

University of Groningen

## The synthesis and properties of some heterocirculens

Dopper, Jan Hendrik

**IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.**

*Document Version*

Publisher's PDF, also known as Version of record

*Publication date:*

1974

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Dopper, J. H. (1974). *The synthesis and properties of some heterocirculens*. s.n.

**Copyright**

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

**Take-down policy**

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

*Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.*

tion was refluxed for  
(6 cc) was distilled  
18 hours, the precipi-  
ed from the solution  
of cold chloroform.  
dissolved in 4 cc of  
. The observed values  
 $n_D^{25} < 0.005^{\circ}$ .  
addition of 5 cc of  
(4 mg) was filtered  
s material showed no

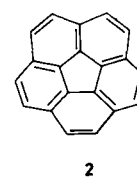
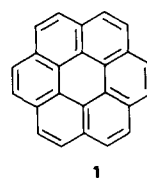
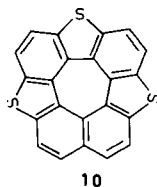
dry THF (15 cc) was  
stirring 21.8 mg (5.2  
125 cc of dry THF.  
tion mixture was re-  
was cooled in an ice  
careful addition of some  
solution and 50 cc of  
e benzene layer was  
CO<sub>2</sub> solution. After  
on of the solvent the  
t p-xylene and chroma-  
r removal of the solvent  
zene. The yield of 15

#### SUMMARY.

In this thesis the synthesis and properties of some hetero-  
circulenes (numbered 10 - 14) is described. The name cir-  
culene as used in this dissertation refers to the circular  
arrangement of the individual aromatic rings within the mo-  
lecule.

In addition to their synthesis we envisioned for the entire  
family of circulenes a number of interesting properties. The  
most important ones are :

1. Planarity vs. non-planarity depending on the relationship  
between the outer- and inner diameter of these "doughnuts",  
the circulenes might :
  - a) assume a bowl-like shape—as in corannulene (2)
  - b) remain planar—as in coronene (1)
  - c) become "corrugated"—as in our compound 10 in which the  
outer diameter is too large for planarity.
2. Optical activity of a suitable dissymmetric circulene would  
be prima facie evidence for its non-planarity.

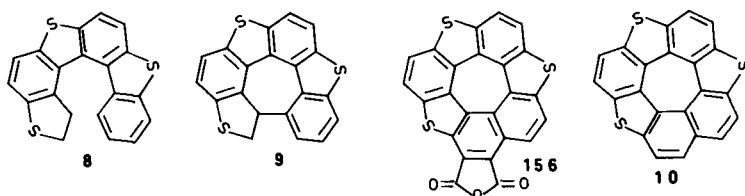


The circulene 10 could be prepared from the heterocirculene 8.  
This use of helicenes as starting materials for the synthesis  
of circulenes prompted us to study alternate routes for the  
former.

In chapter 2 the preparation of eleven new heterohelicenes is  
described. In their syntheses two new elements in heterohelicene  
chemistry have been introduced :

- a) double photocyclizations and
- b) the use of thieno[2.3-b]thiophene (19) as a building block  
for helicenes.

In addition to their synthesis the unusual spectral properties of helicenes containing the thiophene moiety are discussed. In the NMR spectrum of one of the helicenes (e.g. 39) "through-space" coupling is observed.



In chapter 3 the  $\text{AlCl}_3$  catalysed ring closures of some heterohelicenes are described. For this reaction an ionic mechanism is proposed which explains why a terminal thiophene ring is essential for the reaction to occur. The ring closures are limited to [5] and [6] heterohelicenes. An explanation for this phenomenon is presented. Helicenes in which the termini are connected by a sigma bond (e.g. 9) are called dehydrohelicenes. Diels-Alder additions of maleic anhydride to these dehydrohelicenes furnished the anhydrides 156 - 162, which upon decarboxylation gave the circulenes 10 - 14 (chapter 4). The dehydrohelicenes differ from one another in their activity towards Diels-Alder additions. A correlation with calculated para-localization energies is given.

In chapter 5 we deal with the attempts that have been made to demonstrate non-planarity of the circulenes. In these attempts we made use of :

- a) diastereomeric complex formation
- b) the NMR signals from diastereomeric protons and
- c) circular polarization of luminescence.

These attempts were unsuccessful. An explanation for this failure of these attempts is given and the influence of these results upon the development of the concept of "flexibility of aromatics" is indicated.