzo System

Usually the term "benzo" has indicated a benzene ring fused in the *ortho* positions to some other system such as in benzocyclobutane. Years ago Ruzicka *et al.* (10), and more recently Huisgen and his co-workers (11, 12),

had applied this to both the normal *ortho*-bridged systems as well as several *meta*- and *para*-bridged structures, calling the series (IX), the 1,2,3,4-benzocycloalka-1,3-dien-5-ones, and (X), the *meta*- or *para*-benzopolymethylenes.



This system, however, is not always completely obvious and unambiguous. It has not been adopted by other workers.

### *Ansa* System

Lüttringhaus, in his pioneering work of the 1930's and 1940's, recognized certain stereochemical relationships of dissymmetry in these cyclic systems. He observed that appropriately substituted members of the series might exhibit optical isomerism as a result of this general molecular dissymmetry and not by the presence of an asymmetric carbon atom. These concepts and their effects will be discussed later. However, to distinguish these dissymmetric species from the many others which also show similar molecular dissymmetry (diphenyls, spirans, allenes), he chose to name them *ansa* compounds (*ansa*, from the Latin, means handle and was selected since the bridges looked like handles to the ring when portrayed in two dimensions). To be included as an *ansa* compound, by Lüttringhaus' definition, the molecule had to have a ring system condensed with an aromatic nucleus in a position other than *ortho* or *peri*. Although the term *ansa* did not define the detailed spatial relationships within the compound or divulge specific structural information, it did call attention to the fact that a special case of bridging was being considered. Even as late as 1958 (13) the term *ansa* was being used in connection with the bridged ferrocenes.

### Bicyclo System

By the strict rules of nomenclature as accepted and fostered by *Chemical Abstracts*, the simple, mononuclear bridged rings are named as bicyclic compounds, the binuclear ones as tricyclics, the trinuclear ones as quadracy-

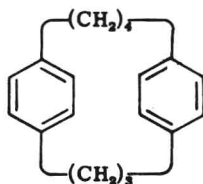


clics, and so on. Thus, by these rules, (I) would be bicyclo[12.2.2]octadeca-14, 16,17-triene, while (VIII) with  $X=CH_2$  and  $n = 5$  would be tricyclo[13.2.2.2.4.7]heneicosa-4,6,15,17,18,20-hexaene.

A complete discussion here of this system would require an inordinate amount of space, and the system is clearly described elsewhere (14, 15). Though the *Chemical Abstracts* systems usually are accepted as the final authority and are prerequisites for publication in most American journals, the names derived therefrom frequently are cumbersome. Many authors thus eschew the use of these names and prefer to adopt or adapt a colloquial system or even devise a new one of their own.

### Cyclophane System

As increasingly greater interest arose in these bridged compounds, it became necessary to define the species more clearly and avoid the indefiniteness lent to them by a variety of nomenclature systems and devices. While the *Chemical Abstracts* systematic approach does unambiguously define these compounds in question, it does not immediately, to most people, conjure up a mental image of the compound nor does it call attention to the most striking characteristic of the class, namely the bridged aromatic system. Consequently, in 1951, Cram and Steinberg (16), proposed the name paracyclophane. This title was to be used for the general class of compounds which would include structures having two benzene rings *vis-à-vis*, held there by methylene bridges attached to the *para* positions of the benzenes. Here then was the first step toward a useful, workable, and distinctive name for the class, one which would single out both the individuality and specificity of the molecule as well as relate something clear and concrete about its structure. At the same time the proposal further indicated that the number of methylenes joining the *para* positions of these rings would be indicated in brackets. By this system [3.4] paracyclophane became a simple, definitive name for a compound such as (XI), a species which by any of the other systems considered thus far could not be known in as simple a manner.



(XI)