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The synthesis and properties of some heterocirculens

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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

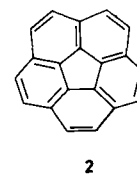
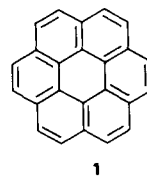
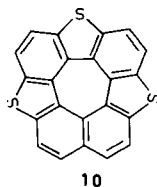
dry THF (15 cc) was
stirring 21.8 mg (5.2
125 cc of dry THF.
tion mixture was re-
was cooled in an ice
careful addition of some
solution and 50 cc of
e benzene layer was
CO₂ solution. After
on of the solvent the
t p-xylene and chroma-
r removal of the solvent
zene. The yield of 15

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.

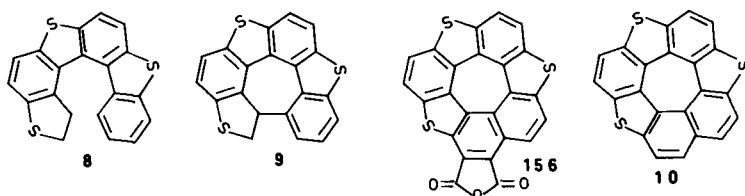


The circulene 10 could be prepared from the heterocirculene 8.
This use of helicenes as starting materials for the synthesis
of circulenes prompted us to study alternate routes for the
former.

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 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.