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978-0-521-10565-1 - The Chemistry of Cyclo-Octatetraene and its Derivatives

G. I. Fray and R. G. Saxton

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# The chemistry of cyclo-octatetraene and its derivatives

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## Foreword

The story of cyclo-octatetraene began in 1911–13 with Willstätter's multistep preparation from pseudo-pelletierine, surely one of the most hopeful synthetic projects ever undertaken in organic chemistry. Although for many years doubt was cast on the validity of this work it was proved in 1947 to have been correct. Yet in view of its inaccessibility, for thirty years after its discovery the likelihood of ever being able either to solve the fascinating theoretical speculation as to whether cyclo-octatetraene was an aromatic compound akin to benzene, or to investigate its properties in any detail, seemed wholly remote.

The writer recalls the almost incredible news reaching this country in 1945 that Reppe had prepared cyclo-octatetraene in kilogram quantities by the polymerisation of acetylene, and his wonder on seeing this beautiful yellow liquid in bulk. Since 1945, and indeed a few years before in Germany, the investigation of this remarkable compound has been pursued in chemical laboratories throughout the world, and has revealed an astonishing variety of chemical behaviour, little of which could have been foretold by application of chemical theory or by analogy with the behaviour of other substances, and in which, in contrast with benzenoid compounds, the cyclo-octatetraene nucleus seldom retains its original structure.

It has long been evident that a comprehensive account of the chemistry of cyclo-octatetraene was needed, not only to summarise the great volume of work that has been done with it but, on the basis of the information disclosed, to lay the foundations of a real knowledge of the chemistry of this hydrocarbon. This timely book by Dr G. I. Fray in collaboration with Dr R. G. Saxton fulfils both these objectives, and generations of chemists who will continue to investigate this versatile hydrocarbon will be grateful to be able to 'look it up in Fray and Saxton'.

W. BAKER

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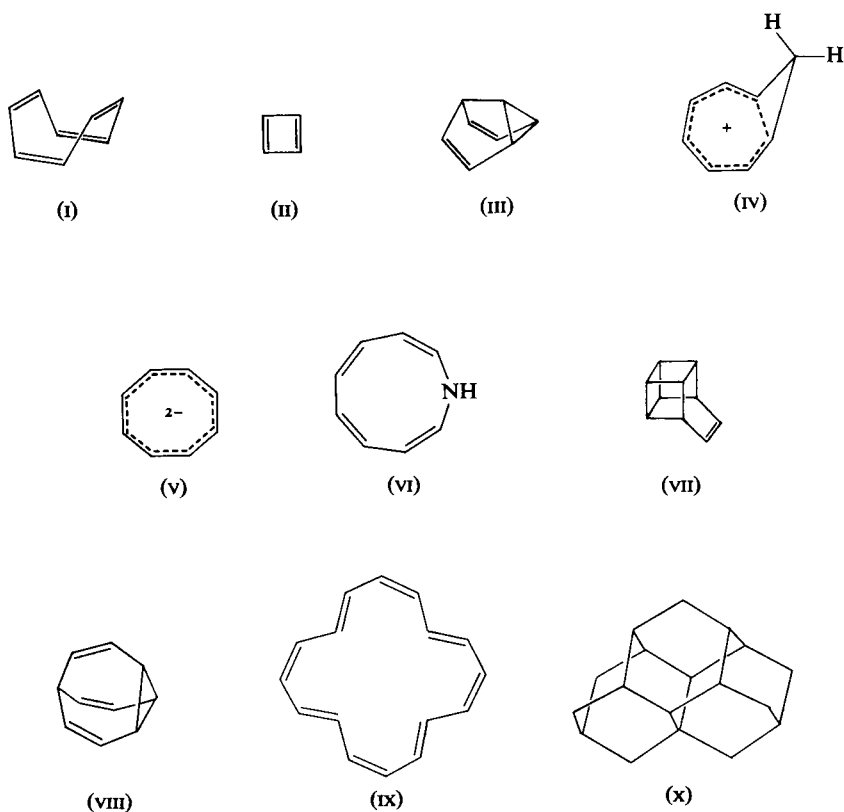
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*For  
Joyce and Patricia*

## Preface

*Z,Z,Z,Z*-Cyclo-octatetraene (COT) (i) has played an outstanding role in many aspects of theoretical and synthetical chemistry. As [8]annulene, the next higher vinylogue of benzene, it is of fundamental importance for the understanding of cyclic alternating  $\pi$ -systems. As a medium-ring polyene, it undergoes a wide variety of reactions which are often accompanied by skeletal transformations, and it is the progenitor of a large number of interesting species including, for example, cyclobutadiene (ii), semibullvalene (iii), the homotropylium cation (iv), the dianion (v), 1H-azonine (vi), basketene (vii), bullvalene (viii), [16]annulene (ix) and triamantane (x).





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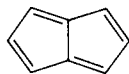
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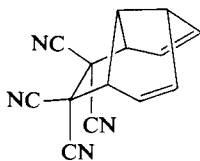
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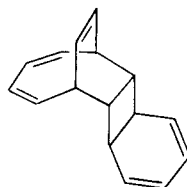
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(xi)



(xii)



(xiii)

COT also forms an exceptional variety of complexes with transition metals. In addition to the interest, from the viewpoint of bonding theory, of these multifarious derivatives (some of which exhibit intriguing fluxional behaviour), modifications of the attached  $C_8H_8$  ligand may occur, leading to systems such as pentalene (xi). Moreover, reactions of metal-coordinated COT can provide routes to systems which are not readily available by the conventional transformations of organic chemistry; examples include the dihydrotriquinacene-derivative (xii) and the COT dimer (xiii).

We feel that our interest in such a molecule needs no apology, and the rapid development of its chemistry during the last decade provides some justification for a new summary of existing knowledge. In chapter 1, the formation, physical properties and chemical reactions of COT are outlined, while chapter 2 deals with substituted (and annulated) derivatives of the parent compound; in order to keep the length of the book within bounds, benzo-derivatives and analogues containing hetero-atoms, e.g. azocines, have been omitted. Chapter 3 attempts to cover, as far as possible, the known chemistry of those compounds which are immediately derivable from COTs. By means of an appendix, prepared after the main typescript had been submitted, we have been able to include additional material from the later literature (up to the end of 1976).

We are indebted to previous reviewers of this field, notably the following:

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July 1977

G.I.F.  
R.G.S